2019

EUROCLAY

International conference on clay science and technology

1st-5th July 2019

PARIS

Sorbonne Université
Campus Pierre et Marie Curie
4, place Jussieu - 75005 Paris

Book of abstracts

ECGA

The Clay Minerals Society

MCM

GFA
Groupe Francais des Argiles

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Table of contents

Foreword

Dear delegates, Colleagues and Friends,

We are delighted to welcome you at the 2019 EUROCLAY Meeting which is organized jointly by the French Clay Group (GFA) on behalf of the European Clay Group Association (ECGA) and the Clay Minerals Society (CMS – 56th annual meeting). This conference will provide a forum for colleagues from both academia and industries throughout the world to exchange results and ideas on Clays and Clay Minerals.

Four days of technical sessions are planned, each starting with a plenary talk given by a CMS awardee (Jackson Award recipient: **Colleen Hansel**, Bailey Award recipient: **Denny Eberl**, Brindley Award recipient: **Bruno Lanson**, and Pioneer Award recipient: **Laurent Michot**). CMG George Brown Award recipient **Toshihiro Kogure** will also deliver a plenary lecture. Two exciting poster sessions are included in the program. A workshop on clay mineral catalysis of organic reactions, organized by Benny Theng, complements this stimulating technical program.

The conference program includes 24 technical sessions covering all aspects of Clay Science from fundamental aspects of crystallography, mineralogy, and modelling, to environmental and geological processes, through materials science and functionalized clays with applications in the fields of health, cosmetics, resources, energy, storage, or building materials. The 600+ abstracts received from the five continents to build this program will provide as many opportunities to gather and discuss with colleagues and students.

Combining scientific and relational aspects was very important to Jean-Louis Robert who, as president of the French Clay Group at the time, proposed and prepared the French candidacy to hold this 2019 Euroclay meeting in Paris.

This candidacy was selected in 2015 at the Edinburgh meeting, where he was also elected as ECGA president for the 2015-2019 term. Jean-Louis Robert then chaired the Euroclay 2019 organizing committee until his passing away in 2017 as the last International Clay Conference was starting.

Making the Euroclay 2019 a success, both from the scientific standpoint and from the social perspective is the best way we could think of to pay tribute to the vivid memory of Jean-Louis Robert and to the contribution of this enthusiastic and accessible scientist to Clay Science.

We are sure we can rely on you to help us make Euroclay 2019 a success.

Welcome to Paris! We sincerely hope that you will enjoy the conference.

Maguy Jaber, Bruno Lanson & Erwan Paineau

1. Euroclay 2019 committees & Clay Minerals Society information

Organizing committee

Maguy Jaber, General Chair
Erwan Paineau, co-chair
Bruno Lanson, co-chair

Cécile Duflot, Graphic Design
Martine Gérard & Christelle Latrille, Social program
Christelle Latrille & Nicolas Michau, Field Trips
Lydie Le Forestier & Erwan Paineau, Abstracts

Thierry Allard, Etienne Balan, Benoît Baptiste, Laurent Caner, Dimitri Deneele, Agnès Elmaleh, Suzie Joncart, Sophie Le Caer, Laurent Michot, Violaine Sautter, Antoine Thill, Fabienne Trolard

International Scientific Committee

Gabriela Carja (Iaşi, Romania)
Özgür Cehgiz (Afyon Kocatepe,Turkey)
Georgios Christidis (Chania, Greece)
Christian Detellier (Ottawa, Canada)
Reiner Dohrmann (Hannover, Germany)
Nathalie Fagel (Liège, Belgium)
Will Gates (Melbourne, Australia)
Katarzyna Górniak (Krakow, Poland)
Ulla Gro Nielsen (Odense, Denmark)
Steve Guggenheim (Chicago, USA)
Steve Hillier (Aberdeen, United Kingdom)
Corina Ionescu (Cluj-Napoca, Romania)
Fakher Jamoussi (Soliman, Tunisia)
Mohamed Khodja (Boumerdiès, Algeria)
Victoria Krupskaya (Moscow, Russia)
Bruno Lanson (Grenoble, France)
Jana Madejova (Bratislava, Slovakia)
Laurent Michot (Paris, France)
Fernando Nieto (Granada, Spain)
Franz Ottner (Wien, Austria)
Sabine Petit (Poitiers, France)
Michael Plötze (Zurich, Switzerland)
Miroslav Pospíšil (Prague, Czech Republic)
Fernando Rocha (Aveiro, Portugal)
Eduardo Ruiz-Hitzky (Madrid, Spain)
Emanuela Schingaro (Bari, Italy)
Rebecca M. Stokes (Houston, USA)
Darko Tibljaš (Zagreb, Croatia)
Asuman Türkmenoğlu (Ankara, Turkey)
Sabine Verryn (Pretoria, South Africa)
Lynda Williams (Tempe, USA)

European Clay Group Association

Presidents of the European Clay Group Association (ECGA)

1987–1991	Fernando Veniale	1991-1995	Radko Kühnel
1995-1999	Emilio Galán	1999-2003	Gerhard Lagaly
2003-2007	Jan Środoń	2007-2011	Celso Gomes
2011-2015	Peter Komadel	2015-2017	Jean-Louis Robert
2017-2019	Miroslav Pospíšil (*ex officio*)		

Past Presidents

Presidents of the "Commission du Groupe Français des Argiles" — National Center for Scientific Research (CNRS)

1947–1954	Jean Orcel	1954-1956	Jean Wyart
1956-1958	Jacques Méring	1958-1961	Stéphane Hénin
1961-1964	Raymond Hocart	1964-1967	Simonne Caillère
1967-1969	Yves Letort		

Presidents of the "Groupe Français des Argiles"

1969–1972	Georges Millot	1973-1975	Georges Pédro
1976-1978	Raymond Wey	1978-1978	Jean Chaussidon
1979-1981	Henri Pézerat	1982-1984	Cyril Tchoubar
1985-1987	Jean Mamy	1988-1990	Bernard Siffert
1990-1994	Médard Thiry	1994-1998	Alain Decarreau
1998-2002	Jacques Yvon	2003-2007	Faïza Bergaya
2007-2011	Jocelyne Brendlé	2011-2015	Jean-Louis Robert
2015-2019	Bruno Lanson		

The Clay Mineral Society Administration

3635 Concorde Pkwy, Suite 500
Chantilly, VA 20151-
1110, USA
Mary Gray, Manager

Executive Committee

President: Lynda B. Williams, Arizona State University
Vice President: Andrey Kalinichev, University of Nantes, France
Secretary: Warren Huff, University of Cincinnati
Treasurer: Paul Schroeder, University of Georgia
Vice-President Elect: Bruno Lanson, CNRS, France
Past President: Douglas K. McCarty, Chevron Inc. (Retired)
Editor-in-Chief: Joseph W. Stucki, University of Illinois

Council

Thru 2019	Thru 2020	Thru 2021
Shane Butler	Arek Derkowski	Janice Bishop
Youjun Deng	Stephen J. Hillier	Anke Neumann
Carolyn Olson	Timothy Fischer	Nikolla Qafoku
Javiera Cervini-Silva	Ana Luisa Barrientos Velazquez	Erwan Paineau

Past presidents

Chairmen of the Interdivisional Committee on Clay Minerals of the National Academy of Sciences—National Research Council

1952–1956	Ralph E. Grim	1960–1962	A. F. Frederickson
1957–1959	Walter D. Keller	1963	Richards A. Rowland

Presidents

1963–1964	Richards A. Rowland
1964–1965	James W. Earley
1965–1966	Haydn H. Murray
1966–1967	Marion L. Jackson
1967–1968	Charles E. Weaver
1968–1969	Paul G. Nahin
1969–1970	George W. Brindley, Katherine Mather
1970–1971	John F. Burst
1971–1972	Sturges W. Bailey
1972–1973	William F. Bradley
1973–1974	John W. Jordan
1974–1975	John C. Hathaway
1975–1976	Stanley B. McCaleb
1976–1977	John Hower
1977–1978	John B. Hayes
1978–1979	Max M. Mortland
1979–1980	Finis Turner
1980–1981	R. Torrence Martin
1981–1982	Joe B. Dixon
1982–1983	William D. Johns
1983–1984	Wayne Hower
1984–1985	Wayne M. Bundy
1985–1986	Marion G. Reed
1987-1988	Necip Guven
1988–1989	William F. Moll
1989–1990	Brij L. Sawhney
1990–1991	Thomas J. Pinnavaia
1991–1992	Robert C. Reynolds, Jr.
1992–1993	David R. Pevear
1993–1994	Dennis D. Eberl
1994–1995	Rossman F. Giese, Jr.
1995–1996	Kenneth M. Towe
1996–1997	Stephen Guggenheim
1997–1998	Joseph W. Stucki
1998–1999	David L. Bish
1999–2000	Patricia M. Costanzo
2000–2001	Darrell G. Schultze
2001–2002	Blair F. Jones
2002–2003	Jessica Elzea Kogel
2003–2004	Kathry L. Nagy
2004–2005	Duane M. Moore
2005–2006	Cliff T. Johnston
2006–2007	Richard K. Brown
2007–2008	Ray E. Ferrell, Jr.
2008–2009	Andrew R. Thomas
2009–2010	Derek C. Bain
2010–2011	Paul A. Schroeder
2011–2012	David A. Laird
2012–2013	Peter Komadel
2013–2014	Michael A. Velbel
2014–2015	W. Crawford Elliott
2015-2016	Prakash B. Malla
2016-2017	Jan Środoń
2017-2018	Douglas K. McCarty
2018-2019	Lynda B. Williams
2019-2020	Andrey Kalinichev

Individual Sustaining Members of the Clay Minerals Society

Richard K. Brown
Randall T. Cygan
Will Gates
Stephen Guggenheim
Marc A. Herpfer
James Matthews
Carolyn G. Olson
Thomas J. Pinnavaia
Paul A. Schroeder
Joseph W. Stucki
Michael A. Velbel
Lynda B. Williams

Awards

Marilyn and Sturges W. Bailey Distinguished Member Award

The Marilyn and Sturges W. Bailey Award, the highest honor of The Clay Minerals Society, is awarded solely for scientific eminence in clay mineralogy (in its broadest sense) as evidenced by the publication of outstanding original scientific research and by the impact of this research on the clay sciences. This Award replaces the Society's Distinguished Member Award and is not restricted to members of the Society.

Distinguished Members

1968 Ralph E. Grim
1969 Clarence S. Ross
1970 Paul F. Kerr
1971 Walter D. Keller
1972 George W. Brindley
1975 Sturges W. Bailey
1975 William F. Bradley
1975 José Fripiat
1977 Marion L. Jackson
1979 Toshio Sudo
1980 Haydn H. Murray
1984 C. Edmund Marshall
1985 Charles E. Weaver
1988 Max M. Mortland
1989 Robert C. Reynolds, Jr.
1990 Joe L. White
1990 John Hower
1991 Joe B. Dixon
1992 Philip F. Low
1993 Thomas J. Pinnavaia
1995 William D. Johns
1996 Victor A. Drits
1997 Udo Schwertmann
1998 Brij L. Sawhney

Bailey Distinguished Members

2000 Boris Zvyagin
2001 Keith Norrish
2002 Gerhard Lagaly
2004 Benny K. G. Theng
2005 M. Jeff Wilson
2006 Frederick J. Wicks
2008 Norbert Clauer
2009 Joseph W. Stucki
2010 José M. Serratosa
2011 Sridhar Komarneni
2012 Akahiko Yamagishi
2013 Stephen Guggenheim
2015 R. James Kirkpatrick
2016 Lisa Heller-Kallai
2018 G. Jock Churchman
2019 Dennis D. Eberl

Marion L. And Chrystie M. Jackson Mid-Career Clay Scientist Award

The Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award recognizes a mid-career scientist for excellence in the contribution of new knowledge to clay minerals science through original and scholarly research. The honoree must be within the ages of 39 and 60.

Jackson Awardees

1992 Joseph W. Stucki
1993 Jan Środoń
1994 Stephen Guggenheim
1995 David L. Bish
1996 Darrell G. Schulze
2001 Cliff T. Johnston
2002 Sridhar Komarneni
2003 Peter Komadel
2004 Fred J. Longstaffe
2005 Samuel J. Traina
2010 Toshihiro Kogure
2011 Douglas K. McCarty
2012 Jeffrey E. Post
2013 George E. Christidis
2014 Will P. Gates

1997 Jerry M. Bigham
1998 Murray McBride
1999 Stephen Boyd
2000 Jillian Banfield
2006 J. Theo Kloprogge
2007 Paul A. Schroeder
2008 Hailiang Dong
2009 Lynda B. Williams
2015 Balwant Singh
2016 Janice L. Bishop
2018 Stephen J. Hillier
2019 Colleen M. Hansel

George W. Brindley Lecture Award

The George W. Brindley Lecture Award recognizes an outstanding clay scientist, someone who is both a dynamic speaker and involved in innovative research, and charges the recipient to deliver a lecture that will infuse The Clay Minerals Society with new ideas. The speaker is challenged to deliver a lecture that Brindley himself would applaud.

Brindley Lecturers

1984 Walter D. Keller
1985 José J. Fripiat
1986 Ralph E. Grim
1987 Sturges W. Bailey
1988 Marion L. Jackson
1989 William D. Johns
1990 Alain Baronnet
1991 Thomas J. Pinnavaia
1992 Philip F. Low
1993 Dennis D. Eberl
1994 Robert C. Reynolds, Jr.
1995 Gerhard Lagaly
1996 Samuel M. Savin
1997 Paul H. Nadeau
1998 Bruce Velde
1999 Richard Eggleton
2000 Duane M. Moore
2001 Robert Schoonheydt
2002 David L. Bish
2003 Alain Manceau
2005 Maria F. Brigatti
2008 Robert J. Gilkes
2009 Michael F. Hochella, Jr.
2010 Randall T. Cygan
2013 Andrey G. Kalinichev
2017 Sridhar Komarneni
2018 Cliff T. Johnston
2019 Bruno Lanson

Pioneer In Clay Science Award

The lecture award recognizes research contributions that have led to important new directions in clay mineral science and technology. The recipient is responsible for delivering a plenary lecture supporting symposia organized for the national meeting.

Pioneer in Clay Science Lecturers

1987 Marion L. Jackson
1988 R. M. Barrer
1989 H. van Olphen
1990 John W. Jordan
1991 Charles E. Weaver
1992 Udo Schwertmann
1993 Linus Pauling
1998 Robert C. Reynolds, Jr.
1999 V. Colin Farmer
2000 William F. Moll
2001 Don Scafe
2002 Victor A. Drits
2003 Vernon J. Hurst
2004 Hideomi Kodama
2009 Haydn H. Murray
2011 Glenn A. Waychunas
2013 Thomas J. Pinnavaia
2014 Douglas W. Ming
2015 Reinhard Kleeberg
2016 Donald L. Sparks
2017 Fred J. Longstaffe

1994 Joe L. White
1995 Rustum Roy
1996 Max M. Mortland
1997 Koji Wada.
2005 Jillian Banfield
2006 Jean-Maurice Cases
2007 Spencer G. Lucas
2008 Emilio Galan
2018 Jan Środoń
2019 Laurent J. Michot

Citation of special recognition

1984 Richards A. Rowland
1984 Ada Swineford
1991 Frederick A Mumpton
1994 Kenneth M. Towe
1996 Don Scafe
2003 William D. Johns
2013 Haydn H. Murray
2014 Warren D. Huff
2015 Stephen J. Hillier
2016 J. Reed Glasmann
2018 Duane M. Moore

Editors of Clays & Clay Minerals

1952	J. A. Pash & M. D. Turner	1975-1978	Richards A. Rowland
1953	Ada Swineford & Norman Plummer	1979-1990	Frederick A. Mumpton
1954	W. O. Milligan	1990-1991	Kenneth M. Towe
1955–1961	Ada Swineford	1991-1995	Ray E. Ferrell, Jr.
1962-1964	William F. Bradley	1995-1998	Wayne H. Hudnall
1964-1969	Sturges W. Bailey	1999-2000	Stephen Guggenheim
1970-1972	Max M. Mortland	2000-2007	Derek C. Bain
1973-1974	William T. Granquist	2008–Present	Joseph W. Stucki

2. Practical information (maps + general agenda)

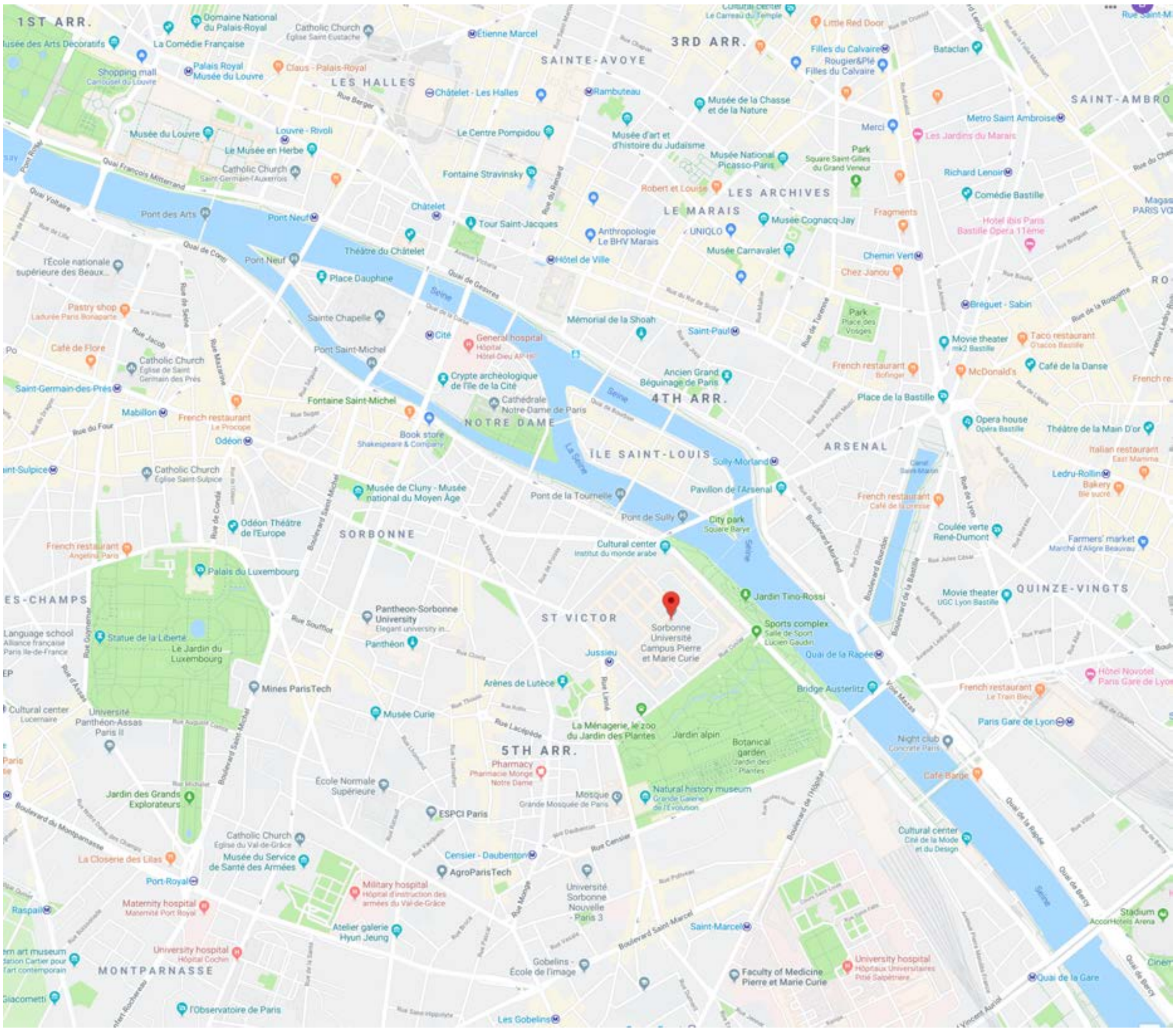
Practiocal Maps & General agenda

Conference venue

Opening ceremony, scientific lectures, poster sessions, and Welcome Party (evening of Monday 1st July) will take place in the Congress Center complex of the Pierre & Marie Curie Campus (Sorbonne University).

The University Campus is located in the center of Paris between the East end of the "Rue des Ecoles", the Seine river banks and the botanical garden ("Jardin des Plantes") that also hosts the Natural History Museum (general map below) and is easily accessed by:

- Metro lines ⑦ or ⑩ (stop Jussieu)
- Bus lines n°24, 63, 67, 86, 87, and 89 (stops in the Campus vicinity)

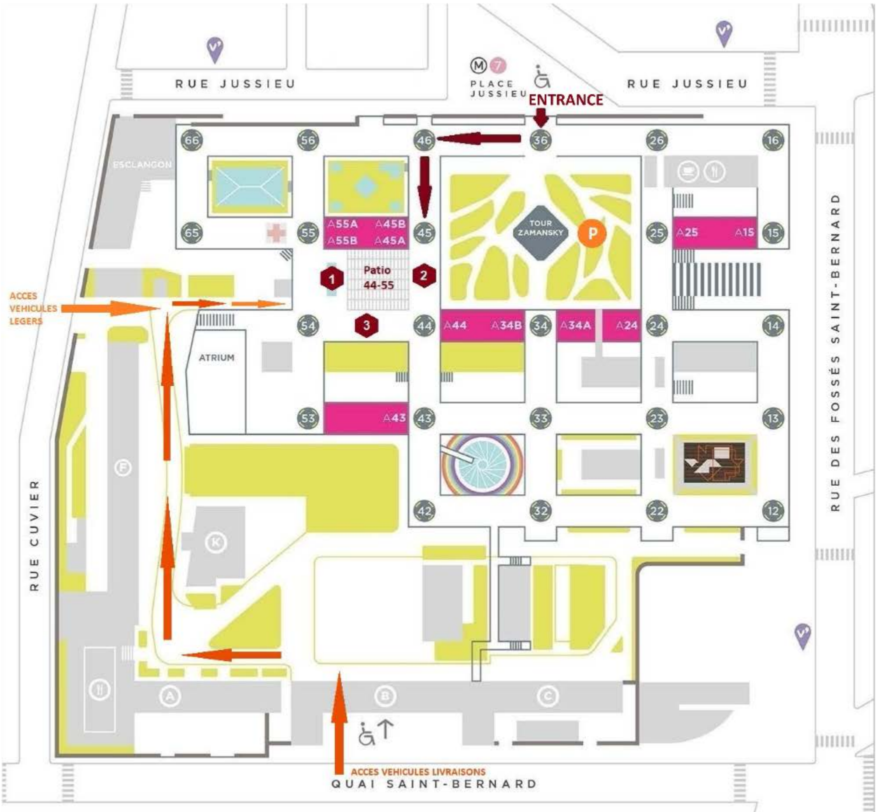


See also the [map on the Euroclay website](#)

Additional information on Paris public transportation may be obtained from https://www.ratp.fr/en

]]>

The main entrance of the Campus is located Place Jussieu (see below)
Directions are indicated by the numbers of the towers on Campus. The conference center is located between towers #44 and #55.



CAMPUS ACCESS

MAIN ACCESS
4, place Jussieu

CONFERENCE CENTER

① **PATIO 44-55 (1)**
Auditorium: 500 seats
with a 400 m² Hall
Outside Patio:
Poster sessions / Coffee breaks

② **BARRE 44-45 / Floor #1 (2)**
Access through Tower 44
Room #108: 120 seats
Room #106: 90 seats

③ **BARRE 44-54 / Floor #1 (3)**
Access through Tower 44
Rooms #105, #107, #109: 80 seats
Room #116: 30 seats
Rooms #112 & #14: 16 seats

ACCESS MAP - PIERRE & MARIE CURIE CAMPUS
Crédits © Sorbonne Université

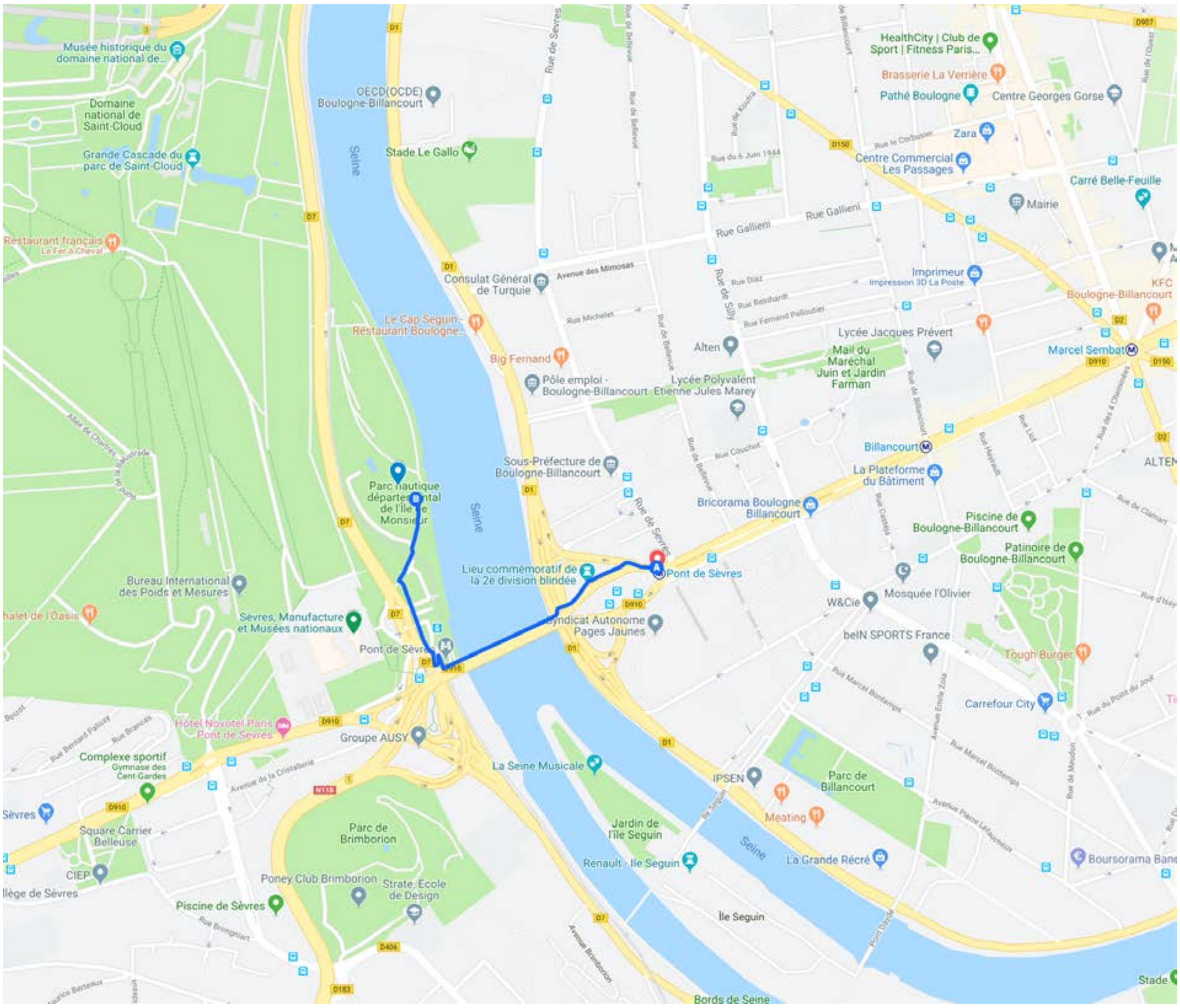
Oral presentations will be given in the Main auditorium (#1 on the map) on the above map, in rooms #106, #108 (located on the first floor above ground between towers #44 and #45 – The so-called “Barre 44-45”, #2 on the map) and in rooms #105 and #109 (located on the first floor above ground between towers #44 and #45 – The so-called “Barre 44-54”, #3 on the map).

Poster sessions, coffee breaks, and exhibitors will be in the outside patio between towers #44 and #55 (Patio 44-55, #1 on the map).

Satellite meetings will be held in rooms #106 (located on the first floor above ground between towers #44 and #45 – The so-called “Barre 44-45”, #2 on the map) and in rooms #107, #112, and #116 (located on the first floor above ground between towers #44 and #45 – The so-called “Barre 44-54”, #3 on the map). See the detailed planning for further information.

Banquet

The banquet will be held at "Parc Nautique de l'île Monsieur" (Ecologic park).
The place may be easily reached by underground ("Métro") public transportation (~40 min from the conference venue). From Jussieu Campus and metro station, use line ⑩ to "*Michel-Ange-Auteuil*" and then line ⑨ to "*Pont de Sèvres*". The map below displays the itinerary from the "*Pont de Sèvres*" stop on line ⑨ to the banquet site (~10 min walk).



See also the map on the Euroclay website
The itinerary from the conference venue to the "Pont de Sèvres" Métro station can be found here (or modified from using your actual location)

Field trips
Detailed information on field trips will be posted on the website and displayed at the conference venue

General agenda

	Scientific sessions	Satellite meetings & activites
Fri June 28th	09:00 am - 5:30 pm Workshop "Clay Minerals and catalysis" (B.K.G. Theng)	5:30 pm - 9:30 pm CMS Executive Committee meeting
Sat June 29th	No scientific activity - Enjoy Paris!	9:00 am - 5:30 pm CMS Council meeting
Sun June 30th	No scientific activity - Enjoy Paris!	6:00 pm - 8:00 pm AIPEA council meeting
Mon July 1st	9:15 am - 9:45 am Opening ceremony	
	9:50 am - 10:45 am CMS Pioneer in Clay Science lecture: Laurent Michot	12:40 pm - 1:40 pm CMS - Past president lunch
	11:10 am - 6:30 pm 5 parallel technical sessions	12:40 pm - 1:40 pm Clay Minerals Editorial board meeting
	1:30 pm - 2:15 pm CMG George Brown lecture: Toshihiro Kogure	
	6:30 pm - 8:30 pm Poster session	6:30 pm - 8:30 pm Wine & Cheese party
Tue July 2nd	8:30 am - 9:25 am / CMS Bailey distinguished member award: Denny Eberl	12:50 pm - 2:00 pm ECGA meeting of Natl Clay Groups
	9:30 am - 5:30 pm 5 parallel technical sessions	12:50 pm - 2:00 pm CMS Sustaining members lunch
	5:30 pm - 7:30 pm Poster session	6:30 pm - 9:00 pm Clays & Clay Minerals Editorial board meeting + dinner
		6:30pm - 7:30 pm Applied Clay Science Executive meeting 8:30pm - 10:30 pm Applied Clay Science Editorial board meeting + dinner
Wed July 3rd	"Field" trips / Enjoy Paris!	5:00 pm - 7:30 pm AIPEA Natl Clay group meeting
Thu July 4th	8:30 am - 9:25 am CMS Jackson mid-career award: Colleen Hansel	12:50 pm - 2:00 pm CMS Business meeting
	9:30 am - 6:00 pm 5 parallel technical sessions	12:50 pm - 2:00 pm GFA Council meeting
		7:00 pm - 11:30 pm Banquet
Fri July 5th	8:30 am - 9:25 am CMS Brindley Clay Science Lecture: Bruno Lanson	1:00 pm - 2:00 pm GFA General Assembly
	9:30 am - 4:20 pm 5 parallel technical sessions	
	4:25 pm - 4:45 pm Closing ceremony	

General planning of technical sessions

Room #106		Room #108		Room #105		Room #109		Auditorium	
Monday		**Monday**		**Monday**		**Monday**		**Monday**	
Session A7 1 of 4	Characterization of clayey nanomaterials	Session E2 1 of 3	General session	Session B1 1 of 3	Clays in fractures	Session C3 1 of 2	Thermal reactions of clays for construction materials	Session D2 1 of 5	LDH for future Earth
Session A7 2 of 4		Session E2 2 of 3		Session B1 2 of 3		Session C3 2 of 2		Session D2 2 of 5	
Session A7 3 of 4		Session E2 3 of 3		Session B1 / 3 of 3 Session B6 / 1 of 3		Session C3 1 of 4	Geotechnical characterization of clayey geomaterials	Session D2 3 of 5	
Tuesday		**Tuesday**		**Tuesday**		**Tuesday**		**Tuesday**	
Session A7 4 of 4		Session A5 1 of 2	Multiscale understanding of interface redox reactions	Session B6 2 of 3	Clays and the origin of life	Session C3 2 of 4		Session D2 4 of 5	
Session A2 1 of 6	Experimental and numerical analysis of clay systems	Session A5 2 of 2		Session B6 3 of 3		Session C3 3 of 4		Session D2 5 of 5	
Session A2 2 of 6		Session B4 1 of 3	Mudrocks	Session B2 1 of 4	Clays and organic matter	Session C3 4 of 4		Session D5 1 of 2	Frontiers and new applications of clay colloids
Session A2 3 of 6		Session B4 2 of 3		Session B2 2 of 4		Session D8 1 of 1	Clays & health	Session D5 2 of 2	
Thursday		**Thursday**		**Thursday**		**Thursday**		**Thursday**	
Session A2 4 of 6		Session B4 3 of 3		Session B2 3 of 4		Session D6 1 of 2	Archaeoceramics	Session D1 1 of 5	Nanotechnology and nanomaterials from clay minerals
Session A2 5 of 6		Session B2 1 of 5	Enironmental pollutant remediation	Session B2 4 of 4		Session D6 2 of 2		Session D1 2 of 5	
Session A2 6 of 6		Session B2 2 of 5		Session E1 1 of 2	Teaching clay science	Session D3 1 of 2	Clays in ceramics	Session D1 3 of 5	
Session A4 1 of 4	1D nanoporous clay minerals	Session B2 3 of 5		Session E1 / 2 of 2 Session D7 / 1 of 3		Session D3 / 2 of 2 Session A3 / 1 of 4		Session D1 4 of 5	
Friday		**Friday**		**Friday**		**Friday**		**Friday**	
Session A4 2 of 4		Session B2 4 of 5		Session D7 2 of 3	Clay mineral synthesis	Session A3 2 of 4	Physico-chemical processes at the clay/water interface	Session D1 5 of 5	
Session A4 3 of 4		Session B2 5 of 5		Session D7 3 of 3		Session A3 3 of 4		Session B7 1 of 2	Diagenesis and low-grade metamorphism
Session A4 4 of 4		Session A1 1 of 1	Reactive transport modelling	Session C4 1 of 1	Photochem. and optical properties of	Session A3 4 of 4		Session B7 2 of 2	

3. Satellite meetings (sorted by convening organization)

Friday June 28th – 9:00 am – 5:30 pm – Room #116 / Building # 44-54
Workshop on “Clay mineral catalysis of organic reactions”
Convener: Benny K.G. Theng

Sunday June 30th – 5:00 – 7:30 pm – Hôtel Le six – 14 rue Stanislas – 75006 Paris
AIPEA Council meeting
Convener: Association Internationale pour l’étude des Argiles (AIPEA)

Wednesday July 3rd – 5:00 – 7:30 pm – Room #106 / Building # 44-45 (90 p.)
AIPEA Meeting of National Clay Groups
Convener: Association Internationale pour l’étude des Argiles (AIPEA)

Tuesday July 2nd – 12:50 – 2:00 pm – Room #116 / Building # 44-54 (30 p.)
ECGA Meeting of National Clay Groups
Convener: European Clay Group Association (ECGA)

Friday June 28th – 5:30 – 9:30 pm – Room #116 / Building # 44-54 (30 p.)
CMS Executive committee Meeting
Convener: Clay Minerals Society (CMS)

Saturday June 29th – 9:00 am – 5:30 pm – Room #116 / Building # 44-54 (30 p.) + Lunch
CMS Council Meeting
Convener: Clay Minerals Society (CMS)

Monday July 1st – 12:40-1:40 pm – Lunch in Room #112 / Building # 44-54 (15 p.)
CMS Past president lunch
Convener: Clay Minerals Society (CMS)

Tuesday July 2nd – 12:40 – 2:00 pm – Lunch in Room #112 / Building # 44-54
CMS Sustaining members lunch
Convener: Clay Minerals Society (CMS)

Thursday July 4th – 12:50 – 2:00 pm –Room #107 / Building # 44-54 (80 p.)
CMS Business meeting
Convener: Clay Minerals Society (CMS)

Thursday July 4th – 12:50 – 2:00 pm –Room #116 / Building # 44-54 (30 p.)
GFA Council meeting
Convener: Groupe Français des Argiles (GFA)

Friday July 5th – 1:00 – 2:00 pm – Room #107 / Building # 44-54 (80 p.)
GFA Business meeting
Convener: Groupe Français des Argiles (GFA)

Monday July 1st – 12:40-1:40 pm – Room #116 / Building # 44-54 (30 p.)
Clay Minerals: Editorial board meeting

Convener: Clay Minerals – Mineralogical Society UK & Ireland / Cambridge University Press

Tuesday July 2nd – 6:30 – 9:00 pm – Room #116 / Building # 44-54 (30 p.)
Clays & Clay Minerals: Editorial board meeting
Convener: Clays & Clay Minerals – Clay Minerals Society / Springer

Tuesday July 2nd – 6:30 – 7:30 pm – Room #114 / Building # 44-54 (15 p.)
Applied Clay Science: Executive meeting
Convener: Applied Clays Science – Elsevier

Tuesday July 2nd – 8:30 – 10:30 pm – Les éditeurs – 4 Carrefour de l'Odéon – 75006 PARIS
Applied Clay Science: Editorial board meeting + dinner
Convener: Applied Clays Science – Elsevier

4. Detailed oral program

List of technical sessions with location of the talks and conveners

Session A1: Challenges in reactive transport modeling of clay systems – Room #108

Christophe TOURNASSAT, Jean-Charles ROBINET

Session A2: Experimental and numerical analysis of clay systems: Bridging time and length scales – Room #106

Jeffery A. GREATHOUSE, Pascale LAUNOIS, Eric FERRAGE, Pierre LEVITZ

Session A3: Physicochemical processes at the clay/water interface – Room #109

Emmanuel TERTRE, Thorsten SCHÄFER, Helge STANJEK

Session A4: 1D Nanoporous clay minerals: Structures, genesis, functionalization, properties and applications – Room #106

Antoine THILL, Lala Setti BELAROUI, Peng YUAN, Faïza BERGAYA

Session A5: Multi-scale understanding of interface redox reactions – Room #108

Sylvain GRANGEON, Francis CLARET, Maria do SAMEIRO MARQUES FERNANDES

Session A7: Characterization of clayey nanomaterials – Room #106

Wen-An CHIOU, Toshihiro KOGURE, Stephan KAUFHOLD, Reiner DOHRMANN, Paul SCHRÖEDER

Session B1: Clay minerals in fracture zones – Room #105

Simon J. KEMP, Horst ZWINGMANN, Anga SCHLEICHER, Juan JIMÉNEZ-MILLÁN

Session B2: The role of clays and modified clays in remediating environmental pollutants – Room #108

Bhabananda BISWAS, Jérôme LABILLE, Benedicte PRELOT

Session B3: Clays and organic matter – Room #105

Michael PLÖTZE

Session B4: Mudrocks: Composition, fabric, and provenance - Fundamental research and practical applications of the data – Room #108

Jean-Francois DECONINCK, Katarzyna GÓRNIAK, Pierre PELLENARD

Session B6: The role of clay minerals in the origin of life – Room #105

Jihua HAO, Isabelle DANIEL, Jean-François LAMBERT

Session B7: Diagenesis and low-grade metamorphism (4th Frey-Kübler Symposium) – Auditorium

Sébastien POTEL, Rafael FERREIRO MÄHLMANN

Session C2: Geotechnical characterization of clayey geomaterials from micro to macro scale: The role of microstructure and anisotropy – Room #109

Philippe COSENZA, Myriam DUC, Pierre DELAGE, Christopher SPIERS

Session C3: Thermal reactions of clays and their application in sustainable construction materials – Room #109

Katja EMMERICH, Jan ELSEN, Sylvie ROSSIGNOL, Franck DEHN

Session C4: Photochemistry, photophysical and optical functionalities of clay mineral based materials – Room #105

Yusuke IDE, Juraj BUJDÁK, Jun KAWAMATA

Session D1: Recent Progress on Nanotechnology and Nanomaterials from Clay Minerals – Auditorium

Eduardo RUIZ-HITZKY, Pilar ARANDA

Session D2: LDH for future health: Advances and challenges in energy, environmental and medical applications – Auditorium

Claude FORANO, Gabriela CARJA, H. Chris GREENWELL

Session D3: Clay and clay minerals in ceramics: From industrial to new hierarchical/textural materials – Room #109

Giséle LECOMTE-NANA

Session D5: Frontier and new applications of clay colloids – Auditorium

Nobuyoshi MIYAMOTO, Josef BREU, Teruyuki NAKATO, Patrick DAVIDSON

Session D6: Archaeoceramics: Raw materials, technology and provenance – Room #109

Corina IONESCU, Elisabetta GLIOZZO

Session D7: Clay mineral synthesis – Room #105

François MARTIN, Sabine PETIT

Session D8: Clays and health: From pelotherapy to drug delivery – Room #109

Stefano LEPORATTI, Rawil FAKHRULLIN

Session E1: Teaching clay science – Room #105

Ray FERRELL

Session E2: General session – Room #108

Maguy JABER, Bruno LANSON, Erwan PAINEAU

Monday July 1st

Hall Auditorium

From 8:00 am: Registration and badge pick-up

Auditorium

9:15-9:45 am Opening ceremony

9:50-10:45 am Clay Minerals Society - Pioneer in clay science lecture

Laurent J. Michot: Crystalline and osmotic swelling of clay minerals. Recent advances Introduction by Maguy Jaber

10:45-11:10 am: Coffee break

Session A7: Characterization of clayey nanomaterials – Room #106

11:10-11:30 am: Wen-An Chiou

The unique role of electron and ion microscopy in nano-clayey materials characterization

11:30-11:50 am: Nia Gray, Stephen Hillier, Peter Holliman, Chris Greenwell, Pablo Cubillas, Chris Kershaw, David Lumsdon, Zabeada Aslam, Rik Brydson

Aspects of the surface and internal structure of halloysite nanotubes as revealed by various microscopy methods

11:50 am-12:10 pm: Anne-Claire Gaillot

Cristal-chemical characterization of clay at the nano and subnanoscale: new opportunities from Cs-corrected TEM in scanning and precession modes

12:10-12:30 pm: Kasimanat Vibulyaseak, Wen-An Chiou, Makoto Ogawa

Characterization of titania nanoparticles in mesoporous silica

Session E2: General session – Room #108

11:10-11:30 am: Peter Uhlík, Peter Koděra, Alexander Kubač, Marek Szczerba, Adrián Biroň, Rastislav Milovský, Boris Bača, Marek Osacký, Ľubica Puškelová

Illite – indicator of hydrothermal alteration conditions in a shallow-dipping epithermal precious and base metal deposit Banská Hodruša, Slovakia

11:30-11:50 am: François Fontaine, Sofie Hollanders, Andreas Hoffmann, Johan Yans, Nathalie Fagel

Characterization and origin of a Fe-rich bentonite from Westerwald (Germany)

11:50 am-12:10 pm: Selahattin Kadir, Nergis Önalgil, Tacit Külah, Hülya Erkoyun, Muhsin Eren, W. Crawford Elliott

Mineralogy, geochemistry, and genesis of bentonites in Upper Cretaceous Bereketli Member of the Reşadiye Formation, Reşadiye (Tokat), Turkey

12:10-12:30 pm: Mango-Itulamya Lavie Arsène, El Ouahabi Meriam, Fagel Nathalie

Properties of the alteration clays of the Schisto-Calcaire and Inkisi Subgroups in the Democratic Republic of Congo and raw earth construction material valorisation

Session B1: Clay minerals in fracture zones – Room #105

11:10-11:50 am: Warr Laurence Noel (**keynote lecture**)

The importance of clay in the faulting and fracturing of rocks

11:50 am-12:10 pm: Anna K. Ksienzyk, Espen Torgersen, Klaus Wemmer, Roelant van der Lelij, Jasmin Schönenberger, Joachim Jacobs, Haakon Fossen, Atle Rotevatn

Clay-gouge bearing faults in the Norwegian basement: K-Ar geochronology and insights into strain localization, mineralogy and temperature conditions

12:10-12:30 pm: John Keeling, Horst Zwingmann, Mark Raven, Peter Self

Fault zones, graphite, and anomalous celadonite/nontronite alteration in deeply weathered high-grade metamorphic rocks of southern Eyre Peninsula, South Australia

Session C3: Thermal reactions of clays and their application in sustainable construction materials – Room #109

11:10-11:30 am: Baptiste Luzu, Myriam Duc, Assia Djerbi, Laurent Gautron

Illitic clay-based geopolymer: the study of the mechanochemical activation duration and coupling with thermal activation

11:30-11:50 am: Mohammadreza Izadifara, Peter Thissen, Annett Steudel, Frank Dehn, Rainer Schuhmann, Katja Emmerich

Formation of metakaolinite and metadickite during dehydroxylation

11:50 am-12:10 pm: Noel N'guessan Essey, Emmanuel Joussein, Marilyne Soubrand, Alexandra Courtin-Nomade, Olivier Grauby, Valentin Robin, Sylvie Rossignol, Nathalie Texier Mandoki, Xavier Bourbon

Importance of (meta)kaolins crystallochemistry toward their alkali treatment reactivity

12:10-12:30 pm: Emilie Emmanuel, Michael Paris, Dimitri Deneel

Characterization and description of alkaline activation of raw kaolin

Session D2: LDH for future health: Advances and challenges in energy, environmental and medical applications – Auditorium

11:10-11:30 am: Nicholai D. Jensen, Suraj S.C. Pushparaj, Laura Lundehøj, Anders BA Andersen, Tae-Hyun Kim, Yusuke Nishiyama, Nghia Dong, Claude Forano, Vanessa Prevot, Ulla Gro Nielsen

Linking the properties of layered double hydroxides to their atomic level structure

11:30-11:50 am: Géraldine Layrac, Mathias Destarac, Simon Harrisson, Didier Tichit, Corine Gérardin

Synthesis of layered double hydroxides through a colloidal route: a comparative study of the behavior of Cu^{2+}/Al^{3+} and Mg^{2+}/Al^{3+} systems

11:50 am-12:10 pm: Iqra Zubair Awan, Giada Beltrami, Thomas Cacciaguerra, Annalisa Martucci, Stefania Albonetti, Fabrizio Cavani, Francesco Di Renzo

The riddle of Cu-layered double hydroxides solved by general principles of hydrotalcite synthesis

12:10-12:30 pm: Meriem Djellali, Pilar Aranda, Eduardo Ruiz-Hitzky

Silica-layered double hydroxide nanostructured materials

Lunch break

Auditorium

1:30-2:15 pm Clay Minerals Groups, Mineralogical Society – George Brown lecture:

Toshihiro Kogure: Visualization of Clays at the Atomic Scale

Introduction by Simon Kemp

Session A7: Characterization of clayey nanomaterials – Room #106

2:20-2:40 pm: Fabien Hubert, Jean-Christophe Viennet, Eleanor Bakker, Eric Ferrage, Bruno Lanson, Baptiste Dazas, Brian Grégoire, Emmanuel Tertre

Occurrence of mixed-layer minerals in temperate soils

2:40-3:00 pm: Eleanor Bakker, Bruno Lanson, Michelle M. Wander, Fabien Hubert

X-ray diffraction full-profile modelling as a tool to assess evolution of soil clay mineralogy arising from agronomic practices: Insights from the Morrow Plots experimental fields

3:00-3:20 pm: Paul A. Schroeder, Daniel D. Richter, Jason C. Austin

Quantification of mixed-layer clays in multiple saturation states using NEWMOD2: Implications for the potassium uplift hypothesis

3:20-3:40 pm: Zbigniew Zagórski, Wojciech Stępień, Łukasz Uzarowicz

Transformations of clay minerals in soils under the influence of chemical changes induced by long-term fertilizing experiments

3:40-4:00 pm: Bussaraporn Patarachao, Daniel Tyo, Andre Zborowski, Krystal Davis, Judy Kung, Samson Ng, Patrick Mercier

Profile Refinement for XRD Analysis of Illite-Smectite Interstratification in Clays from Athabasca Oil Sands

4:00-4:25 pm: Coffee break

Session A7: Characterization of clayey nanomaterials – Room #106

4:25-4:45 pm: G. Monet, S. Rouzière, E. Paineau, Z. Chai, L.-M. Liu, G. Teobaldi, P. Launois

Structural resolution of clay-like nanotubes

4:45-5:05 pm: Mathilde Poirier, Yannick Millot, Elisa Silva Gomes, Maguy Jaber, Virginie Herledan, Guillaume Laugel, Pierre Micoud, François Martin, Hélène Lauron-Pernot, Hervé Toulhoat

Probing the surface chemistry of nano-layered silicates: a combined experimental and theoretical approach

5:05-5:25 pm: Pierre Levitz, Laurent Michot

Structural modeling of flocculation of clay suspensions as probed by small angle scattering and TXM imagery: The q^{-3} dilemma

5:25-5:45 pm: G. Martin-Gassin, B. Gregoire, B. Prelot, P.M. Gassin

Molecular adsorption at layered interfaces investigated by Second Harmonic Scattering

5:45-6:05 pm: Brian Grégoire, Laurent Grasset, Fabien Hubert, Eric Ferrage, Emmanuel Tertre, Baptiste Dazas, Thomas Dabat, Sabine Petit

Model-Based Analysis of organo-clay thin films experimentally probed by polarized ATR-FTIR spectroscopy

6:05-6:25 pm: Stephen Hillier, Jeff Armstrong, Nia Gray, Tom Headen, Sanghamitra Mukhopadhyay, Andrew Seel, Aasim Shaffi, Neal Skipper

Neutron scattering experiments to determine the structure and dynamics of interlayer H_2O in halloysite nanotubes

Session E2: General session – Room #108

2:25-2:45 pm: Javier García-Rivas, Mercedes Suárez, Emilia García-Romero

On the influence of the presence of oriented fibers within random powders of palygorskite in X-Ray diffractograms

2:45-3:05 pm: Aron Knoblich, Reinhard Kleeberg

Improving the preparation method and structural description of illite-smectite interstratifications for X-ray powder diffraction analysis

3:05-3:25 pm: Alena Kremleva, Sven Krüger, Notker Rösch

Quantum chemical modelling of Fe(III) and Fe(II) in 2:1 dioctahedral smectites

3:25-3:45 pm: Erick Ramanaidou, Ian C Lau, Monica leGras

A toolkit for the characterization of kaolinite and smectite in the mining industry

3:45-4:05 pm: Amélia Paula Reis, Cristiana Costa, Denise Terroso, Fernando Rocha

Mineralogy of indoor dust collected from households in urban and peri-urban areas of Estarreja, an industrial Portuguese city

4:05-4:30 pm: Coffee break

Session E2: General session – Room #108

4:30-4:50 pm: Marie-Noëlle de Noirfontaine, Mireille Courtial, Sandrine Tusseau-Nenez, Frédéric Dunstetter, Dominique Gorse-Pomonti

Electron radiation damages to lamellar hydroxides: the case of portlandite and brucite

4:50-5:10 pm: Thierry Allard, Celia Montes, Guilherme TaitsonBueno, Luciana Peirera, Bruna Fernandes Soares, Nadia do Nascimento, Maximilien Mathian, Etienne Balan, Cécile Gautheron

Dating supergene kaolinites by electron paramagnetic resonance spectroscopy: what have we learned from the latest studies?

5:10-5:30 pm: Maximilien Mathian, Guilherme Taitson Bueno, Etienne Balan, Madeleine Selo, Emmanuel Fritsch, Thierry Allard

Investigating the Acrisol/Ferralsol transition in Amazonia: new insights from EPR dating of kaolinites

5:30-5:50 pm: Noémi M. Nagy, Eszter Mária Kovács, Dóra Buzetzky, József Kónya

Phosphate sorption of soils with different clay content

5:50-6:10 pm: Fugen Dou, Xiufen Li, Youjun Deng

Effect of vermiculite clays on the performance of urease inhibitors in soil ammonia volatilization

6:10-6:30 pm: Nikolaos Athanasakis, Georgios E. Christidis Demetrios Marinakis

Rheological properties of trioctahedral smectite and sepiolite suspensions after dynamic aging at High Temperatures

Session B1: Clay minerals in fracture zones – Room #105

2:30-2:50 pm: Arkadiusz Derkowski, Marek Szczerba, Małgorzata Lempart, Artur Kuligiewicz

Is dehydroxylation a sole trigger of radiogenic argon diffusion in micas?

2:50-3:10 pm: I. Tonguç Uysal

Rb–Sr dating of fault gouges

3:10-3:30 pm: Jeremy Rushton, Simon J. Kemp, David Schofield, Antoni Milodowski, Matthew Horstwood, Horst Zwingman, Matthew Free, Ben Gilson

Clay minerals as a key to seismic hazard assessment for a New Nuclear Build: Wylfa Head, Anglesey, North Wales

3:30-3:50 pm: Ahmed Abd Elmola, Martine Buatier, Patrick Monié, Delphine Charpentier, Pierre Labaume

^{40}Ar/^{39}Ar radiometric dating of thrust activity using synkinematic clay minerals: a case study from the Axial Zone of the Pyrenees

3:50-4:15 pm: Coffee break

Session B1: Clay minerals in fracture zones – Room #105

4:15-4:35 pm: Delphine Charpentier, Ahmed Abd Elmola, Martine Buatier, Manuel Munoz, Gaetan Milesi, Vincent Trincal, Pierre Lanari, Pierre Labaume

Redox conditions registrated by phyllosilicates in a thrust fault (Pic de Port Vieux fault, Pyrenees)

4:35-4:55 pm: Masakazu Niwa, Koji Shimada, Shigeru Sueoka

Thermal constraints on clay growth in fault gouge and their relationship with fault zone evolution: Case study of gouges from granitic rock in central Japan

4:55-5:15 pm: Balboa I., Suárez M., Gómez-Barreiro J., García-Romero E.

Mineralogical changes related to a fault zone: La Barquilla fault zone, Salamanca, Spain

Session B6: The role of clay minerals in the origin of life – Room #105

5:15-5:35 pm: J.-C. Viennet, S. Bernard, P. Jacquemot, C. Le Guillou, E. Balan, L. Delbes, B. Rigaud, T. Georgelin, M. Jaber

Searching for organic biosignatures on Mars: Experimental perspectives

5:35-5.55 pm: Joseph R. Michalski

Formation of clay minerals in the earliest phases of geological activity on Mars, with implications for origin of life

5:55-6:15 pm: Fabien Baron, Anne Gaudin, Jean-Pierre Lorand, Nicolas Mangold

New constraints on Early Mars weathering conditions from an experimental approach on rock simulants

Session C3: Thermal reactions of clays and their application in sustainable construction materials – Room #109

2:25-2:45 pm: Svetlana Petlitckaia, Sylvie Rossignol, Ameni Gharzouni, Nathalie Texier-Mandoki, Xavier Bourbon

Thermal behavior of several clay mixtures

2:45-3:05 pm: Ameni Gharzouni , Isabel Sobrados, Sylvie Rossignol

Reactivity of different flash-calcined clays for geopolymer synthesis

3:05-3:25 pm: Colin Dupuy, Ameni Gharzouni, Nathalie Texier-Mandoki, Xavier Bourbon, Sylvie Rossignol

Control of the binder setting time, pH value and viscosity of the Callovo-Oxfordian argillite in alkali-activated grout – role of additives

3:25-3:45 pm: Ugo De Filippis, Elodie Prud'homme, Sylvain Meille

Study of the interaction between clays and alkali-activated slag's hydrates in stabilized poured earth concrete

3:45-4:05 pm: Stephan Partschefeld, Adrian Tutal, Jens Schneider, Andrea Osburg

Flow agents for calcium-free binder systems

4:05-4:35 pm: Coffee break

Session C2: Geotechnical characterization of clayey geomaterials from micro to macro scale: The role of microstructure and anisotropy – Room #109

4:35-4:55 pm: Myriam Duc, Alain Le Kouby, Fabien Szymkiewicz, Joali Paredes-Marino

Behavior of clay-rich soil /cement mixtures prepared by deep soil mixing method

4:55-5:15 pm: Candy Mariel Juego and Petronilo Paña

Geotechnical Characterization of Zeolite Deposits in Mangatarem, Pangasinan, Philippines

5:15-5:35 pm: Laila Mesrar, Ahmed Benamar, Anne Pantet , Hamza Mesrar, Raouf Jabrane

Physical and mechanical properties improvement of Miocene marls (Morocco) after doping with metal oxide

5:35-5:55 pm: Fernando Rocha, Cristiana Costa, Deborah Arduin

Alkaline activation of rammed earth material – properties improvement for sustainable conservation and rehabilitation

5:55-6:15 pm: Timothy Wangler

Swelling damage and inhibition in a Swiss clay-bearing heritage sandstone

Session D2: LDH for future health: Advances and challenges in energy, environmental and medical applications – Auditorium

2:20-2:40 pm: Vanessa Prevot, Mohamed Mousa, Marko Pavlovic, Istvan Szilagyi, Claude Forano

Aerosol approach toward functional nanostructured Layered Double Hydroxide microspheres

2:40:3:00 pm: Laura Lundehøj, Cejna A. Quist-Jensen, Claude Forano, Vanessa Prevot, Morten L. Christensen, Ulla G. Nielsen

Toward the use of layered double hydroxides for phosphate recycling from wastewater

3:00-3:20 pm: Martine Mallet, Mustapha Abdelmoula, Zhou Yin, Hans Christian Hansen, Christian Ruby

Structural and phosphate adsorption properties of nano-sized ferric oxyhydroxides produced by oxidation of Fe^{II}-Fe^{III} layered double hydroxides (green rust)

3:20-3:40 pm: Chérif Morcos, Alain Seron, Romain Rodrigues, Ioannis Ignatiadis, Theodore Tzedakis, Stéphanie Betelu

Electrolytically supported processes of capture and release of CO_2

3:40-4:00 pm: Grégory Lefèvre, Thomas Degabriel, Athénaïs Davantès, Dominique Costa

Layered double hydroxides and polyoxometalates: the perfect match

4:00-4:25 pm: Coffee break

Session D2: LDH for future health: Advances and challenges in energy, environmental and medical applications – Auditorium

4:25-4:45 pm: Domenica Tonelli, Elisa Musella, Isacco Gualandi, Erika Scavetta, Marco Giorgetti

Layered Double Hydroxides for energy applications

4:45-5:05 pm: Noriyuki Sonoyama, Satoshi Yoshida, Takashi Inaba, Atsushi Nakayabu

Reaction Mechanism of Layered Double Hydroxide as the Cathode Material of Nickel Secondary Battery

5:05-5:25 pm: Hani Farhat, Claude Forano, Christine Mousty

Glucose oxidase@CoMn Layered Double Hydroxides modified electrodes for electrochemical detection of glucose

5:25-5:45 pm: Gilles Villemure

Preparation of a Ni-Al-LDH Containing Intercalated Borate Counter Ions. Comparison of its Storage Capacity with Similar LDHs Containing other Counter Ions for Use as Cathode Materiel in Nickel Secondary Cells

5:45-6:05 pm: Manon Wilhelm, Alexandre C. Bastos, João Tedim, Mário S.G. Ferreira

Determination of relevant parameters for the design of Ni-Fe layered double hydroxide based electrocatalysts for water splitting

6:05-6:25 pm: Daojin Zhou, Pengsong Li, Xiaoming Sun

Layered double hydroxides-based catalysts for electrochemical water splitting

Patio 44-55

6:30-8:30 pm Poster session #1 – Posters from sessions A2, A5, A7, B1, B3, B4, C2, C3, D2, D5, D8, E2

Wine & Cheese welcome party

Tuesday July 2nd

Hall Auditorium

From 8:00 am: Registration and badge pick-up

Auditorium

8:30-9:25 am Clay Minerals Society – Bailey Distinguished member award:

Dennis D. Eberl: Memoir of an Illitist
Introduction by Lynda Williams

Session A7: Characterization of clayey nanomaterials – Room #106

9:30-9:50 am: Mark Raven, Peter Self

Dehydration and intercalation behavior of the unique "Patch Clay" halloysite using in-situ XRD

9:50-10:10 am: Myriam I. Agnel, Sylvain Grangeon, François Fauth, Erik Elkaïm, Francis Claret, Marjorie Roulet, Fabienne Warmont, Christophe Tournassat

Ion exchange in fougèrite: influence of crystal size and structural defects

10:10-10:30 am: Stephan Kaufhold, Reiner Dohrmann

About the Critical Coagulation Concentration of Allophane and dioctahedral Smectite

10:30-10:50 am: Youjun Deng, Darren Andrew Chevis, Chia-Wei Lin

Ion sieving effects on Cs incorporation and exchange in cancrinite and sodalite formed in highly alkaline solutions

10:50-11:20 am: Coffee break

Session A2: Experimental and numerical analysis of clay systems: Bridging time and length scales – Room #106

11:20 am-12:00 pm: Simon R. Larsen, Laurie P. Aldridge, Leander Michels, Will P. Gates, Éverton C. dos Santos, Leide P. Cavalcanti, Jon Otto Fossum, Heloisa N. Bordallo (**keynote lecture**)

Water mobility and its influence in the capture and retention of CO_2 in the interlayer space of Fluorohectorite clay minerals

12:00-12:20 pm: Marek Szczerba, Douglas K. McCarty, Arkadiusz Derkowski

Molecular dynamics simulations of interactions of organic molecules found in oil with smectite: influence of brine chemistry on oil recovery

12:20-12:40 pm: R. James Kirkpatrick, Geoffrey M. Bowers, H. Todd Schaef, John S. Loring, Eric D. Walter, Sarah D. Burton, David W. Hoyt, Sydney S. Cunniff, Randolph K. Larsen IV

Chemical trapping of CO_2 by smectite clays under supercritical conditions

Session A5: Multi-scale understanding of interface redox reactions – Room #108

9:45-10:15 am: Caroline Peacock, Amy Atkins, Sam Shaw, Zhongkuan Wu, Xionghan Feng, Fan Liu (**keynote lecture**)

Mineralogical controls on Earth's climate

10:15-10:35 am: Marina Karpov, Bettina Seiwert, Vered Mordehay, Thorsten Reemtsma, Tamara Polubesova, Benny Chefetz

Mechanisms of oxytetracycline oxidation by Fe(III)- and Mn(IV)-containing minerals

10:35-10:55 am: Lorella Masci, Benoît Dubacq, Anne Verlaguet, Christian Chopin, Franck Bourdelle, Vincent De Andrade, Julien Siebert, Nicolas Wehr, Clément Herviou, Laura Airaghi

A XANES, EELS and EPMA study of Fe^{3+} in natural and synthetic chlorite: Substitutions and importance of oxychlorite

10:55-11:25 am: Coffee break

Session A5: Multi-scale understanding of interface redox reactions – Room #108

11:25-11:55 am: Michel Sassi, Anxu Sheng, Odeta Qafoku, Mark E. Bowden, Alpha T. N'Diaye, Carolyn I. Pearce, Richard N. Collins, Juan Liu, Kevin M. Rosso (**keynote lecture**)

Atomically-Resolved Transformation Pathways of Ferrihydrite to Goethite

11:55 am-12:15 pm: James Entwistle, Maggie White, Drew E. Latta, Michelle M. Scherer, Anke Neumann

Mixed-valent iron precipitates formed via interfacial electron transfer at clay minerals control chlorinated contaminant reduction

12:15-12:35 pm: Martine Gérard, Florian Lahrouch, Aisha Kanzari, Michael Descostes

Migration and stabilization of uranium in clayey weathered waste rocks

Session B6: The role of clay minerals in the origin of life – Room #105

9:40-10:00 am: Isabelle Daniel, Jihua Hao, Ulysse Pedreira-Segade, Hervé Cardon, Laurent Michot

Effect of pressure on the adsorption on nucleotides on clays – would this favor the emergence of life on the Hadean ocean floor?

10:00-10:20 am: Hussein Jaafar Kanbar, Michael Holmboe

Linking the geochemical composition of lake sediments to DNA sorption and preservation

10:20-10:40 am: Xiandong Liu, Yingchun Zhang, Xiancai Lu (**invited lecture**)

Surface complexation of organic groups on clay surfaces: insight from first principles simulations

10:40-11:10 am: Coffee break

Session B6: The role of clay minerals in the origin of life – Room #105

11:10-11:30 am: Bénédicte Ménez, Céline Pisapia, Muriel Andreani, Frédéric Jamme, Quentin P. Vanbellingen, Alain Brunelle, Laurent Richard, Paul Dumas, Matthieu Réfrégiers (**keynote lecture**)

On the key role of Fe-rich saponite for the abiotic synthesis of amino acids in the oceanic lithosphere

11:30-11:50 am: Pierre Mignon, Jihua Hao, Isabelle Daniel, Mariona Sodupe

Adsorption of RNA/DNA nucleobases and nucleotides on clay surfaces. On the role of mineral composition

11:50 am-12:10 pm: Pierre Jacquemot, Maguy Jaber, Sylvain Bernard, Thomas Georgelin

Experimental fossilization of biomolecules and micro-organisms in clays

12:10-12:30 pm: Jean-François Lambert, Maguy Jaber, Thomas Georgelin, Gianmario Martra, Yuriy Sakhno

How good are clay minerals for biopolymers formation?

Session C2: Geotechnical characterization of clayey geomaterials from micro to macro scale: The role of microstructure and anisotropy – Room #109

9:35-9:55 am: Katherine L. Hull, Younane N. Abousleiman

In Situ Scanning Electron Microscopy Analysis of Nanoindentation Pop-Ins in High Clay Content Shale

9:55-10:15 am: Marine Bonnet, Laurent Caner, Paul Sardini

Mineralogical and petrographic characterisations of a granite weathering profile from South Brazil

10:15-10:35 am: Yiming Liu, Xinchao Liao, Guofang Xu, Henglin Xiao

Influence of principal stress direction on mechanical behavior of rocks by three-dimensional discrete element method analyses

10:35-10:55 am: Kexin Yin, Anne-Laure Fauchille, Khaoula Othmani, Giulio Sciarra, Panagiotis Kotronis, Francois Bertrand, Yannick Benoit, Samuel Branchu

Influence of sample preparation on the microstructure of sand-clay mixtures

10:55-11:25 am: Coffee break

Session C2: Geotechnical characterization of clayey geomaterials from micro to macro scale: The role of microstructure and anisotropy – Room #109

11:25-11:45 am: Christina Kapralou, Thanasis Karalis, Monika Zervaki, Christos Dedeloudis

Bentonite low permeability barrier in highly ionic strength environment: interaction with silica

11:45 am-12:05 pm: Nadia Mokni, Agustín Molinero Guerra, Yu-Jun Cui, Pierre Delage, Patrick Aimedieu, Michel Bornert, Anh Minh Tang

Impact of initial structural heterogeneities on the long term hydro-mechanical behaviour of a bentonite pellet/powder mixture. Experimental and modelling results

12:05-12:25 pm: Matthias Schellhorn, Ralf Diedel, Katja Emmerich, Florian Christ, Wiebke Baille

Composition and properties of Westerwald bentonites and their usage for high swelling pressure sealing in underground mining and nuclear waste deposits

12:25-12:45 pm: María Victoria Villar, Rubén Javier Iglesias, Ana María Melón

Changes in the exchangeable cation complex of montmorillonite during oedometer tests

Session D2: LDH for future health: Advances and challenges in energy, environmental and medical applications – Auditorium

9:40-10:00 am: Paul Legentil', Geneviève Chadeyron, Fabrice Leroux, Sandrine Therias, Anthony Barros, Rodolphe Valleix, Philippe Boutinaud and Damien Boyer

Enhanced stability of quantum dots InP/ZnS by intercalation in a layered double hydroxides matrix to provide sustainable solutions for lighting applications

10:00-10:20 am: Elise Duquesne, Stéphanie Betelu, Denis Limagne, Michel Goldmann, Cyrille Bazin, Alain Seron, Ioannis Ignatiadis, Hubert Perrot, Ozlem Sel, Catherine Debiemme-Chouvy

In the depth understanding of reversible ionic transfers of Layered Double Hydroxides by *in operando* electrochemical and gravimetric measurements coupled with Grazing Incidence Wide Angle X-ray Scattering

10:20-10:40 am: Vera R. Leopoldo Constantino

Layered Double Hydroxides and their nanohybrids: characterization, biocompatibility, and biological activities

10:40-11:00 am: Nawal Fodil Cherif, Vanessa Prévot, Oualid Hamdaoui, Fabrice Leroux, Vera R. Leopoldo Constantino, Christine Taviot-Gueho

Layered double hydroxides @ Fe_3O_4 nanoparticles for drug release of ciprofloxacin

11:00-11:30 am: Coffee break

Session D2: LDH for future health: Advances and challenges in energy, environmental and medical applications – Auditorium

11:30-11:50 am: Corina Eugenia Ignat, Iuliana Biru, Horia Iovu, Gabriela Carja

On the tunability of micro/nanoparticulates of ibuprofen/layered double hydroxides dry-powders for targeting pulmonary delivery

11:50 am- 12:10 pm: Mariana Pires Figueiredo, Alfredo Duarte, Christine Taviot-Gueho, Fabrice Leroux, Vera Regina Leopoldo Constantino

Iron-based layered double hydroxides as drug carriers: advantages and challenges

12:10-12:30 pm: Hyoung-Jun Kim, Sung Hoon Kim, Yoon Suk Kim, Jae-Min Oh

Surface roughness dependent cellular uptake behavior of layered double hydroxide nanoparticle

12:30-12:50 pm: Yasuaki Tokudome, Gowsihan Poologasundarampillai, Kenji Okada, Masahide Takahashi

Layered Double Hydroxide Nanoclusters toward Correlative Imaging in Biomedical Applications

Lunch break

Session A2: Experimental and numerical analysis of clay systems: Bridging time and length scales – Room #106

2:20-2:40 pm: Narasimhan Loganathan, Geoffrey M. Bowers, Brice F. Ngouana Wakou, Andrey G. Kalinichev, R. James Kirkpatrick, A. Ozgur Yazaydin

Methane/carbon dioxide partitioning in clay nano- and meso-pores: molecular dynamics modeling with constant reservoir composition

2:40-3:00 pm: C. Ignacio Sainz-Díaz, A. Borrego-Sánchez

Adsorption of pharmaceutical compounds confined in clay nanospaces by molecular modeling

3:00-3:20 pm: Jennifer A.R. Willemsen, Satish C.B. Myneni, Ian C. Bourg

Adsorption of phthalate esters on smectite clay surfaces: a molecular dynamics simulation and experimental study

3:20-3:40 pm: Vassilis Gionis, Georgios D. Chryssikos

Reactions on clay surfaces monitored by infrared spectroscopy

3:40-4:10 pm: Coffee break

Session A2: Experimental and numerical analysis of clay systems: Bridging time and length scales – Room #106

4:10-4:30 pm: Laurent Brochard, Tulio Honorio

Thermo-poro-mechanics under adsorption capturing the anomalous thermal pressurization of water in clay

4:30-4:50 pm: Sara Bandera, Catherine O’Sullivan, Stefano Angioletti-Uberti, Paul Tangney

Particle-scale simulation of clay compression

4:50-5:10 pm: Doriana Vinci, Bruno Lanson, Martine Lanson, Valérie Magnin, Nathaniel Findling, Baptiste Dazas, Eric Ferrage

Influence of Layer Charge (Location and Amount) on the Hydration Properties of Synthetic Na-Saturated Smectites

5:10-5:30 pm: Leander Michels, Yves Méheust, Mario A. S. Altoé, Éverton C. dos Santos, Henrik Hemmen, Roosevelt Droppa Jr., Jon O. Fossum, Geraldo J. da Silva

Water vapor diffusive transport in a smectite clay: Cationic control of normal versus anomalous diffusion

Session B4: Mudrocks: Composition, fabric, and provenance - Fundamental research and practical applications of the data – Room #108

2:15-2:35 pm: H. Albert Gilg

A new genetic classification of bentonite deposits

2:35-2:55 pm: Michael Wilson, Andrew Hurst, Anne Wilkins, Lyudmyla Wilson, Leon Bowen

Multiple aeolian dust parageneses in loessite: mineralogical evidence for the volcanic contribution from the Early Triassic of the Central North Sea

2:55-3:15 pm: Giovanni Zanoni, Branimir Šegvić, Thomas Boulesteix, Jesús Solé

Crystal growth of illite in Pennsylvanian shale of the American Mid-Continent region – inferences from clay mineralogy and K-Ar ages

3:15-3:35 pm: Andrea Schicker, Susanne Gier, Jürgen Schieber, Peter Krois

Diagenesis of a Malmian source rock, Vienna Basin: Focus on matrix and pores

3:35-4:05 pm: Coffee break

Session B4: Mudrocks: Composition, fabric, and provenance - Fundamental research and practical applications of the data – Room #108

4:05-4:25 pm: Rute Coimbra, Fernando Rocha, Federico Olóriz

3D mapping of mineralogical (XRD) data: method and applications

4:25-4:45 pm: Jean-François Deconinck, Stephen P. Hesselbo, Pierre Pellenard

Climatic and sea-level control of Pliensbachian clay mineral sedimentation in the Cardigan Bay Basin, Llanbedr (Mochras Farm) borehole Wales

4:45-5:05 pm: Catherine Lerouge, Mathieu Debure, Jacques Brulhet, Christine Fléhoc, Sylvain Grangeon, Catherine Guerrot, Benoit Henry, Nicolas Maubec, Romain Millot, Eric Proust, Philippe Landrein, Benoit Madé, Francis Claret, Jean-Charles Robinet

Weathering processes in the Gault Clay formation, Paris Basin

5:05-5:25 pm: Larissa de Santana do Nascimento, Everton Bongiolo, Reiner Neumann, James B. Gill, Ann-Sophie Jonas

The role of Kuroshio Current in the sedimentation of Izu-Bonin-Mariana rear arc (IODP Expedition 350): evidence from clay minerals (<1 Ma)

Session B3: Clays and organic matter – Room #105

2:10-2:30 pm: Balwant Singh, Sabina Yeasmin (**inivited lecture**)

The role of clay minerals in the preservation of organic carbon in the soil

2:30-2:50 pm: Tatiana Alekseeva, Berta Zolotareva

Soil humin and kerogen. Clay mineralogy stabilizing effect

2:50-3:10 pm: Thibault Duteil,Raphael Bourillot, Pieter Visscher, Brian Gregoire, Olivier Braissant, Benjamin Brigaud, Maxime Virolle, Julius Nouet, Eric Portier, Patricia Patrier, Etienne Gontier, Isabelle Svahn

Biofilm exopolymeric substances induce the aggregation of clay and sand in sedimentary environments

3:10-3:30 pm: Marie-Agnès Courty , Ahmad Hamdan, Jean-Michel Martinez, Erwan Oliviero

Longlived organo-clay nanocomposites formed in the atmosphere by plasma discharges

3:30-4:00 pm: Coffee break

Session B3: Clays and organic matter – Room #105

4:00-4:30 pm: Wenlu Li, Peng Liao, Trey Oldham, Yi Jiang, Chao Pan, Songhu Yuan, John D. Fortner (**keynote lecture**)

Real-time Evaluation of Natural Organic Matter Deposition Processes onto Model Environmental Surfaces

4:30-4:50 pm: Tamara Polubesova, Shani Avneri-Katz, Yaniv Olshansky, Robert B. Young, Thomas Borch, Benny Chefetz

Adsorptive transformation of organic matter by mineral surfaces

4:50-5:10 pm: Herve Goure-Doubi, Céline Martias, Agnès Smith, Nicolas Villandier, Vincent Sol, Vincent Gloaguen, Geneviève Feuillade

Adsorption of fulvic and humic like acids on surfaces of clays: relation with SUVA index and acidity

5:10-5:30 pm: Paweł P. Ziemiański, Arkadiusz Derkowski, Marek Szczerba

High-pressure adsorption of methane on clay minerals – texture versus structure

Session C2: Geotechnical characterization of clayey geomaterials from micro to macro scale: The role of microstructure and anisotropy – Room #109

2:25-2:45 pm: Thomas Dabat, Fabien Hubert, Erwan Paineau, Pascale Launois, Claude Laforest, Brian Grégoire, Baptiste Dazas, Emmanuel Tertre, Alfred Delville, Eric Ferrage

A general orientation distribution function for clay particles

2:45-3:05 pm: Florian Christ, Matthias Schellhorn, Frank Diedel, Wiebke Baille

Effect of compaction induced anisotropy on the swelling pressure development of a natural Ca-saponite

3:05-3:25 pm: Maoz Dor, Yael Mishael′ , Simon Emmanuel

Effect of Salinity on Clay-Mineral Nano- to Micron-Structural Assembly: Characterization by AFM, cryo-TEM and Cryo-SEM

3:25-3:45 pm: Laurent Arbaret, Yasmina Boussafir

Effect of wetting and drying cycles on compacted silt from Loire's Levee: evolution of permeability and 3D textural analyses with X-Ray tomography

3:45-4:15 pm: Coffee break

Session D8: Clays and health: From pelotherapy to drug delivery – Room #109

4:15-4:35 pm: Rocío García-Vázquez, Ediana P. Rebitski, Lucia Viejo, Cristobal de los Ríos, Eva M. García-Frutos, Margarita Darder

Clay-based bionanocomposites for controlled delivery of neuroprotective drugs in the treatment of Alzheimer’s disease

4:35-4:55 pm: Yusuke Toyota, Masami Okamoto, Shuichi Arakawa

New opportunities for drug delivery carrier of natural allophane nanoparticles on human lung cancer A549 cells

4:55-5:15 pm: Grace Anne O. Galingana, Bethune Karla B. Cortez, Mitch-Irene Kate G. Oyales, Leslie Joy L. Diaz

Functionalization of montmorillonite clay via intercalation of amino acids for anti-acne clay mask formulation

5:15-5:35 pm: Ruth Osovsky, Shiraz Cherf , Shiri Karagach, Yael Mishael

Decontamination of Sarin in Water by Designed Oxime-Clay Composites

Session D5: Frontier and new applications of clay colloids – Auditorium

2:10-2:30 pm: Jun Kawamata, Yuki Higashi, Takashi Nagashita, Yasutaka Suzuki, Teruyuki Nakato, Toshiaki Iwai

Optical manipulation of oxide nanosheets

2:30-2:50 pm: Erwan Paineau, Geoffrey Monet, Véronique Peyre, Claire Goldmann, Stéphan Rouzière, Pascale Launois

Colloidal properties of imogolite nanotubes

2:50-3:10 pm: Kazuhiro Shikinaka

Stimuli-responsive colloidal assembly consisting of imogolite, cylindrical clay

3:10-3:30 pm: Ahmed Aït Aghzzaf Aziza Khalil, Benaïssa Rhouta, Emmanuel Rocca, Delphine Veys-Renaux

Functionalized clay minerals as “smart materials” for corrosion inhibition in paints

3:30-4:00 pm: Coffee break

Session D5: Frontier and new applications of clay colloids – Auditorium

4:00-4:20 pm: Theresa Schilling, Zuyuan Wang, Konrad Rolle, Patrick Hummel, Alexandra Philipp, George Fytas, Markus Retsch, Josef Breu

Tunable thermoelastic anisotropy in Bragg stacks with extreme polymer confinement

4:20-4:40 pm: Zoltán Somosi, István Szilágyi, István Pálinkó

Influence of Polyelectrolyte Mono- and Bilayer Formation on the Charging and Aggregation of Layered Double Hydroxide Nanoparticles

4:40-5:00 pm: Teruyuki Nakato, Wataru Ishitobi, Miho Yabuuchi, Emiko Mouri

Electric alignment of liquid crystalline binary colloids of niobate and clay nanosheets

5:00-5:20 pm: Riki Kato, Ryo Iwashita, Nobuyoshi Miyamoto

Liquid crystal phase of clay nanosheet dispersed in *N*, *N*-dimethylformaide / water mixture

Patio 44-55

5:30-7:30 pm Poster session #2 - Posters from sessions A1, A3, A4, B2, B6, B7, C4, D1, D3, D6, D7, E1

Thursday July 4th

Hall Auditorium

From 8:00 am: Registration and badge pick-up

Auditorium

8:30-9:25 am Clay Minerals Society – Marion L. and Chrystie M. Jackson mid-career award:

Colleen Hansel: How microbes break the cryptic manganese cycle to form manganese oxides
Introduction by Yuanzhi Tang

Session A2: Experimental and numerical analysis of clay systems: Bridging time and length scales – Room #106

9:40-10:20 am: Yasine Sakhawoth, Laurent Michot, Pierre Levitz, Anne-Laure Rollet, Juliette Sirieix-Plénet, Natalie Malikova (**keynote lecture**)

Flocculation of clay colloids: combining scattering and imagining techniques

10:20-10:40 am: Thomas R. Underwood, Ian C. Bourg

Properties of clay-rich fine-grained sedimentary rocks from large scale molecular dynamics simulations

10:40-11:10 am: Coffee break

Session A2: Experimental and numerical analysis of clay systems: Bridging time and length scales – Room #106

11:10-11:30 am: Maria Jansson, Samuel Lenton, Tomás S. Plivelic, Marie Skepö

Structural behavior of Na-Laponite clay dispersions upon addition of charged polymers

11:30-11:50 am: Emmanuel Tertre, Baptiste Dazas, Frederick Delay, Alfred Delville, Fabien Hubert, Brian Gregoire, Eric Ferrage

Finite element model constrained by self-diffusion and selectivity coefficients to predict the dynamic exchange of cations in the interlayer of swelling clay minerals

11:50 am-12:10 pm: Jeffery A. Greathouse, Tuan A. Ho, Louise J. Criscenti

Mechanism of montmorillonite interlayer hydration from potential of mean force molecular dynamics simulations

12:10-12:30 pm: Pauline Simonnin, Virginie Marry, Benoît Noetinger, Carlos Nieto-Draghi, Benjamin Rotenberg

Mineral- and Ion-Specific Effects at Clay−Water Interfaces: Structure, Diffusion, and Hydrodynamics

Session B4: Mudrocks: Composition, fabric, and provenance - Fundamental research and practical applications of the data – Room #108

9:45-10:05 am: Gourfi A., Daoudi L., Rhoujjati A., Benkaddour A., Fagel N.

Clay sedimentation control in dam reservoir of a semi-arid region: example of Takerkoust (Western High Atlas, Morocco)

10:05-10:25 am: Katarzyna Górniak

Cemented micro-scale fractures in impure chalk sequence: towards understanding clay origin in black chalk exemplified by the Grybów Marls (Oligocene, Outer Carpathians, Poland)

10:25-10:45 am: Gaël Cherfallot, Pierre Levitz, Loïc Barré, Pauline Michel, Eric Kohler

Mudrocks pore space storage capacities investigated by small-angle neutron scattering intensities ratio

10:45-11:15 am: Coffee break

Session B2: The role of clays and modified clays in remediating environmental pollutants – Room #108

11:15-11:55 am: Lydie Le Forestier (**keynote lecture**)

Are clays relevant materials to have both high sorption and suitable hydraulic properties for the retention of metal pollutants and pharmaceuticals ? Application to waste landfill and waste water treatment

11:55 am-12:15 pm: Tomasz Bajda, Magdalena Tuchowska, Barbara Muir, Mariola Kowalik, Robert P. Socha

Sorption of molybdates and tungstates on modified smectites

12:15-12:35 pm: Saba Akbar, Mohammad Saleem Akhtar, Ahmad Khan, Biao Huang, Aiqin Wang, Mazhar Iqbal, Youjun Deng

Efficacy of indigenous clays of Pakistan in reducing the toxicity of aflatoxin to broiler chickens

Session B3: Clays and organic matter – Room #105

9:30-9:50 am: Jock Churchman

Effects of additions of organic matter or clays on carbon retention in soils

9:50-10:10 am: Andrey Alekseev, Tatiana Alekseeva, Pavel Kalinin, Genady Mitenko, Aleksandr Buhonov

Clay-organic complexes of the modern steppe soils and paleosols of East European Plain of Russia in relationship with climatic parameters

10:10-10:30 am: Sofia N. Lessovaia

Clay mineral assemblages and organic matter in stony soils of cold environment

10:30-10:50 am: Wenfeng Tan, Mingxia Wang, Luuk Koopal

A vision for transformation of iron oxides with organic molecules and their effect on soil aggregates

10:50-11:20 am: Coffee break

Session B3: Clays and organic matter – Room #105

11:20-11:40 am: Francesca Sollecito, Alain Emmenegger, Michael Plötze, Alexander M. Puzrin, Claudia Vitone, Federica Cotecchia

The influence of organic contaminants on clayey soil plasticity and strength

11:40 am-12:00 pm: Nikolaos Apeiranthitis, H. Chris Greenwell, Anke Neumann, Cedric Carteret

Na-Ca-K cation selectivity in reduced iron-bearing clay minerals and implications to low-salinity water flooding

12:00-12:20 pm: Nipada Santha, Pablo Cubillas, Chris Greenwell

Analysis of TGA-MS investigations on oil compounds adsorption on kaolinite and pyrophyllite

12:20-12:40 pm: Daniel Svensson, Birgitta Kalinowski, Patrik Sellin, Stephanie Turner, Mark Dobson

The activity of sulfate reducing bacteria in bentonite as a function of water and lactate availability

Session D6: Archaeoceramics: Raw materials, technology and provenance – Room #109

9:35-9:55 am: Corina Ionescu, Volker Hoeck

Multi-analytical approach of the composition and provenance of ancient ceramics

9:55-10:15 am: Marie-Agnès Courty, Valentine Roux

Unusual clay pastes of Southern Levant Chalcolithic ceramics linking exceptional meteorological events and population dispersal

10:15-10:35 am: Delia Carloni, Branimir Šegvić, Mario Sartori, Giovanni Zanoni, Marie Besse

On a variety of clay matrices of prehistoric pottery from the megalithic cemetery of Petit-Chasseur site (Sion, Western Switzerland) – the tool to investigate cultural identities?

10:35-10:55 am: Zoila Luz Epossi Ntah-Kroll, Jacques Richard Maché, Giuseppe Cultrone

Mineralogical, chemical and physical study of ceramics from Nditam (Centre, Cameroon/ west central Africa): preliminary results

10:55-11:25 am: Coffee break

Session D6: Archaeoceramics: Raw materials, technology and provenance – Room #109

11:25-11:45 am: Alberta Arena, Giacomo Eramo, Italo M. Muntoni, Vedran Barbarić, Irena Radić Rossi

Technology vs. typology transfer in seaborne interactions: the Bronze Age

pottery in Central Adriatic

11:45 am-12:05 pm: Martin Auer, Barbara Borgers, Corina Ionescu, Franz Neubauer, Zsolt Kasztovszky, Katalin Gméling

Compositional and Technological characterisation of 2nd-5th c. AD ceramic bowls in south-western Austria

12:05-12:25 pm: Elisabetta Gliozzo, Maria Turchiano

Clay availability, ceramic production and import: the case of Apulian pottery and building materials.

12:25-12:45 pm: El Halim M., Daoudi L., El Alaoui El Fels A., Rebbouh L., El Ouahabi M., Fagel N.

Characterization and evolution over time of chemical composition of Moroccan architectural ceramics glazes: example of Saadian tombs

Session D1: Recent Progress on Nanotechnology and Nanomaterials from Clay Minerals – Auditorium

9:30-10:00 am: Goeun Choi, Jin-Ho Choy (**keynote lecture**)

A New Challenge for Boron Neutron Capture Therapy; Clay Nanovehicle Smuggles ^{10}B Clusters into Cells

10:00-10:20 am: Fidel Antonio Castro-Smirnov, Olivier Piétrement, Pilar Aranda, Jean-Rémi Bertrand, Eric Le Cam, Eduardo Ruiz-Hitzky, Bernard S. Lopez

Sepiolite as a new nanocarrier for DNA transfer into mammalian cells

10:20-10:40 am: Sergey V. Kraevskiy, Nikolay A. Barinov, Dmitry V. Klinov

Visualization DNA-montmorillonite complexes with atomic-force microscopy

10:40-11:00 am: Bernard S. Lopez, Fidel A. Castro-Smirnov, David Adame Brooks, Olivier Piétrement, Pilar Aranda, Jean-Rémi Bertrand, Eric Le Cam, Eduardo Ruiz-Hitzky

Health impact of sepiolite fibrous clay mineral

11:00-11:30 am: Coffee break

Session D1: Recent Progress on Nanotechnology and Nanomaterials from Clay Minerals – Auditorium

11:30-11:50 am: Siwada Deeepracha, Makoto Ogawa

Hybridization of titania with clay minerals as photocatalysts

11:50 am-12:10 pm: O. Lakbita, S. Ghazi, B. Rhouta, F. Maury, F. Senocq, M. Amjoud, L. Daoudi

On the key role of palygorskite on monitoring the phase composition of Ag_2CO_3 in palygorskite-based nanocomposites and correlation with their visible photocatalytic activities

12:10-12:30 pm: Kazuko Fujii, Hideo Hashizume, Shuichi Shimomura, Takatsugu Wakahara, Toshihiro Ando

Synthesis of an imidazoline-nickel phyllosilicate monolith and its optical properties

12:30-12:50 pm: Thomas Thiebault, Jocelyne Brendlé, Grégoire Augé, Lionel Limousy

Raw and amphoteric surfactant-modified Laponites®: application in the field of competitive adsorption of Cs and Sr

Lunch break

Session A2: Experimental and numerical analysis of clay systems: Bridging time and length scales – Room #106

2:10-2:30 pm: Sébastien Le Crom, Jean-Charles Robinet, Christophe Tournassat, Virginie Marry

Multi-scale modeling of clay mesopores: comparison between Molecular Dynamics and Poisson-Boltzmann

2:30-2:50 pm: Hejian Zhu, Andrew Whittle, Roland Pellenq

Multiscale Modelling of Clay Aggregate Behaviour

2:50-3:10 pm: Alberto Leonardi, David L. Bish

Characterization of defect creation in kaolinite: Bridging powder X-ray diffraction with atomistic simulations

3:10-3:30 pm: Iuliia Androniuk, Brice F. Ngouana Wakou, Andrey G. Kalinichev

Ionic adsorption on the (010) and (110) edge surfaces of kaolinite: Molecular dynamics simulation with updated ClayFF potential

3:30-3:50 pm: Daniel Moreno Rodríguez, Eva Scholtzová, Ľuboš Jankovič, Daniel Tunega

Atrazine-Montmorillonite/Beidellite intercalates: a Density Functional Theory study

3:50-4:20 pm: Coffee break

Session A4: 1D Nanoporous clay minerals: Structures, genesis, functionalization, properties and applications – Room #106

4:20-4:40 pm: G. Monet, Z. Chai, E. Paineau, L.-M. Liu, G. Teobaldi, S. Rols, P. Launois

Unique properties of alumino-germanate imogolite nanotubes as water nanocontainers

4:40-5:00 pm: Alejandro Fernandez-Martinez, Adam F. Wallace, Jinhui Tao, Ian C. Bourg, Mark R. Johnson, Gabriel J. Cuello, Laurent Charlet

Curvature-induced hydrophobicity at imogolite-water interfaces: 'The nanotube effect'

5:00-5:20 pm: Roberto Nasi, Pierre Picot, Antoine Thill, Filomena Sannino, Olimpia Oliviero, Serena Esposito, Marco Armandi, Barbara Bonelli

Hybrid organic-inorganic nanotubes selectively adsorb some organic pollutants from aqueous phases

5:20-5:40 pm: Rafael I. González, Javier Rojas-Nunez, Felipe J. Valencia, Samuel Baltazar, Francisco Munoz, Miguel Kiwi

Molecular dynamics simulation of an isolated aluminosilicate nanotube (imogolite) in water: Diameter effect on the water properties

5:40-6:00 pm: Tobias Lange, Thibault Charpentier, Frédéric Gobeaux, Sophie Charton, Fabienne Testard, Antoine Thill

The reaction of decylphosphonic acid and imogolite yields a composite material of residual imogolite and lamellar phase

Session B2: The role of clays and modified clays in remediating environmental pollutants – Room #108

2:15-2:35 pm: Monica Granetto, Luca Serpella, Tiziana Tosco

Assessment of reduced environmental impact of novel clay-based herbicide formulations through saturated and unsaturated column tests and volatilization quantification

2:35-2:55 pm: Pierre Mignon, Bruno Lanson, Emmanuelle Vulliet

Adsorption of Emerging Micro-Pollutants on Clay Minerals

2:55-3:15 pm: Ines Mulder, Benjamin Heyde, Linda Bisping, Stefanie Glaeser,Valerie Sentek, Wulf Amelung, Kornelia Smalla, Sven Jechalke, Jan Siemens

Sequestration of quaternary ammonium compounds by soil smectites – implications for antibiotic resistance development

3:15-3:35 pm: Yael Zvulunov, Zohar Ben-Barak-Zelas, Ayelet Fishman, Adi Radian

Self-Regenerating Bio-Clays for Formaldehyde Wastewater Remediation

3:35-3:55 pm: Libia Nayane F. de Queiroga, Maria Gardênnia da Fonseca, Ieda M. G. Santos, Maguy Jaber, Francisco Rodrigues

Amino-imine functionalized bentonites: from environmental remediation to new pigments

3:55-4:25 pm: Coffee break

Session B2: The role of clays and modified clays in remediating environmental pollutants – Room #108

4:25-4:45 pm: Karima Hamdi Alaoui, Clément Levard, Jérôme Labille, Muhammad Bin Norharizam, Amélie Guillon, Isabelle Baudin, Naïma Rachid, Corinne Chaneac, José Sanchez Marcano, Marie-Pierre Belleville, Mohamed Bizi

Clay hybridized with nanoparticles for removal of antibiotics in water usage cycle

4:45-5:05 pm: Kh Ashraf Uz-Zaman, Bhabananda Biswas, Md. Mahmudur Rahman, Ravi Naidu

Smectite-supported nano zero valent iron for efficient removal of toxic arsenic from water

5:05-5:25 pm: Ying Li, Xiaoliang Liang, Joseph W. Stucki, Hongping He, Jianxi Zhu

Effect of isomorphous substitution on the reducing capability of magnetite coupled with aqueous Fe^{2+}

5:25-5:45 pm: Mingce Long, Yue Pan, Hamed Vafaei Molamahmood

Efficient Fe/Montmorillonite based Fenton-like oxidation for environment cleanup

Session E1: Teaching clay science – Room #105

2:10-2:30 pm: Youjun Deng

Enhancing the understanding of clay mineralogy concepts by active interacting with students with real and virtual models as well as field, lab, and class room demonstrations

2:30-2:50 pm: Warren D. Huff

Teaching clay science with today's technology

2:50-3:10 pm: Agustín Cota, Adolfo Miras, Domingo Martín

G.E.S.U.S., a didactic resource for learning space groups of symmetry

3:10-3:30 pm: Fernando Nieto

Virtual teaching on mineralogy, identification techniques and their crystallographic basis at the University of Granada

3:30-3:50 pm: Lynda B. Williams

Teaching the art of solid-state stable isotope measurements in clays: What can be learned from nanometric isotope analyses?

3:50-4:20 pm: Coffee break

Session E1: Teaching clay science – Room #105

4:20-4:40 pm: Eulalia Zumaquero, M.Pilar Gomez-Tena, Jessica Gilabert, Eva María Diaz

Quantification of minority minerals present in clays related to acid emissions in tiles manufacturing by Evolved Gas Analysis methodology

4:40-5:00 pm: Ann Bourgès, Anne Bouquillon, Anne-Solenn Le Hö, Anne Liégey, Patricia Patrier

Clay minerals in cultural heritage, how to teach a wide panel of materials and issues?

5:00-5:20 pm: Michael Holmboe

ATOM - Atomistic Topology Operations in Matlab: A general framework for construction and analysis of atomistic geochemical systems

Session D7: Clay mineral synthesis – Room #105

5:20-5:40 pm: Noel N'guessan Essey, Emmanuel Joussein, Marilyne Soubrand, Alexandra Courtin-Nomade, Sylvie Rossignol, Nathalie Texier Mandoki, Xavier Bourbon

Use of synthetic kaolinite to understand the kaolin reactivity in alkaline media

5:40-6:00 pm: Salma Baraka, Nicolas Bion, Kerya Bouearan, Claude Fontaine, Rachid Brahmi, Sabine Petit, Florence Epron, Laurent Caner

Catalytic performances of Ni-containing smectites

Session D3: Clay and clay minerals in ceramics: From industrial to new hierarchical/textural materials – Room #109

2:15-2:35 pm: Philippe Blanchart, Gisèle Lecomte, Nicolas Tessier Doyen (**keynote lecture**)

Clays and clay minerals in ceramics: engineering properties of textured materials

2:35-2:55 pm: Imane Daou, Gisèle L. Lecomte-Nana, Nicolas Tessier-Doyen, Claire Peyratout, René Guinebretière

Structural evolution of textured phyllosilicate materials probed by in situ high temperature X-ray diffraction

2:55-3:15 pm: Youssef Chalouati, Khaled Othmen, Faouzi Mannai, Ali Bennour, Ezzedine Srasra

Chemical and mineralogical compositions, thermal behavior and ceramic applications of the Oligo-Miocene clays from Nefza and Sejnène regions (Northwest Tunisia)

3:15-3:35 pm: Fakher Jamoussi, Béchir Moussi, Oumaima Grine, Emna Fakhfakh, Mondher Hachani, Walid Hajjaji, Alberto Lopez Galindo, Johan Yans, Pascal Pilate, Fernando Rocha, João Labrincha & Michele Dondi

Valorization of Tunisian clays in the ceramics field

3:35-3:55 pm: Aghiles Hammas, Gisèle-Laure Lecomte-Nana, Imane Daou, Claire Peyratout, Fatima Zibouche

Effect of magnesite on the microstructural and mechanical properties of Cordierite-Mullite Ceramics prepared by tape casting process

3:55-4:25 pm: Coffee break

Session D3: Clay and clay minerals in ceramics: From industrial to new hierarchical/textural materials – Room #109

4:25-4:45 pm: E. M. Seftel, V. Van Acker, M. Mertens, B. Michielsen, P. Cool

Clay-based structured composites for oxyanions uptake from aqueous waste effluents

4:45-5:05 pm: Mohamed Mouafon, Gisèle Lecomte-Nana, Dayirou Njoya, Nicolas Tessier-Doyen, Daniel Njopwouo

Comparative effect of bovine bone ash and cassava starch on the microstructure of porous ceramics using kaolinite clays from Cameroon

Session A3: Physicochemical processes at the clay/water interface – Room #109

5:05-5:25 pm: Stamatina Karakitsiou, Athanassios Karalis, Emmanouil Vamvounis

Evaluation of Milos' bentonites with respect to aflatoxin adsorption and governing mechanisms of clay surface / aflatoxin molecule interaction

5:25-5:45 pm: Natacha Van Groeningen, Iso Christl & Ruben Kretzschmar

Influence of Mn(II) on the sorption of Cd(II) to clay minerals

Session D1: Recent Progress on Nanotechnology and Nanomaterials from Clay Minerals – Auditorium

2:20-2:40 pm: Ahmed Borgini, Cédric Gasperini, Thierry Gefflaut, Christine Guerard-Helaine, Virgile Helaine, Marielle Lemaire, Caroline Vachias, Vanessa Prévot, Claude Forano

Water/Water Pickering emulsions stabilized by Layered Double Hydroxides nanoparticles for enzyme encapsulation

2:40-3:00 pm: Giulia Lo Dico, Bernd Wicklein, Lorenzo Lisuzzo, Giuseppe Lazzara, Pilar Aranda, Eduardo Ruiz-Hitzky

Conducting sepiolite-halloysite multicomponent nanoarchitectures for electrochemical devices applications

3:00-3:20 pm: Chris Breen, Francis Clegg, Marianne Labet-Eyley, Neil Bricklebank, Louise Freeman-Parry, Keith Miller, Lukáš Petra

Clay polymer composites for sustained release antimicrobial wound dressings

3:20-3:40 pm: Mei Long, Yi Zhang, Aidong Tang, Huaming Yang

Nanoclay composites for biomedical application

3:40-4:00 pm: Ediana P. Rebitski, Margarita Darder, C. Ignacio Sainz-Diaz, Pilar Aranda, Raffaele Carraro, Eduardo Ruiz-Hitzky

Theoretical and experimental investigation on the intercalation of metformin into layered clay minerals

4:00-4:30 pm: Coffee break

Session D1: Recent Progress on Nanotechnology and Nanomaterials from Clay Minerals – Auditorium

4:30-4:50 pm: Kirill Shafran, Patrick Jenness, Jane Doyle

Laponite® Family of Synthetic Clays: History, Present Status, and Trends

4:50-5:10 pm: María P. Pico, Daniel Alonso-Domínguez, Belén Marcos, Margarita Darder, Rafael Pérez-Castells, Pablo Marco-Gardoqui, Pilar Aranda, Eduardo Ruiz-Hitzky

Sepiolite from Spanish deposits in Toledo and its derived organoclay materials

5:10-5:30 pm: Serena Riela, Giuseppe Cavallaro, Giuseppe Lazzara, Marina Massaro

Panoramic overview of chemical modification of halloysite nanotubes and applications thereof

5:30-5:50 pm: Martin Rieß, Kilian Bärwinkel, Markus M. Herling, Hiroshi Sato, Liangchun Li, Yamini S. Avadhut, Tobias W. Kemnitzer, Kalo, Jürgen Senker, Ryotaro Matsuda, Susumu Kitagawa, Rainer Schobert, Josef Breu

Microporous Organically Pillared Layered Silicates (MOPS) – A versatile class of functional porous materials with structural flexibility

Ecologic Park - L'île Monsieur (See map and/or website)

7:30-11:30 pm Banquet

Friday July 5th

Hall Auditorium

From 8:00 am: Registration and badge pick-up

Auditorium

8:30-9:25 am Clay Minerals Society – George W. Brindley Clay science lecture:

Bruno Lanson: Crystal structure of defective lamellar minerals and their X-ray identification: Implications for reactivity

Introduction by Eric Ferrage

Session A4: 1D Nanoporous clay minerals: Structures, genesis, functionalization, properties and applications – Room #106

9:40-10:00 am: Emiliano Poli, Joshua D. Elliott, Sergey Chulkov, Matthew B. Watkins, Gilberto Teobaldi

The role of cation-vacancies for the electronic and optical properties of aluminosilicate imogolite nanotubes: a non-local, linear-response Time-Dependent Density Functional Theory study

10:00-10:20 am: Andrei A. Krasilin

An energy model for studying of size parameters and chemical composition features of hydrosilicate nanoscrolls

10:20-10:40 am: Emmanuel Joussein, Alexandra Courtin, Erwan Paineau, Delphine Vantelon, Pascale Launois, Marilyne Soubrand

Unravel the famous halloysite structural charge and interlayered cations from X-ray absorption spectroscopy investigations

10:40-11:00 am: C. Ignacio Sainz-Díaz, Bruno Escribano, Julyan Cartwright

Aluminum silicate tubes by chemical gardens formation, new insights in the formation of tubular halloysite

11:00-11:30 am: Coffee break

Session A4: 1D Nanoporous clay minerals: Structures, genesis, functionalization, properties and applications – Room #106

11:30-11:50am: Rawil Fakhrullin

Imaging clay nanoparticles *in vitro* and *in vivo* using dark field hyperspectral microscopy

11:50 am-12:10 pm: Jeroen S. van Duijneveldt, Phillip Woolston, Claudia Ferreiro Córdova

Colloidal liquid crystals of sepiolite in oil thanks to polar activators and dispersants

12:10-12:30 pm: Youcef Yahia, Fátima García-Villén, Amel Djelad, Lala Setti Belaroui, Rita Sanchez-Espejo, Mohamed Sassi, Alberto López-Galindo, César Viseras

Preparation and physicochemical characterization of Chitosan–Algerian Palygorskite composite beads as drug carriers

12:30-12:50 pm: Tan Tze Haw, Pooria Pasbakhsh

Using halloysite nanotubes in fabrication of sustainable cementitious composites for construction and building applications

Session B2: The role of clays and modified clays in remediating environmental pollutants – Room #108

9:45-10:05 am: Hideo Hashizume

Decomposition of polycyclic aromatic hydrocarbons in the presence of hydrogen, carbon dioxide and ammonium gases with a clay mineral

10:05-10:25 am: Endene Emmanuel, Lee Li Yong, Vivi Anggraini, Pooria Pashkbaskh

Stabilization/solidification of lead (Pb) and zinc (Zn) contaminated marine clay using halloysite nanotubes

10:25-10:45 am: Pierre Picot, Thibaud Coradin, Antoine Thill

Methyl-imogolite: a new hybrid nanotube for water remediation

10:45-11:05 am: R. Benhiti, R. Aziam, A. Ait Ichou, C. Carja, M. Zerbet, F. Sinan, M. Chiban

Characterization and comparative study of anionic clays prepared by standard coprecipitation and urea methods for phosphate removal

11:05-11:35 am: Coffee break

Session B2: The role of clays and modified clays in remediating environmental pollutants – Room #108

11:35-11:55 am: Ruta Ozola, Maris Klavins, Marta Jemeljanova, Juris Burlakovs

Clay minerals and ionic liquids or humic acids composites for applications in wastewater treatment

11:55 am-12:15 pm: Thimo Philipp, Katja Schmeide, André Rossberg, Nina Huittinen, Thorsten Stumpf

Influence of pH, carbonate and calcium concentration on U(VI) retention by clay minerals at (hyper)alkaline conditions – A batch sorption and spectroscopy study

12:15-12:35 pm: Mathieu Debure, Christophe Tournassat, Catherine Lerouge, Benoît Madé, Jean-Charles Robinet, Ana María Fernández, Sylvain Grangeon

Retention of arsenic, chromium and boron on an outcropping clay-rich rock formation (the Tégulines Clay, eastern France)

12:35-12:55pm: Dóra Buzetzky, Noémi M. Nagy, József Kónya
The role of silver-bentonite in sorbing long-lived anionic radioactive species

Session D7: Clay mineral synthesis – Room #105

9:30-9:50 am: Cyril Aymonier, Marie Claverie, Marta Diez-Garcia, François Martin

Supercritical solvothermal flow synthesis of nanominerals

9:50:10:10 am: Hella Boumaiza, Liva Dzene, Jocelyne Brendlé, Lionel Limousy, Patrick Dutournié, Christelle Martin, Nicolas Michau

Synthesis of iron rich clays in the Fe/Si system using statistical experimental design

10:10-10:30 am: Mathilde Poirier, François Martin, Nicolas Trcera, Delphine Vantelon, Cécile Quantin

Mg and Si-K edge X-ray absorption study of synthetic talc with various crystallinity

10:30-10:50 am: Erwan Paineau, Pascale Launois

Synthetic imogolite nanotubes: a flexible building block with multipurpose applications

10:50-11:10 am: Chaoqun Zhang, Sabine Petit, Hongping He, Qi Tao, Fabien Baron

The crystal growth of smectite: A study based on crystal-chemistry and morphology

11:10-11:40 am: Coffee break

Session D7: Clay mineral synthesis – Room #105

11:40 am-12:00 pm: Marion Bruneau, Jocelyne Brendlé, Simona Bennici, Sylvain Pluchon

Formation of organic-inorganic hybrids having a talc-like structure: influence of the synthesis parameters

12:00-12:20 pm: Dylan Chaillot, Jocelyne Brendlé, Simona Bennici

Formation of new organic-inorganic hybrid materials having a lamellar structure by sol-gel process

12:20-12:40 pm: Daniel Roland Wagner, Kevin Ament, Josef Breu

Synthesis and application of hectorite intercalated nanoparticles

12:40-13:00 pm: Keith Morrison, Ty Samo, Gabriela Loots

Synthesizing antibacterial minerals

Session A3: Physicochemical processes at the clay/water interface – Room #109

9:35-9:55 am: Xinyi Shen, Ian C. Bourg

Free energy of interaction of two smectite clay nanoparticles in liquid water

9:55-10:15 am: Virginie Marry, Emmanuelle Dubois, Sébastien Le Crom, Eric Ferrage, Laurent Michot

Diffusion mechanisms in clays with octahedral and tetrahedral substitutions: coupling quasi-elastic neutron scattering and molecular dynamics simulations

10:15-10:35 am: Ayumi Koishi, Sang Soo Lee, Paul Fenter, Alejandro Fernandez-Martinez, Laurent Michot, Ian Bourg

Surface Hydrophobicity and Energetics at Mica-Water Interfaces

10:35-10:55 am: René Schliemann, Inna Kurganskaya, Sergey V. Churakov

Molecular mechanism of dissolution, growth and ion uptake at the clay mineral/water interface

10:55-11:15 am: Lucía Pérez Ramírez, Anthony Boucly, Fabrice Bournel, Jean Jacques Gallet, François Rochet, Virginie Marry, Emmanuelle Dubois, Laurent J. Michot

The hydration behavior of mineral clays monitored by NAP-XPS

11:15-11:45 am: Coffee break

Session A3: Physicochemical processes at the clay/water interface – Room #109

11:45 am-12:05 pm: Patrick Loch, Matthias Daab′, Natalie J. Eichstaedt, Andreas Edenharter, Christoph Habel, Sabine Rosenfeldt, Josef Breu

The Onset of Osmotic Swelling in 2:1 Layered Silicates

12:05-12:25 pm: Ashish Rajyaguru, Jingyi Wang, Sébastien Savoye, Charles Wittebroodt, Olivier Bildstein, Valéry Detilleux, Emilie l’Hôpital, Fabien Bernachy-Barbe, Vincent Lagneau

Impact of pore size and surface charge on precipitation processes in clay systems: Case of barite precipitation in compacted kaolinite and illite

12:25-12:45 pm: Marie-Claire Pignié, Antoine Thill, Sophie Le Caër

H_2 production from radiolysis of water confined in imogolite nanotubes. Impact of water content and surface chemistry

Session D1: Recent Progress on Nanotechnology and Nanomaterials from Clay Minerals – Auditorium

9:40-10:00 am: Fabrice Leroux, Adam A. Marek, Grazia Totero, Laura Sisti, Annamaria Celli, Christine Taviot-Guého, Vincent Verney, Thomas Stimpfling, Pierre Vialat, Horst Hintze-Bruening, Patrick Keil, Viacheslav Shkirskiy, Polina Volovitch, Kevin Ogle

Fine Tuning for Matching (Multi)-Properties for polymer: the amazing LDH green toolbox

10:00-10:20 am: Christoph Habel, Marius Schöttle, Matthias Daab, Natalie J. Eichstaedt, Daniel R. Wagner, Hadi Bakhshi, Jasmin Schmid, Elena Doblhofer, Seema Agarwal, Marcus A. Horn, Josef Breu

Bionanocomposites as “green” alternatives for commercial food packaging materials

10:20-10:40 am: Amos Pasder, Yael Mishael

Controlling the Architecture of Grafted Polymer-Clay Composites for Enhanced Sorbent Performance

10:40-11:00 am: Fuchuan Ding, Jingjing Liu, Luyi Sun

Biomimetic Polymer/Clay Nanocoatings with Exceptional Mechanical, Barrier, and Flame Retardant Properties from One-Step Co-assembly

11:00-11:20 am: Won Jun Lee, Erwan Paineau, David B. Anthony, Yulin Gao, Hannah S. Leese, Stéphan Rouzière, Pascale Launois, Milo S. P. Shaffer

Strong healable fibers with imogolite nanotubes

11:20-11:50 am: Coffee break

Session B7: Diagenesis and low-grade metamorphism (4th Frey-Kübler Symposium) – Auditorium

11:50 am-12:10 pm: Iuliu Bobos, Dennis D. Eberl, Lynda B. Williams

Crystal growth of NH_4-illite in the hydrothermal system of Harghita Bãi (Eastern Carpathians) deduced from crystal thickness distributions and light (B and Li) isotopic composition

12:10-12:30 pm: Jan Środoń, Oksana Kuzmenkova, Jan J. Stanek, Sabine Petit, Daniel Beaufort, H. Albert Gilg, Sirle Liivamägi

Fe-smectites as the main products of basalt hydrothermal alteration: example from the Ediacaran flood basalts of the East European Craton

12:30-12:50 pm: Lan Nguyen-Thanh, Rafael Ferreiro Mählmann, Johann-Gerhard Fritsche, Thao Hoang-Minh, Rainer Petschick, Thomas Reischmann, Heinz-Dieter Nesbor, Myriam Ruttmann

Clay Minerals and Mineralization of Permian Illite in a Geothermal Drillhole – Northern Upper Rhein Graben, Germany

Lunch break

Session A4: 1D Nanoporous clay minerals: Structures, genesis, functionalization, properties and applications – Room #106

2:20-2:40 pm: Mingxian Liu, Xiaohan Yang, Jun Zhang, Jingqi Zheng, Xiang Cao, Hongzhong Liu, Rong-Rong He

Functionalization of halloysite nanotubes as drug carrier for treatment of breast cancer

2:40-3:00 pm: Lorenzo Lisuzzo, Giuseppe Cavallaro, Stefana Milioto, Filippo Parisi, Giuseppe Lazzara

Hybrid nanoarchitectures based on Halloysite Nanotubes and polymers for drug delivery

3:00-3:20 pm: Guanzheng Zhuang, Maguy Jaber, Zepeng Zhang

Inspiration from Maya blue: a new durable pigment with super-hydrophobicity based on nanotubular halloysite

3:20-3:40 pm: Giuseppe Cavallaro, Farida Akhatova, Rawil Fakhrullin, Giuseppe Lazzara, Stefana Milioto, Yuri Lvov

Selective adsorption of keratin onto halloysite nanotubes: colloidal stability, thermodynamics and applications

3:40-4:00 pm: Giuseppe Lazzara, Giuseppe Cavallaro, Filippo Parisi, Stefana Milioto

Halloysite nanotubes for conservation of artworks: novel protocols for consolidation and surface cleaning

Session A1: Challenges in reactive transport modeling of clay systems – Room #108

2:20-3:00 pm: Carl I. Steefel, Christophe Tournassat, Josep Soler (**keynote lecture**)

A mean electrostatic model for ion transport through heterogeneous clay

3:00-3:20 pm: Thomas Gimmi, Andreas Jenni, Peter Alt-Epping, Philipp Krejci (**invited lecture**)

Ion transport in clays: Comparing ion-exchange, surface-diffusion, and diffuse-layer modeling approaches

3:20-3:40 pm: Josep M. Soler, Carl I. Steefel, Thomas Gimmi, Olivier X. Leupin, Veerle Cloet (**invited lecture**)

Modeling the effect of ionic strength on diffusion. The DR-A experiment in Opalinus Clay at Mont Terri

3:40-4:00 pm: Andrés Idiart, Marcelo Laviña, Benoit Cochepin, Antoine Pasteau, Isabelle Munier

Development of a chemo-mechanical model of a bentonite-sand sealing component

4:00-4:20 pm: Jonathan C. Pistorino, Ruth M. Tinnacher, Christophe Tournassat

A Prediction of Uranium(VI) Diffusion in Montmorillonite at Various Chemical Solution Conditions

Session C4: Photochemistry, photophysical and optical functionalities of clay mineral based materials – Room #105

2:20-2:40 pm: Juraj Bujdák, Tímea Baranyaiová, Táňa Sebechlebská

On the mechanism of molecular aggregation of dyes in colloidal dispersions of clay minerals. The effect of temperature

2:40-3:00 pm: Ikumi Akita, Yohei Ishida, Tetsu Yonezawa

A real-space investigation of excited energy transfer reaction in quantum dots assembly on silicate surfaces through electron tomography

3:00-3:20 pm: Yasutaka Suzuki, Ayaka Shiosaki, Mana Nagase, Seiji Tani, Jun Kawamata

Thermochromic response of smectite-organic dye hybrid materials

3:20-3:40 pm: Yusuke Ide, Satoshi Tominaka, Esmail Doustkhah

Utilization of zeolitic but unique microchannels within layers of a layered silicate, Magadiite

3:40-4:00 pm: Masaya Miyagawa, Akane Shibusawa, Kengo Nishio, Hideki Tanaka

Introduction of hierarchical structure for enhanced photocatalytic activity of Cu nanoparticles hybridized with saponite nanosheets

4:00-4:20 pm: Chitiphon Chuaicham, Keiko Sasaki

Synthesis of Sepiolite/g-C_3N_4/Pd Nanoparticles Composites for Surface Plasmon Resonance Enhanced Visible-Light-Driven Photocatalytic Degradation of Rhodamine B

Session A3: Physicochemical processes at the clay/water interface – Room #109

2:20-2:40 pm: Paul Wersin, Marek Pekala, Andreas Jenni, Lukas Aschwanden, Hélène Vigier-Gailhanou, Mathieu Debure, Catherine Lerouge

Constraints of sulphate in the porewater of a clay rock

2:40-3:00 pm: Patrik Sellin, Daniel Svensson, Ursula Alonso, Tiziana Missana, Hanna Kronberg, Miguel García Gutiérrez, Jesús Morejón, Manuel Mingarro, Ana María Fernández, Magnus Kronberg

Interaction between a bentonite barrier and a dilute groundwater – flocculation and the impact of gravity

3:00-3:20 pm: W.P. Gates, G.G. Carnero-Guzman, L.P. Aldridge, H.N. Bordallo, R.A. Mole, G.N. Iles, A. Klapproth, A. Bouazza

Unfrozen water in clays and the freezing characteristic curve of geosynthetic clay liners

3:20-3:40 pm: Imane Guetni, Isabelle Bihannic, Fabien Thomas, Jérôme Duval, Yves Waldvogel, Manuel Pelletier, Claire Marlière, David Rousseau, Frédéric Villiéras

Clay-polymer interaction in enhanced oil recovery: impacts of clay type, ionic strength and hardness

3:40-4:00 pm: Jebril Hadi, Paul Wersin, H. Niklaus Waber, Martin Mazurek

Cation exchange capacity (CEC) measurements of Opalinus clay: comparison of operational conditions

4:00-4:20 pm: Nirrit Cohen and Adi Radian

Bacteria-Clay Surface Interactions Mediated by Amyloid Fibers

Session B7: Diagenesis and low-grade metamorphism (4th Frey-Kübler Symposium) – Auditorium

2:20-2:40 pm: Rafael Ferreiro Mählmann, Sébastien Potel, Lan Nguyen-Thanh, Rainer Petschick, Meinert Rahn

Determination of a normal palaeo-geothermal gradient comparing the reaction progress of clay minerals calibrated with organic maturity indices

2:40-3:00 pm: Hülya Erkoyun, Selahattin Kadir, Tacit Külah

Mineralogy, geochemistry and genesis of clays interlayered coal seams succession in the Neogene lacustrine Orhaneli and Keles coal deposits, Bursa, western Turkey

3:00-3:20 pm: Pierre Malie, Rafael Ferreiro Mählmann, Sébastien Potel., Tatiana Maison, Frank Chanier, Geoffroy Mahieux, Julien Bailleul

Low-grade metamorphic study to precise the geodynamic history and hydrocarbon migration system of the Hikurangi Prism (North island, New Zealand)

3:20-3:40 pm: Branimir Segvic, Giovanni Zanoni

Formation of Eogenetic Chlorite in Verdine Facies Sedimentary Rocks from the Gabon Basin in West Africa

3:40-4:00 pm: Ernst Spiridonov, Julia Gritsenko, Sergey Belyakov, Vladimir Ladygin, Julia Frolova, Inna Kulikova, Evgeniy Sereda, Aleftina Serova

Low-grade metamorphism on the East Siberian Platform as ore preparation, ore-forming, ore-transforming process

4:00-4:20 pm: Olga V. Dorzhieva, Victor A. Drits, Boris A. Sakharov, Sergei V. Zakusin, Olga V. Andreeva, Victoria V. Krupskaya

Structural features of clay minerals in metasomatites at the Antei-Streltsovskoe uranium deposit (Russia)

Auditorium

4:25-4:45 pm: Closing ceremony

5. Detailed poster program

Monday July 1st

Patio 44-55

6:30-8:30 pm Poster session #1 – Posters from sessions A2, A5, A7, B1, B3, B4, C2, C3, D2, D5, D8, E2

Wine & Cheese welcome party

Session A2: Experimental and numerical analysis of clay systems: Bridging time and length scales

1. Fevronia Andreou, Eirini Siranidi, Vassilis Gionis, Georgios D. Chryssikos: NMF in kaolinite: Intercalation kinetics by Near-Infrared spectroscopy

2. Ian C. Bourg, Francisco J. Carrillo, Xinyi Shen, Thomas Underwood: Coupled hydrology, chemistry, and mechanics of fine-grained soils and sedimentary rocks

3. Eric Ferrage, Thomas Dabat, Patrice Porion, Fabien Hubert, Erwan Paineau, Baptiste Dazas, Brian Grégoire, Emmanuel Tertre, Alfred Delville: A combined experimental and numerical analysis of anisotropic diffusion of water in clay porous media

4. Eirini Siranidi, Vassilis Gionis, Georgios D. Chryssikos: The effect of hydration on the vibrational spectrum of hectorite

5. Peter Grancic, Daniel Tunega: Molecular Modelling of Bioorganoclays

6. Jerry Lindholm, Michael Holmboe: Atomistic views on smectite interlayers from molecular simulations and XRD profile modelling

7. Kristoffer W. Bø Hunvik, Leide Cavalcanti, Matthias Daab, Konstanse K. Seljelid, Vegard Josvanger, Roosevelt D. Droppa, Barbara Pacáková, Paulo H. Michels-Brito, Kenneth D. Knudsen, Josef Breu, Jon Otto Fossum: The Role of Interlayer Cations for CO_2 Capture in a Smectite Clay

8. Maria Jansson, Axel Thuresson, Tomás S. Plivelic, Jan Forsman, Marie Skepö: The effect of the relative permittivity, the counterion charge ratio and the temperature on the structural properties and swelling of montmorillonite

9. Geoffrey M. Bowers, John S. Loring, H. Todd Schaef, Eric D. Walter, Randolph K. Larsen IV, Sarah D. Burton, David W. Hoyt, R. James Kirkpatrick: Smectite-methane interactions: in situ high T and P XRD, IR, and ^{13}C NMR studies

10. Mariola Kowalik, Marek Szczerba, Michał Skiba: Structure of glycerol-Mg-smectites/vermiculites complex based on molecular dynamics and implementation of the model for XRD modelling

11. Sylvia M. Mutisya, Andrey G. Kalinichev : Thermodynamics of CO_2 rich fluids in cement nanopores from atomistic simulations

12. Brice F. Ngouana Wakou, Andrey G. Kalinichev: Surface complexation of metal cations at the (010), and (110) edges of montmorillonite: MD computer simulation with updated ClayFF potential

13. Monique Estelle Charrier, Lan Nguyen-Thanh, Blanca Bauluz, Thao Hoang-Minh, Rainer Petschick, Rafael Ferreiro Mählmann: Mineralogical Alteration of Fe-smectite in High Alkaline Solutions

14. Daniel E. González-Santamaría, Raúl Fernández, Ana I. Ruiz, Almudena Ortega, Jaime Cuevas: Surface reactivity in cement mortars/bentonite interface experiments for the upscaling to an in-situ demonstration of nuclear waste clay barrier

15. Eva Scholtzová, Luboš Jankovič, Peter Škorňa, Daniel Moreno Rodriguez, Daniel Tunega: Tetraalkylphosphonium beidellite intercalates – structural stability by DFT method

16. Fevronia Andreou, Eirini Siranidi, Vassilis Gionis, Georgios D. Chryssikos, Arkadiusz Derkowski: NMF-intercalated kaolinite: a comparative vibrational and XRD investigation

17. Peter Škorňa, Eva Scholtzová, Ľuboš Jankovič, Daniel Tunega: Structural properties and spectroscopic characterization of choline-beidellite and acetylcholine-beidellite intercalates

18. Thomas R. Underwood, Edo Boek, H. Chris Greenwell: Salinity-driven wettability alterations on clay minerals surfaces: a molecular dynamics study

19. Doriana Vinci, Bruno Lanson, Martine Lanson, Valérie Magnin, Nathaniel Findling: Hydration properties of synthetic Na-saturated stevensites

20. Hejing Wang, Ting Li, Yu Yan, Mengyao Chen, Xiaoli Wang: Row-indexing and its application in structural analysis for clay minerals

21. Narasimhan Loganathan, A. Ozgur Yazaydin, R. James Kirkpatrick, Geoffrey M. Bowers: Tuning the hydrophobicity of layer-structure silicates to promote adsorption of non-aqueous fluids: Effects of F^- for OH^- substitution on CO_2 partitioning into smectite interlayers

Session A5: Multi-scale understanding of interface redox reactions

22. Iuliu Bobos, Carlos Sá, Fernando Noronha: The redox state exchanges between Fe and Mn distribution in chlorites and fluid in the magmatic-hydrothermal system of Borralha, Portugal

23. Harry Brooksbank, Anke Neumann: Impact of multiple redox cycles on the reactivity and structure of iron-bearing clay minerals

24. Andrew Hambly, Jeroen Van Duijneveldt, Paul J Gates: Oxidation of Carotene by Acid Treated Montmorillonite

25. Miroslav Honty, Lander Frederickx, Dipanjan Banerjee, Alwina Hoving: Fe valence state & distribution in the various size fractions of the Boom Clay

26. Małgorzata Lempart Arkadiusz Derkowski: Hydrogen liberation during heating of phyllosilicates

27. Christos Vasilopanagos, Chris Greenwell, Anke Neumann: Redox sensitive clay minerals: implications for fines migration and enhanced oil recovery

Session A7: Characterization of clayey nanomaterials

28. Ikumi Akita, Yohei Ishida, Tetsu Yonezawa: Direct imaging of monolayer silicate nanosheet by aberration corrected scanning transmission electron microscopy

29. Andre L. V. Carmo, Rômulo S. Angélica, Simone P. A. Paz: Sodium deactivation of Brazilian bentonite varieties

30. Ali Asaad, Fabien Hubert, Eric Ferrage, Emmanuel Tertre: Mineralogical and morphological characterization of different size fractions of Na- saturated Illite du Puy

31. Fernando García Tomás, Joaquín Bastida, Pablo Pardo, Rafael Ibañez, Marek Kojdecki, Mercedes Suárez: Multiple light scattering, sedimentation behaviour of suspensions and crystallite size features of reference clay minerals

32. E.C. dos Santos, W.P. Gates, L. Michels, J.O. Fossum, H.N. Bordallo: Fluorohectorite, a promising material for drug delivery

33. Bella B. Zviagina, Victor A. Drits, Olga V. Dorzhieva: Structural factors affecting the crystal-chemical variability in Al-rich K-dioctahedral $2M_1$ micas

34. Maricris Jimenez, Candy Mariel Juego, Maybellyn Zepeda: Contribution to the zeolite deposits in Mangatarem, Pangasinan, Philippines

35. Ryosuke Kikuchi, Toshihiro Kogure: Nanoscopic structures and chemistry of mixed-layer biotite-vermiculite in the weathering profile in Abukuma granitic rocks in the eastern part of Fukushima, Japan

36. Toshihiro Kogure, Linwei Tian, Yohichi Sakai, Taiga Okumura, Jing Sun, Tsutomu Takayama, Changzhong Liao, Kaimin Shih, Dong Liu: Acicular chamosite in the coal mined in southern China, as potential cause of lung cancer in the area

37. Victoria V. Krupskaya, Olga V. Dorzhieva, Sergei V. Zakusin, Petr Belousov, Ekaterina Tyupina: Structural features of montmorillonites as a key for understanding the stability of bentonite buffer for isolation of radioactive waste

38. Jerry Lindholm, Michael Holmboe: Accuracy of force fields for atomistic modelling of alcohols in nano-confined clay environments

39. Eliana Satiko Mano, Danilo Pineschi, Laurent Caner, Sabine Petit, Arthur Pinto Chaves, André Sampaio Mexias: Mineral characterization of Ni-bearing mixered-layered clay minerals from Niquelandia deposit at Brazil

40. Michel Terray: Interlayer hydration of clays depending on humidity

41. Xiaoli Wang, Reinhard Kleeberg, Kristian Ufer: Investigation of layer charge density of dioctahedral smectites by the Rietveld method

Session B1: Clay minerals in fracture zones

42. Ahmed Abd Elmola, Patricia Patrier, Michael Descostes, Marine Ballini, Daniel Beaufort: Clay signature of fluid flows associated to the major Arlit fault: a case study of Teloua formation-Tim Mersoï Basin, Niger

43. Matoussi Kort Hanene, Sghair Dallel, Laridhi Ouazaa Néjia: New investigations of the hydrothermal signature of clay minerals in the Upper Cretaceous shaly gas/oil reservoir: Tunisian Eastern margin and the Pelagic Sea

44. Annina Margreth, Ola Fredin, Giulio Viola, Jochen Knies, Ronald Sørlie, Jan-Erik Lie, Horst Zwingmann, Roelant van der Lelij, Thomas Scheiber, Jasmin Schönenberger, H. Albert Gilg: Timing and interplay of faulting, hydrothermal alteration and weathering processes of the Rolvsnes granodiorite in southwestern Norway

45. Katharina Methner, Horst Zwingmann, Andreas Mulch, Alfons Berger, Andrew Todd, Marco Herwegh: Testing high-voltage electrical discharges in disintegrating fault claystone for isotopic dating and fluid tracing using hydrogen isotopes

46. Rodrigo W. Lopes, Christophe Renac, André S. Mexias, Lauro V.S. Nardi, Eduardo Fontana, Márcia E.B. Gomes, Aurélie Barats: Mineral assemblages and temperature associated with copper enrichment in the Seival area (Neoproterozoic Camaquã Basin of Southern Brazil)

47. Anja Schleicher, Maria Jose Jurado: Linking faults, fractures and clay minerals occurrence with fluid transport in the accretionary prism of the Nankai Trough, Japan

48. Ho Sim, Yungoo Song, Seongsik Hong, Donghoon Chung, Woohyun Choi: Estimation of fault moving sense at Yangsan fault zone in Pohang area, using the Shape Preferred Orientation(SPO) analysis

49. Asuman Günal Türkmenoğlu, Hasan Sarıkaya: Fault clays formed in the North Anatolian Fault Zone at Gerede area, Turkey

50. Roelant van der Lelij, Clea Fabian, Jasmin Schönenberger, Ruikai Xie, Marit Sigrid Halle: K-Ar geochronology of illite bearing clays using multicollector noble gas mass spectrometry and full major element characterization on particle size fractions generated by continuous flow centrifugation

51. Wen Chen, Shuangfeng Zhao, Xia Yuan: New progress in $^{40}Ar/^{39}Ar$ dating technique for ultrafine minerals

Session B3: Clays and organic matter

52. Ferran Bagaria, David García, Lara Duro, Stéphane Brassinnes: Isolation of solid organic matter from complex clay matrices

53. Javiera Cervini-Silva, Gerardo Ruiz, José Manuel Hernández, Sergio Hernández, Eduardo Palacios, Perla Morales Gil, Kristian Ufer, Ruth Jacquelin Rosa Cruz, Maripaz Orta, Stephan Kaufhold: Methane production and carbon assimilation in nontronite at 25 °C

54. Romain V.H. Dagnelie, Ning Guo, Jean-Charles Robinet: Unravelling reactive transfer of organic molecules in clays

55. E.A. Henry, E. Montarges-Pelletier, J.F.L. Duval, I. Bihannic, C. Caillet, A. Zegeye, S. Migot, R. Gley, Y. Waldvogel: Synthesis and characterisation of suspension of aggregated Illite particles with polysaccharide or Iron oxyhydroxide

56. Yoshikazu Kameshima, Ryusei Nishimura, Shunsuke Nishimoto, Michihiro Miyake: Preparation of gallate / layered double hydroxide composite and its application to environmental purification

57. Julia Tourtelot, Loren Masson, Myriam Duc, Jeanne-Sylvine Guedon, Laurent Brochard, Matthieu Vandamme, Robert Le Roy, Erwan Hamard, Chloé Fourdrin, Thomas Barré, Jean-Didier Mertz, Ann Bourgès, Emmanuel Keita: Earthen construction in future urban area

58. A. Lebreton, C. Biache, C. Lorgeoux, A. Cébron, T. Beguiristain, M. Pelletier, P. Faure: Impact of the mineralogy on petroleum-contaminated soil combining mineral and organic geochemistry and microbiology approaches

59. Amy Lewis, Binoy Sarkar, Mark Hodson, Simon Kemp, David Beerling: Adsorption of an artificial Acid Root Exudate to clays: methodology and preliminary results.

60. Nicolas Maubec, Nicolas Devau, Nicole Baran: Use of X-ray diffractometry and analysis of the atomic pair distribution function to study the interactions between smectite and emerging organic pollutants

61. Monsueto Cardoso da Rocha, Elton Marks de Araujo Braz, Luzia Maria Castro Honorio, Pollyana Trigueiro, Maria Gardênnia Fonseca, Edson Cavalcanti da Silva Filho, Santiago Medina Carrasco, Cesar Viseras Iborra, Josy Anteveli Osajima: Adsorption and photostability of tetracycline onto different clays

62. Lior Levy, Adi Radian: Gallic Acid Interactions with Iron-Coated Smectites

63. Mélanie Lundy, Romain V.H. Dagnelie, Emilie Thory, Claude Le Milbeau, Christophe Tournassat, Patrick Ollivier, Yanick Lettry, Stefan Wechner, Jean-Charles Robinet: Fate of α-isosaccharinic acid in Callovian-Oxfordian clay-rich rock studied by *in situ* experiment

64. Julia Schlosser, Georg H. Grathoff, Arkadiusz Derkowski, Stephan Kaufhold, Laurence N. Warr: The influence of K-bearing organic acids on the alteration of smectite: New experimental results

65. Usa Srisai: Clay minerals of some Paddy soils in the Southern of Thailand

66. Zeb Teichert, Maitrayee Bose, Lynda B. Williams: Lithium isotope systematics in coal

67. Peter Uhlík, Rastislav Milovský, Ľubica Puškelová, Lenka Marková: The relation of weathering of granitoides and soil organic matter formation in the alpine terrain depending on altitude, The High Tatras, Slovakia

Session B4: Mudrocks: Composition, fabric, and provenance - Fundamental research and practical applications of the data

68. Victor Fontdevila, Oriol Oms, Pablo Pardo, Joaquín Bastida: Clay Mineralogy of the K/P transition in Tremp Group (Tremp basin, South Pyrenees).

69. Hyen Goo Cho, Jae Young Choi, Hyo Jin Koo: Provenance Study of 99MAP-P63 Core Sediments in the East China Sea

70. A. El-Shater, S. A. Abu Seif: Eocene Esna Shale as a new source for modern and archaeological pottery in Egypt

71. Lander Frederickx, Miroslav Honty, Mieke De Craen, Gert Jan Weltje, Jan Elsen: Prediction of Boom Clay characteristics using grain size data

72. Paola Mameli, Giovanni Mongelli, Rosa Sinisi, Giacomo Oggiano: Different alterations paths of alluvium derived from the Variscan basement in different time: Cretaceous and Messinian alterites of Sardinia (Italy)

Session C2: Geotechnical characterization of clayey geomaterials from micro to macro scale: The role of microstructure and anisotropy

73. Renata Adamcova, Magdalena Kondrcova: Hydromechanical properties of a commercial bentonite from Slovakia

74. Nurgul Alibekova, Askar Zhussupbekov, Zhumabike Ospanova: Evaluation of the geotechnical properties of clay soils of Astana using GIS-technology

75. M. S. Biju, D. N. Arnepalli: Gas permeation characteristics of biopolymer-modified fine-grained geomaterial

76. Florian Christ, Maximilian Schoen, Arash A. Lavasan: Excavation damaged zone in Opalinus clay induced by mechanized tunneling

77. Giuseppe Cultrone, Natalie Saenz, Eduardo Sebastian: Waste addition in brick manufacture. Improvement of the technical qualities of bricks for use in construction and restoration work

78. Philipp Braun, Pierre Delage, Siavash Ghabezloo, Jean Sulem, Nathalie Conil: The peculiar thermal effect of transverse anisotropy on the thermal response of the Callovo-Oxfordian claystone

79. Stephen Hedan, Anne-Laure Fauchille, Dimitri Prêt, Philippe Cosenza: Deterministic inference of Representative Elementary Area of clay rock at the mesoscopic scale

80. María Victoria Villar, Rubén Javier Iglesias, Beatriz Carbonell, Carlos Gutiérrez-Álvarez, Pedro Luis Martín: Evolution of a bentonite barrier initially inhomogeneous upon hydration

81. Hamza Mesrar, Laila Mesrar, Ahmed Benamar, Anne Pantet, Raouf Jabrane: Effect of cement on mechanical properties of bricks

82. Paul H. Nadeau, Pål Østebø Andersen, Dhruvit Satishchandra Berawala: Towards zero carbon emission power via CO_2 increased shale energy recovery

83. Yuto Nishiki, Tsutomu Sato, Tsubasa Otake: Formation of low-crystalline magnesium silicate at Kamuikotan metamorphic belts, Hokkaido, Japan

84. Cristiana Costa, Fernando Rocha, Lahcen Daoudi, Carla Candeias, Nathalie Fagel: Using multivariate techniques to assess the effects of raw materials source and manufacture of Rammed-earth and Coating on conservation: the case of Badii Palace (Marrakech, Morocco)

85. Dominik Zangerl, Molly Williams, Martin Ziegler, Simon Loew: Microstructure and micromechanical properties of EDZ, tectonic, and drilling-induced fractures in the Opalinus Clay shale

86. M. Zhang, C.J. Spiers: Effect of CO_2 on stress-strain cycling behaviour of smectites under geological storage conditions

Session C3: Thermal reactions of clays and their application in sustainable construction materials

87. Youssef Chalouati, Khaled Othmen, Faouzi Mannai, Ali Bennour, Ezzedine Srasra: Mineralogical composition, firing behavior and potential use of Tunisian Clay as Raw Material in geopolymer cement

88. E. Bonet-Martínez, L. Pérez-Villarejo, P. J. Sánchez-Soto, E. Castro, D. Eliche- Quesada: Effects of raw yellow clay addition on geopolymer synthesized from metakaolin

89. S. Martínez-Martínez, D. Eliche-Quesada, L. Pérez-Villarejo, P. J. Sánchez-Soto, A. Christogero, D. Kanellopoulou, G. N. Angelopoulos: Design of eco-cement clinker by valorizing wastes from the ceramic, the marble and the aluminum industries

90. H. Slimanou, N. Bouzidi, D. Eliche-Quesada: Port dredge sediments as raw materials in the manufacture of fired clay bricks

91. R. C. Kaze, G. L. Lecomte-Nana, M. Lacroix, E. Kamseu, U. Chinje Melo: Effect of solution type and temperature on the strengthening of laterite (Cameroon) based geomaterials: Rheological and micro calorimetry analyses

92. Jean-Frank Wagner: Alkali activation of gravel wash mud with KOH and NaOH

Session D2: LDH for future health: Advances and challenges in energy, environmental and medical applications

93. Anders B. A. Andersen, Nicholai D. Jensen, Yusuke Nishiyama, Nghia Dong, Ulla Gro Nielsen: Synthesis optimization and structural characterization of MAl_4 layered double hydroxides with M = Co(II), Ni(II), and Zn(II)

94. Bakhtyar K. Aziz, Dler M. Salh, Stephan Kaufhold: Characterization of (natural, acid activated and Ce-Al_{13}/pillared) Darbandikhan clay and their efficiency for the removal of Methyl orange as a model anionic dye

95. Gabriela Carja, Diana Gilea, Elena Seftel, Myriam Mertens, Pegie Cool: Mixed oxides obtained from Au/ZnCuLDH nanostructures with plasmonic photocatalytic response under simulated solar light

96. Belayneh Bekele, Laura Lundehøj, Nicholai Daugaard Jensen, Ulla Gro Nielsen, Claude Forano: Sequestration of orthophosphate by Ca_2Al-NO_3 Layered Double Hydroxide – Insight into reactivity and mechanism

97. Claude Forano, Karen M. Mantovani, Christine Mousty, Vanessa Prévot, Bianca R. Brito, Fernando Wypych, Shirley Nakagaki: Novel multifunctional core-shell material based on SiO_2@LDH/Gox/metalloporphyrin for hybrid catalysis

98. Do-gak Jeung, Hyoung-jun Kim, Jae-min Oh: Encapsulation of doxorubicin into polymer modified layered double hydroxide for effective cellular drug delivery

99. Nam-Ho Kim, Hyoung-Mi Kim, Jae-Min Oh: Reduction assisted exfoliation of ferric containing layered double hydroxide

100. Tae-Hyun Kim, Changyong Lu, Hans Chr. Bruun Hansen, Ulla Gro Nielsen: Investigation of phosphate removal efficacy of layered double hydroxide and their hybrid with magnetic nanoparticles

101. Eszter Mária Kovács, Marcell Balogh, József Kónya, Noémi M. Nagy: Sorption of $^{131}I^-$, $^{36}Cl^-$ and $^{99m}TcO_4^-$ Anions by ZnAl and MgAl Layered Double Hydroxides

102. Natálie Dvorníková, Petr Kovář, František Kovanda: Hydrotalcite-like hosts intercalated with atorvastatin

103. A. Misol, A. Morato, F.M. Labajos, V. Rives: Influence of media synthesis and thermal post-treatments on the properties of the Layered Double Hydroxides

104. Nestroinaia O.V., Tarasenko E.A., Yapryntsev M.N., Smalchenko D.E., Lebedeva O.E.: Sorption properties of natural hydrotalcite

105. Diego Perera, Ella Fidment, Hugh Christopher Greenwell: Andy Whiting: Production of ketones derived from fatty acids using a layered double hydroxide catalyst derived from waste-material: An efficiency and parameters comparison study

106. P. Koilraj, A. Aidoudi, C. Mousty, M. Takemoto, M. Takahashi, Y. Tokudome, V.Prévot: Preparation of NiAl Layered Double Hydroxide thin films and their electrochromic properties

107. Milan Pšenička, Jakub Škoda, Miroslav Pospíšil: Sulindac and Mefenamic acid intercalated into LDHs described by combination of DFT and classical MD simulations

108. Karolina Rybka, Jakub Matusik: Physico-chemical studies of Mg/Fe and Mg/Al Layered Double Hydroxides obtained via transformation of minerals

109. Ryltsova I.G., Tarasenko E.A., Nestroynaya O.V., Lebedeva O.E.: Synthesis and Study of Layered Double Hydroxides with Magnetic Properties

110. Leticia Santamaría, María López, Marcos García-Padial, Miguel Ángel Vicente, Raquel Trujillano, Sophia A. Korili, Antonio Gil: Drugs adsorption by hydrotalcite-like compounds synthesized from aluminium saline slag wastes

111. E. M. Seftel, S. Mullens, B. Michielsen: Sorption of metal oxyanions from complex solutions by layered double hydroxide (LDHs) type anionic clays

112. Elena M. Seftel, Radu G. Ciocarlan, Hao Wang, Bert Cuypers, Myrjam Mertens, Sabine Van Doorslaer, Yan Wu, Pegie Cool: ZnTi layered double hydroxides as photocatalysts for salicylic acid degradation under visible light irradiation

113. Noriyuki Sonoyama, Tomoki Ota , Shizuka Yamada: Synthesis and Electrochemical Properties of Layered Double Hydroxide Coated Electrodes Fabricated by Electrodeposition Method

114. Tiphaine Tailliez, Liliane Guerlou-Demourgues: Buserite and asbolane type manganese-cobalt-nickel phases for supercapacitors

115. Yasuaki Tokudome, Masanori Takemoto, Vanessa Prevot, Claude Forano, Ulla Gro Nielsen, Kenji Okada, Masahide Takahashi: Pseudomorphic Replication of Nano-sized Amorphous Aluminum Hydroxide into LiAl Layered Double Hydroxide

116. Alejandro Jiménez, Vicente Rives, Miguel A. Vicente, Raquel Trujillano, Elena Pérez, Francisco M. Labajos, Antonio Gil, Sophia Korili: Preparation of hydrocalumite from aluminium saline slags

117. Elena Zhitova, Sergey Krivovichev, Igor Pekov: Structural characterization of chlorine Layered Double Hydroxides

Session D5: Frontier and new applications of clay colloids

118. Paraskevi Efstathiou, Athanasios Karalis, Christos Dedeloudis: A rheological approach on the study and determination of fundamental structural parameters of hydrated bentonite systems.

119. Mahmoud Ramadan, Mervat S. Hassan: Enhance oil production throughout inhibition of fines migration using nano-drilling fluids

120. Paulo H. Michels-Brito, Antonio M. Gasperini, Ximena Puentes-Martinez, Leide P. Cavalcanti, Josef Breu, Koiti Araki, Kenneth D. Knudsen, Jon Otto Fossum: Clay nanoparticle organization at the air-liquid interface

121. Ana Catarina Trindade, Susete Fernandes, Ville Liljeström, Matthias Daab, Josef Breu, Maria Helena Godinho, Jon Otto Fossum: Iridiscent Cellulose-Clay Nano Structures

122. Shinya Yamamoto, Nobuyoshi Miyamoto: Angular-independent Structural Color of Liquid Crystalline Colloids of Fluorohectorite Clay Nanosheets

123. Daisuke Yoshioka, Yasumitsu Nishimura: Localized Surface Plasmon Resonance of Noble Metals Supporting onto Titanate Nanosheets

Session D8: Clays and health: From pelotherapy to drug delivery

124. Giuseppa Biddeci, Serena Riela, Marina Massaro, Tania Salerno, Paola Bonaccorsi, Anna Barattucci, Aurora Mancuso, Gaetano Spinelli, Francesco Di Blasi: Study of uptake mechanism for halloysite nanotubes in different cell lines

125. Ana Borrego-Sánchez, Carola Aguzzi, César Viseras, Ignacio Sainz-Díaz: Nanomaterial based on interaction of ethambutol with palygorskite as a tuberculostatic medicine

126. Bethune Karla B. Cortez, Grace Anne O. Galingana, Mitch-Irene Kate G. Oyales, Leslie Joy L. Diaz: Simultaneous exfoliation and functionalization of montmorillonite clay via high speed mechanical milling

127. María Virginia Fernández-González, Juan Manuel Martín-García, Alberto Molinero, Ana Cervera, M. Isabel Carretero, Rafael Delgado: Use of clays in peloids' manufacture for cosmetic use

128. Juliana da Silva Favero, Venina dos Santos, Valeria Weiss-Angeli, Lucas Bonan Gomes, Diego Gusmão Veras, Norberto Dani, André Sampaio Mexias, Carlos Pérez Bergmann: Evaluation and characterization of Melo Bentonite clay for cosmetic applications

129. Leander Michels, Everton dos Santos, Barbara Pacakova, Kristoffer Hunvik, Leide P. Cavalcanti, Koiti Araki, Heloisa N. Bordallo, Kenneth D. Knudsen, Jon Otto Fossum: In-situ intercalation of pharmaceutics in smectite clays

130. Ruta Ozola, Maris Klavins, Linards Klavins, Marta Jemeljanova, Juris Burlakovs: Preparation and characterization of natural anthocyanin and montmorillonite composites

131. Florence Thiriez: For a global mapping of customary uses of alumina silicates in primary health care

Session E2: General session

132. Patricia Aparicio, José Luis Mas, Emilio Galán, Domingo Martín: An approach to geological interpretation using Uranium and Thorium isotopes in kaolinitic clays

133. Ana María Fernández, Xabier Arroyo, D.M. Sánchez-Ledesma, Darío Chinchilla, Fernando Nieto: Applying chlorite as a thermometer in the FEBEX *in situ* test

134. Paolo Andre D. Benavides, Stephen Guggenheim, August F. Koster van Groos: Effects of CO_2 Pressure, Temperature and Brine Composition on the Interlayer Spacing of a Mg-exchanged Montmorillonite

135. Fatima Zohra El Berrichi, Besma Zadam, Diaa Obaid, Asma Mayoufi, Patricia Beaunier, Franck Launay: Oxidation of Benzyl alcohol over Nanoporous Ruthenium supported on DD3 kaolin

136. Debarghya Chakraborty, Koushik Halder: Effect of clay anisotropy on the probabilistic bearing capacity of strip footing under eccentric load

137. Hyen Goo Cho, Jeong-Kyu Jang, Hyo Jin Koo: Clay Mineralogy of 420 Mud Volcano in the Beaufort Sea, Arctic

138. Fabiola D. S. Curbelo, Alfredo I. C. Garnica, Giovanna L. R. Leal, Paula A. N. Costa, Guilherme N. A. Melo, Agostinho C. B. Junior, Maria G. Fonseca, Júlio Cézar O. Freitas: Use of organoclays in microemulsion-based drilling fluids

139. Ludovic Dore, Yasmina Boussafir, Christophe Chevalier: Utilization of computer vision for characterizing the sensitivity to disaggregation of soils immersed in water

140. W. Crawford Elliott, Daniel Gardner, Prakash Malla, Ed Riley, Ya Peng Yu: Heavy rare-earth element enrichments in kaolin gangue materials

141. Sarah Figowy, Benoît Dubacq, Philippe D’Arco, Yves Noël, Benoît Villemant, Benoît Caron: Thermodynamics and partitioning of halogens (F, Cl, Br, I) in phyllosilicates: analytical petrology coupled to geochemical modelling

142. Erin Gibbons, Richard Léveillé, Kim Berlo: Identification and Characterization of Phyllosilicates by Laser-Induced Breakdown Spectroscopy

143. Elisa Laita, Blanca Bauluz, Alfonso Yuste, Marcos Aurell, Beatriz Bádenas, José Ignacio Canudo: Mineralogical and textural characterization of the Barremian lateritic paleosols of the Oliete sub basin (Lower Cretaceous, NE Spain)

144. Mandana Peresson, Birgit Jochum, David Ottowitz, Robert Supper: Mineralogical composition of a clayey landslide, Wolfsegg am Hausruck, Upper Austria

145. Nattaporn Prakongkep, Robert Gilkes, Sumitra Wattana, Supaluck Pakankul, Chanida Kerdchana, Worachart Wisawapipat, Jean-Louis Janeau: The Influence of Soil Mineralogy on Soil Crust Morphology

146. Tetsuichi Takagi, Mayumi Jige, Mihoko Hoshino, Katsuhiro Tsukimura: Iron oxidation and leaching with intense kaolinization - implication of the formation of sedimentary kaolin deposits

147. Darko Tibljaš, Darko Hanžel, Zvonka Gverić: Mössbauer study of bentonites from Croatia and neighbouring countries

148. Molly Williams, Martin Ziegler, Simon Loew: Identification of self-sealing mechanisms in 10–20 year old excavation damaged zones through mineralogical, petrophysical, and geochemical tests and SEM imaging

149. Ingeborg Wimmer-Frey, Christian Benold, Peter Filzmoser, Maria Heinrich, Gerhard Hobiger, Can Mert, Julia Rabeder, Heinz Reitner, Jürgen Reitner: Gone with the wind: Integrative evaluation of Austrian loess and loess loam deposits by sedimentological, mineralogical and rock chemical analyses

Patio 44-55

5:30-7:30 pm Poster session #2 - Posters from sessions A1, A3, A4, B2, B6, B7, C4, D1, D3, D6, D7, E1

Session A1: Challenges in reactive transport modeling of clay systems

1. Peter Alt-Epping, Marek Pekala, Paul Wersin, Petteri Pitkänen, Ignasi Puigdomenech: Modelling sulfide fluxes and corrosion rates of copper canisters in a KBS-3 repository using a Donnan equilibrium approach.

2. Francis Claret, Mathieu Debure, Stephane Gaboreau, Carl Steefel, Christophe Tournassat, Yannick Linard: Multi-component reactive transport in a claystone: Insights from a ten-year alkaline in situ injection experiment

3. Lizaveta Fralova, Grégory Lefèvre, Benoît Madé, Romain Dagnelie: Transport of uranium in Clay rocks: studies on the effect of chemical perturbations

4. Emilie Coene, Andrés Idiart, Ola Wessely, Patrik Sellin: Modelling radionuclide diffusion through compacted bentonite in a nuclear waste repository vault

5. Tomoya Iioka, Masao Uyama,Hiroyuki Saito: Relation between Corrosion Behavior of Steel Rod and Bentonite Particle Size

6. M.G. Khramchenkov, E.M. Khramchenkov, R.M. Usmanov: A new model of mass transport in clays and its experimental verification

7. Sergey V. Kraevsky, Christophe Tournassat, Andrey G. Kalinichev, Marylène Vayer, Brice F. Ngouana Wakou: Identification of montmorillonite particle edge orientations by atomic-force microscopy

8. Qinfu Liu, Yongjie Yang, Shuai Zhang, Zhichuan Qiao, Kenan Zhang: Spiral growth of kaolinite nanocrystals and its constraint to the morphology of kaolinite aggregation

9. Christophe Tournassat, Carl I. Steefel: Modeling diffusion processes in the presence of a diffuse layer at charged mineral surfaces. A benchmark exercise.

10. Lixia Yan, Runliang Zhu: Significantly different effects of graphene oxide and fullerol on the phase transformation of ferrihydrite

Session A3: Physicochemical processes at the clay/water interface

11. Mary R. Arenberg, Yuji Arai: Ligand specific suppression of hydrogen peroxide generation in ultraviolet irradiated titanium dioxide

12. Zachary Burton, Janice Bishop, Peter Englert, Christian Koeberl, Everett Gibson: Clays from Antarctica Dry Valleys provide analogues for clays formed under cold, dry conditions on Mars

13. Javiera Cervini-Silva, Eduardo Palacios, Virginia Gomez-Vidales: Nontronite as natural source and growth template for (nano)maghemite [γ-Fe_2O_3] and (nano)wüstite [$Fe_{1-x}O$]

14. Ruarri J. Day-Stirrat, L. Taras Bryndzia, Anja M. Schleicher, Rieko Adriaens, Ronny Hofmann, Peter B. Flemings: Hydration behavior by X-ray diffraction profile fitting of smectite-bearing minerals in a Plio-Pleistocene mudrock from Eugene Island, Gulf of Mexico

15. Elise Duquesne, Stéphanie Betelu, Alain Seron, Ioannis Ignatiadis, Hubert Perrot, Ozlem Sel, Catherine Debiemme-Chouvy: Tuning redox state and ionic transfers of nano-Mg/Fe-(4/2) Layered Double Hydroxides using electrochemical and gravimetrical techniques

16. N. J. Kollannur, D. N. Arnepalli: Influence of acid and alkali treatment on physical and surface charge properties of clayey soils

17. Christelle Latrille, Olivier Bildstein: Cesium sorption on Ca-vermiculite: comparison with Ca-illite and Ca-smectite behavior

18. P. Nørnberg, H.P. Gunnlaugsson, K. Finster, S.K. Jensen: Iron oxides formed in an experimental forest fire related to the presence of hematite and maghemite in Weichselian sediments in Denmark

19. Mathilde Payen, Olivier Bildstein, Christelle Latrille: Kinetics of cesium sorption on Ca-illite: experiments and modelling

20. Sanchez-Encinar A., Lamarca-Irisarri D., Van Driessche A.E.S., Huertas F.J.: Effect of organic acids and ammonium ion on the dissolution kinetics of natural and K-saturated montmorillonite

Session A4: 1D Nanoporous clay minerals: Structures, genesis, functionalization, properties and applications

21. Muriel Andrade, Catalina Orellana, Mercedes Becerra-Herrera, Karen Manqián-Cerda, Nicolás Arancibia-Miranda: Imogolite as a sorbent phase for pharmaceutical products microextraction in water

22. Yamina Benaissa, Lala Setti Belaroui: Macroscopic identification of a bacterium found in Algerian palygorskite

23. Lamia Dali Youcef, Lala Setti Belaroui, Alberto Lopez Galindo: Hydrothermal treatment of natural Algerian palygorskite to produce LTA zeolite

24. Yuanfeng Cai: Products and mechanism study in acid-palygorskite reactions

25. Laura Pardo, Marta Domínguez Maqueda, Juan Antonio Cecilia, Rosa Serrano Soto, Manuel Pozo, Miguel Ángel Moriñigo, Francisco Franco: Adsorption of *Salmonella* by natural clays and clay-based advanced materials in contaminated waters

26. Rokhaya Sylla Gueye, Catherine Davy, Augustin Ndiaye, Adama Diedhiou, Mamadou Baldé, Thomas Yoro Tine, Idrissa Ndoye, Matar Seck, Djibril Fall, Alassane Wele, Frédéric Skoczylas, Mouhamadou Bassir Diop: Characterizations of attapulgite mbodiene for pharmaceutical trials preformulations

27. Rachid Hamar, Alberto Lopez Galindo, Lala Setti Belaroui: Synthesis and characterization of palygorskite modified with zinc oxide

28. Wenxiu Rao, Guocheng Lv, Libing Liao, Lefu Mei, Hao Liu: Enhanced Degradation of Rh 6G by Zero Valent Iron Loaded on Two Typical Clay Minerals with Different Structures under Microwave Irradiation

29. Peng Fan, Hao Liu, Libing Liao, Guocheng Lv, Lefu Mei: High performance supercapacitor of polyaniline Nanotubes synthesized from halloysite template

30. Rui Ma, Wei Tang, Pan Hu, Yao Li, Zhiyan Liu, Peishan Liao: Nanostructured organic-amine-decorated 13X zeolite for reversible CO_2 capture

31. Jakub Matusik, Karolina Rybka, Paulina Maziarz, Jakub Hyla, Joanna Kuzdro, Bartosz Toboła: Halloysite-LDH heterostructured materials: performance in removal of selected anions from aqueous solutions

32. Jianle Weng, Libing Liao, Guocheng, Hao Liu, Lefu Mei: Probing the interactions between lucigenin and phyllosilicates with different layer structures

33. Jinan Niu, Aichun Wu, Duoxiao Wang, Lu Zhou: Computer simulation of mechanical properties of kaolinite nanotubes with different orientations

34. Choong Yi, Justin Wong, Daniel Kong, Ehsan Zeimaran, Pooria Pasbakhsh: Effect of various nano-clays on structural and mechanical properties of fly ash-based geopolymers

35. Pierre Picot, Thibaud Coradin, Antoine Thill: Modification of the internal cavity of methyl-imogolite

36. Ruhaida Rusmin, Binoy Sarkar, Yanju Liu, Ravi Naidu: Australian palygorskite for treating Pb (II) contaminated water

37. Xiaohan Yang, Mingxian Liu: Preparation of cellulose nanofiber/ halloysite nanotubes composite films and study on performances of the film

38. Cristina Fernández-Barranco, Antonio Esteban, Marta Sacristan, Africa Yebra-Rodriguez: Sepiolite as nucleating agent of extruded polystyrene composite foams

39. Peng Yuan, Yanfu Wei, Dong Liu, Hongchang Liu, Junming Zhou, Peixin Du, Yaran Song: Activation of Halloysite and Kaolinite by Introducing Lanthanum Oxycarbonate Nanoparticles via Co-calcination for Efficient Phosphate Removal

40. Shuai Zhang, Qinfu Liu, Lihui Liu, Zhichuan Qiao, Yongjie Yang: Genesis of palygorskite from Baiyanghe Formation of Neogene in Yangtaiwatan basin, north Gansu province, China

41. Junming Zhou, Peng Yuan, Baifa Zhang, Dong Liu: Co-existence of Clay Minerals and Nano-sized Cerium Mineral in Bachi Rare Earth Deposit, in Guangdong Province, China

42. Yongfeng Zhu, Wenbo Wang, Taotao Lu, Yuru Kang, Li Zong, Qin Wang, Aiqin Wang: Hierarchically porous adsorbent prepared from eco-friendly Pickering MIPEs for high-efficient adsorption of Rb^+ and Cs^+

Session B2: The role of clays and modified clays in remediating environmental pollutants

43. Heini M. Reijonen, Masakazu Ito, Susanna Arvilommi, Jojo Garcia, Erik P. Kremer, Simon Norris, Nick Jefferies, W.Russell Alexander: Preliminary results of the IBL (International Bentonite Longevity) project

44. Almudena Gómez Avilés, Jorge Bedia, Sellaoui Lotfi, Juan Jose Rodriguez, Carolina Belver: Adsorption of emerging contaminants on derived clay materials

45. Petr Belousov, Anna Semenkova, Anna Romanchuk, Viktoria Krupskaya: Neptunium (V), uranium (VI), cesium (I) and strontium (II) uptake by various natural filtration and non-filtration sorbents

46. Carmen B. Molina, A. Gomez-Aviles, Carolina Belver, Juan J. Rodriguez: Removal of emerging pollutants in aqueous phase by CWPO and photo-assisted CWPO with Fe-TiO_2 delaminated clays

47. Carmen B. Molina, A. Boukhemkhem, Carolina Belver, Juan J. Rodriguez: Fe-modified kaolin as catalyst for CWPO of phenolic compounds

48. Leonard Böhm, Rolf-Alexander Düring, Jan Siemens: Sediment clay minerals as longterm sink for hydrophobic organic chemicals?

49. M. Boumelik, M. Zahraoui, M. Belhachemi: Removal of Malachite Green Dye onto Natural Clays: Equilibrium Isotherms and Kinetics Studies

50. Leticia de Melo, Michelle Saltarelli, Eduardo José Nassar, Emerson Henrique de Faria, Katia Jorge Ciuffi, Miguel Angel Vicente, Raquel Trujillano, Vicente Rives, María Elena Pérez, Francisco M. Labajos, Antonio Gil, Sophia Korili: Kaolinite-Fe-TiO_2 composites as potential photocatalysts for acetylsalicylic acid removal

51. Dler M. Salh, Bakhtyar K.Aziz, Kaufhold S.: Characterization of Tagaran natural clay and its efficiency for removal of cadmium(II) from Sulaimani industrial zone sewage

52. Soumia Zen, Fatima Zohra El Berrichi, Nadjib Abidi, Joelle Duplay, Amane Jada, Brahim Gasmi: Activated Algerian kaolins as low-coast potential adsorbents for the removal of Derma Blue R67 acid dye

53. Meriam El Ouahabi, Safae Oumnih, Elkhadir Gharibi, Achraf Harrou, Nathalie Fagel: Potentiality of raw bentonite for removal of heavy metals from acidic phosphogypsum waste

54. Abdelhak Maazouzi, Driss Lahcene, Asma Behilil, Brahim Zahraoui, Meriem Belhachemi, Abdelkader Badri, Abderrahim Choukchou-Braham: Fe_2O_3/Clay as useful heterogeneous Fenton catalyst for the elimination of Congo Red

55. Tiziana Missana, Ursula Alonso, Miguel García-Gutierrez, Manuel Mingarro, Ana María Fernández: Evaluation of clay-based geochemical barriers for cadmium migration.

56. Denise B. França, Maria G. Fonseca, Francisco Rodrigues, Pollyana Trigueiro, Edson Cavalcanti da Silva Filho, Josy Anteveli Osajima, Maguy Jaber: Alkylpyridinium montmorillonite as new adsorbent for diclofenac

57. Yulia Izosimova, Irina Gurova, Inna Tolpeshta: Sorption Of Cu^{2+} Ions And Humic Acids From Aqueous Solutions By Modified Bentonite

58. Luboš Jankovič: Sorption an textile dye to clay modified with phosphonium surfactants

59. Nataša Jović-Jovičić, Irena Ilić, Sanja Marinović, Marija Ajduković, Predrag Banković, Zorica Mojović, Tihana Mudrinić, Aleksandra Milutinović-Nikolić: Cobalt impregnated smectites (raw and acid activated) as catalysts in organic dye oxidation process in the presence of peroxymonosulfate generated radicals

60. Ahmad Khan, Mohammad Saleem Akhtar, Saba Akbar, Biao Huang, Aiqin Wang, Mazhar Iqbal, Youjun Deng: Mineral characterization of Pakistan's indigenous clays for their potential use as aflatoxin adsorbent

61. Kazuki Kobayashi, Yohey Hashimoto: Effects of pH values and polyborate anions on boron coprecipitation with calcium carbonate

62. Marina Kryuchkova, Elvira Rozhina, Rawil Fakhrullin: Kaolin clay alleviates toxicity of graphene oxide in aqueous environments

63. Jana Madejová, Peter Komadel, Helena Pálková: Infrared spectroscopy in studies of acid-treated clay minerals

64. Sanja Marinović, Marija Ajduković, Tihana Mudrinić, Nataša Jović-Jovičić, Zorica Mojović, Aleksandra Milutinović-Nikolić, Predrag Banković: The effect of different reaction parameters on catalytic oxidation of tartrazine induced by Oxone® activated by cobalt impregnated aluminium pillared montmorillonite

65. Domingo Martín, Patricia Aparicio, Emilio Galán: Time evolution of the mineral carbonation of ceramic bricks in a simulated pilot plant using a common clay as sealing material at superficial conditions

66. Matthias Monneron--Gyurits, Emmanuel Joussein, Marilyne Soubrand, Alexandra Courtin-Nomade: Synthesis and characterization of zinc-bearing silicates phases: a new way to assess health risks from polluted sites

67. Marek Osacký, Martina Vítková, Ľuboš Jankovič, Adriana Czímerová, Helena Pálková, Pavol Hudec, Jaroslav Sedláček: Role of mineralogy, chemistry and surface properties of different zeolitic materials synthesized from perlite by-product on retention of selected elements from soil pore water.

68. Helena Pálková, Martin Barlog, Lukáš Petra, Jana Madejová, Erik Šimon, Małgorzata Zimowska: Influence of dry grinding on the structure of dioctahedral and trioctahedral smectites and organo-modified smectites

69. Heini Reijonen, Jukka Kuva, Pasi Heikkilä: Description of bentonite textures and structural characteristics through 3D analysis

70. Ana I. Ruiz, Raúl Fernández, Mónica Martínez, Olga Fafila, Begoña Mayans, Enrique Eymar, Jaime Cuevas: Stevensite-geofilter effectifivity for antibiotics sorption in wastewater treatments

71. Mismel Ruiz-Garcia, Mario Villalobos-Peñalosa, Nadia Valentina Martinez-Villegas, Francisco Romero: Humic acids influence on the thallium-potassium cation exchange behavior of illite

72. Luca Serpella, Monica Granetto, Tiziana Tosco: Assessment of reduced environmental impact of a novel clay-based herbicide formulation: release and volatilization tests

73. Michal Slaný, Ľuboš Jankovič, Jana Madejová: Effect of chain length and surfactant loading on the self-assembly of primary alkylammonium cations on montmorillonite

74. Satoko Tezuka, Kouki Hoshi: Anion exchange properties of monoclinic lithium-aluminum layered double hydroxides synthesized by simplified method with bayerite

75. Magdalena Tuchowska, Tomasz Bajda: Modification of bentonite with mixed cationic-nonionic surfactants

76. Beatriz González, Bárbara Muñoz, Miguel Ángel Vicente, Raquel Trujillano, Vicente Rives, Leticia Santamaría, Antonio Gil, Sophia A. Korili: Photocatalytic removal of 1,2,4-trichlorobenzene by montmorillonite-TiO_2 nanocomposites

77. Yu Liang, Mingxia Wang, Wenfeng Tan: Al-substitution-induced defect sites enhance adsorption of Pb^{2+} on hematite

78. Laurence Noel Warr: Biocompatible smectite-talc mineral flakes for enhancing the biodegradation of marine oil spills

79. Magdalena Wołowiec, Małgorzata Komorowska-Kaufman, Alina Pruss, Grzegorz Rzepa, Tomasz Bajda: Characterization of aluminum-based drinking water treatment residuals

80. Zhongkuan Wu, Caroline L. Peacock, Bruno Lanson, Fan Liu, Xionghan Feng, Hui Yin, Lirong Zheng: Transformation of Co-containing birnessite to todorokite: Effects of Co on the transformation and implications for Co mobility

81. Brahim Zahraoui, Driss Lahcene, Abdelkader Badri, Abdelhak Maazouzi: Removal of chromate from wastewater using modified montmorillonite obtained by intercalation with Iron and Aluminum

82. S. Zakusin, O. Dorzhieva, E. Tyupina, P. Belousov, V. Krupskaya: The influence of acid modification on the sorption of radioactive and stable isotopes of Cs and Sr on bentonites

Session B6: The role of clay minerals in the origin of life

83. Svetlana Batasheva, Elvira Rozhina, Rawil Fakhrullin: Studying the interaction of halloysite nanotubes with nucleotides and nucleic acids

84. Pablo del Buey, M. Esther Sanz-Montero, Olivier Braissant, Óscar Cabestrero, Pieter.T Visscher: The role of natural microbial extracellular polymeric substances on fibrous Mg-clays formation

85. Gilles Montagnac, Jihua Hao, Ulysse Pedreira-Segade, Isabelle Daniel: Detection of nucleotides absorbed onto clay by UV Resonant Raman spectroscopy: preliminaries to the search for biological traces on Mars

86. Simon Duval, Fabienne Trolard, Olivier Grauby, Frauke Baymann, Wolfgang Nitschke: Fougerite, the key mineral to understand bioenergetics mechanisms at the origin of life?

87. Jihua Hao, Laurent J. Michot, Isabelle Daniel: Effects of transition metals on the adsorption of nucleotides onto clay mineral surfaces: implications for the origin of life

88. Shunta Higashino, Ryohei Kawakita, Tsubasa Otake, Tsutomu Sato: Effect of Mg-silicate formation on hydrogen generation during low temperature serpentinization

89. Barbara Lafuente, Genesis Berlanga, Thomas Bristow: Use of clay minerals as indicators of the paleoenvironments of Ediacaran multicellular life in the Doushantuo Formation (South China)

90. Ulysse Pedreira-Segade, Jihua Hao′, Angelina Razafitianamaharavo, Manuel Pelletier, Virginie Marry, Sébastien Le Crom, Laurent J. Michot, Isabelle Daniel: Influence of cationic valence on the adsorption of nucleotides onto montmorillonite: a Molecular Dynamics study

91. Fabrícia de Castro Silva, Luciano Clécio Brandão Lima, Edson Cavalcanti da Silva Filho, Maria Gardênnia da Fonseca, Jean-François Lambert, Maguy Jaber: Adsorption of amino acids in clay minerals and their possible contribution to the origin of life

92. Pollyana Trigueiro, Luís Humberto de Oliveira, Edson Cavalcanti da Silva Filho, Josy Anteveli Osajima, Maria Gardênnia Fonseca, Thomas Georgelin, Maguy Jaber: RNA-exchanged montmorillonite complexes in prebiotic chemistry

Session B7: Diagenesis and low-grade metamorphism (4th Frey-Kübler Symposium)

93. Mikhail Chernov, Ruslan Kuznetsov, Viktoriya Krupskaya, Sergey Zakusin, Vyatcheslav Sokolov: Nanoparticles In Hydrothermal Clays (South Kamchatka, Russia)

94. Ruslan Kuznetsov, Ilya Bol'shakov, Mikhail Chernov, Julia Frolova, Vyatcheslav Sokolov: Properties of hydrothermally modified rocks of the Pauzhetskoye field

95. Navot Morag, Ofra Klein-Ben David: Clay Minerals composition of the Late Neoproterozoic Zenifim Formation (southern Israel)

96. Jasmin Schönenberger, Håkon Rueslåtten, Marco Brönner: Tropical paleo-weathering and variations in clay mineralogy in the Ramså Basin, northern Norway

97. Ernst Spiridonov, Vladimir Ladygin, Julia Frolova, Oleg Lavrov, Elena Putintseva, Evgenia Semikolennykh, Vyacheslav Sokolov, Michael Chernov: Agates in the low-grade metamorphic volcanic rocks: “bearing”, “existence”, “extinction”

98. Ernst Spiridonov, Elena Putintseva, Alexey Ariskin, Evgeniy Kislov, Inna Kulikova, Oleg Nabelkin, Georgy Nikolaev: Geochemistry and mineralogy of REE in low-grade metamorphosed magmatic rocks and problems of their Sm/Nd dating

99. Katarzyna Luberda-Durnaś, Marek Szczerba, Jan Środoń: Crystallinity of hematite as a potential indicator of diagenetic grade

100. Hejing Wang, Jian Zhou, Jiali An, Guanyu Wang, Yu Yan, Mengyao Chen: Very low to low-grade metamorphism of Precambrian in Fanjingshan area, Guizhou, China

Session C4: Photochemistry, photophysical and optical functionalities of clay mineral based materials

101. Maya Aimeur, Faiza Zermane, Michel Baudu: Elaboration of hybrid photosensitizer based on natural clays for water micropollutants photodegradation

102. Tímea Baranyaiová, Juraj Bujdák, Táňa Sebechlebská: Effect of ionic strength on the molecular aggregation of cationic dye in colloidal dispersions with montmorillonite particles

103. M. Barlog, H. Pálková, J. Bujdák: Spectroscopic study of organo-smectites and cationic laser dye hybrid systems

104. Silvia Belušáková, Rebeca Sola-Llano, Iñigo Lopez Arbeloa, Virginia Martínez-Martínez, Juraj Bujdák: Resonance energy transfer between dye molecules in hybrid films of a layered silicate including the effect of dye surface concentration

105. Peter Boháč, Adriana Czímerová, Ryo Sasai, Juraj Bujdák: Hybrid systems based on layered silicate and cyanine dyes prepared by LBL method for studying FRET phenomenon

106. Elena-Florentina Grosu, Gabriela Carja, Renato Froidevaux: Self-assembled gold nanoparticles on layered double hydroxide matrix as a photocatalyst for Horseradish Peroxidase activation and cofactor regeneration

107. Elena-Florentina Grosu, Gabriela Carja, Renato Froidevaux: Combining photo- and enzymatic-catalysis for phenol removal using Horseradish Peroxidase, ZnMeLDH (Me=Al, Cr) and their derived mixed oxides

108. Driss Lahcene, Asma Behilil, Brahim Zahraoui, Meriem Belhachemi, Abdelhak Maazouzi, Abdelkadeur Badri, Abderrahim Choukchou-Braham: Incorporation of ZnO into clay volcanic (sericite-clinochlore) by impregnation Method for photo-degradation of the methylene blue dye under solar

109. Luciano Clécio Brandão Lima, Fabrícia de Castro Silva, Edson Cavalcanti da Silva Filho, Maria Gardênnia da Fonseca, Maguy Jaber: Hybrid pigments clay-anthocyanin: slipping between the sheets

110. Kengo Nishio, Masaya Miyagawa, Hideki Tanaka: Photoluminescent Cu nanoparticles induced by energy transfer on saponite nanosheets

111. Graycyelle R. S. Cavalcanti, Guanzheng Zhuang, Francisco Rodrigues, Maria G. Fonseca, Maguy Jaber: New routes of synthesis to obtain hybrid pigments based on carminic acid

112. Misa Sugiura, Mai Sueyoshi, Ryuichi Seike, Takayoshi Hayashi, Tomohiko Okada: Crystal growth of an expandable layered silicate on fluorophlogopite surface

Session D1: Recent Progress on Nanotechnology and Nanomaterials from Clay Minerals

113. Tihana Mudrinić, Sanja Marinović, Zorica Mojović, Aleksandra Milutinović-Nikolić, Marija Ajduković, Nataša Jović-Jovičić, Predrag Banković: Carbon paste electrode modified with cobalt-impregnated pillared smectite for analytical detection of glucose

114. Goeun Choi, Jin-Ho Choy: Injectable Drug Delivery System with an Anionic Clay for Chemotherapy

115. Koutsopoulou Eleni, Christidis Georgios, Marantos Ioannis: Effect of layer charge and charge distribution on the formation of smectite- chitosan nanocomposites

116. Koutsopoulou Eleni, Papagiannopoulos Aristeidis, Christidis Georgios: Surface Plasmon Resonance investigation of clay and organo-clay film formation on Au/water interface

117. Fatima Zohra El Berrichi, Ibtissem Slatni, Nor el Houda Ferdjaoui, Joelle Duplay: Mesoporous silica synthesised by a local kaolin as efficient adsorbent for the real effluent textile treatment

118. S. Ghazi, O. Lakbita, B. Rhouta, F. Maury, L. Daoudi: Direct TiO_2 immobilization onto palygorskite nanofibers by one-pot mechanical synthesis: characterizations and photocatalytic activity

119. Elena-Florentina Grosu, Renato Froidevaux, Gabriela Carja: Gold release from AuNP/ZnAlLDH mediated by Horseradish Peroxidase and AuNP influence on enzyme activity

120. Luboš Jankovič, Juraj Kronek, Jana Madejová, Viktor Hronský: Intercalation of montmorillonite with functionalized surfactant

121. Paulina Maziarz, Jakub Matusik: Effectiveness of As(V) removal from wastewaters by layered double hydroxides impregnated with Fe oxide

122. Małgorzata Zimowska, Jacek Gurgul, Robert P. Socha, Helena Pálková, Kazimierz Łątka, Leszek Matachowski: Laponite® derived porous heterostructures for hydrogen production

123. Marina Massaro, Carmelo G. Colletti, Giuseppe Lazzara, Serena Riela: Multifunctional carrier based on clay minerals for drug delivery applications

124. Cristina Ruiz-García, Francisco Heras, Miguel Ángel Gilarranz, Pilar Aranda, Eduardo Ruiz-Hitzky: Carbon-sepiolite nanostructured materials incorporating Pd nanoparticles as improved catalysts for hydrodechlorination processes

125. Zita Timár, Claude Forano, Vanessa Prevot, Claire Richard, Pál Sipos, István Pálinkó: Zn_2Al- and Mg_2Al-layered double hydroxides as nanoreactors in the photoinduced interlayer isomerization of *E*-cinnamate

126. Yasushi Umemura, Masanari Hirahara, Yoshihiro Miyauchi, Hiroki Goto: Application of electrospray spreading to organo-clay hybrid film preparation by a modified Langmuir–Blodgett technique

Session D3: Clay and clay minerals in ceramics: From industrial to new hierarchical/textural materials

127. Angel Sanz, Joaquín Bastida, Angel Caballero, Marek Kojdecki: Crystallite size evolution of mullite in whiteware triaxial porcelains made from two different kaolin raw materials

128. Jemaa Amakrane, Kamal El Hammouti, Ali Azdimousa, Meriam El Ouahabi, Frédéric Collin, Abdelali Gourfi, Nathalie Fagel: Mineralogical and physicochemical characterization for the valorization of the Miocene formations of the Taourirt basin (Eastern Morocco)

129. Elisa Laita, Blanca Bauluz, Alfonso Yuste, Maria José Mayayo: High-temperature phases in fireclays by spontaneous coal combustion process

130. Gisèle Laure Lecomte-Nana, Imane Daou, Edouard Bareil, Claire Peyratout: Understanding the interactions of surfactants and clays used for the shaping of textured silicate ceramics

Session D6: Archaeoceramics: Raw materials, technology and provenance

131. Giacomo Disantarosa, Giacomo Eramo: The cargo of amphorae and the ceramics of the shipwrecks *La Madonnina A* and *B* (Campomarino, Maruggio - Taranto, Italy)

132. Ágnes Gál, Corina Ionescu, Volker Hoeck, Mátyás Bajusz, Vlad A. Codrea, Lucian Barbu-Tudoran: Compositional constraints in inferring the provenance of 2nd c.AD pottery from Roman *Napoca*

133. Elisabetta Gliozzo: Stamped bricks and tiles from southern Tuscany (Italy): the exploitation of local raw materials and the imports

134. Corina Ionescu, Andreea Drăgan, Ágnes Gál, Elisabetta Gliozzo, Lucian Barbu-Tudoran: Roman amphoras from an Iron Age settlement at the Danube

135. Artur Kuligiewicz, Arkadiusz Derkowski: How to properly describe mass gain in dehydroxylated clay mienrals?

Session D7: Clay mineral synthesis

136. Fabien Baron, Sabine Petit, Alain Decarreau: Experimental evidence of the metastability of nontronite

137. Krzysztof Bahranowski, Agnieszka Klimek, Adam Gaweł, Katarzyna Górniak, Alicja Michalik, Ewa M. Serwicka: Structural transformations of calcined [Ti,Zr]-pillared montmorillonites in relation to thermal evolution of hydrolysates obtained from [Ti,Zr]-pillaring solutions

138. Renata S. Nascimento, Bruno A. M. Figueira, Thays Lavra, Igor A. R. Barreto, Marcondes L. da Costa, José Rivas Mercury, Herbert Pöllmann: Hydrothermal synthesis of layered and tunnel manganese oxides from Mn mining residues from Amazon (Brazil)

139. Martine Lanson, Jean-Louis Robert, Bruno Lanson, Valérie Magnin, Nathaniel Findling, Baptiste Dazas, Eric Ferrage: Hydrothermal synthesis of trioctahedral smectites with an extended compositional range

140. Renata S. Nascimento Bruno A. M. Figueira, Alex J. F. Cabral, Igor A. R. Barreto, Marcondes L. da Costa, Herbert Pöllmann: TG-DTA and synchrotron-radiation X-ray diffraction investigations of nanopyroaurite-type material obtained from bauxite washing residues

141. Sabine Petit, Fabien Baron, Alain Decarreau: The role of interlayer cations on the stability and on the crystal-chemistry of nontronite

142. Peter C. Ryan, F. Javier Huertas: Arsenic speciation in trioctahedral clays: insights from a serpentine synthesis study

Session E1: Teaching clay science

143. Ray E. Ferrell, Jr.: Massive open online clay course, a 21st century approach to teaching clay science

6. Abstracts

Clay signature of fluid flows associated to the major Arlit fault: a case study of Teloua formation-Tim Mersoï Basin, Niger

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The Tim Mersoï sedimentary basin is located on the NE of Niger republic (West Africa) and it is filled mainly with detrital materials transported from the Aïr Mountains to the East. The largest tectonic structure impacting the Tim Mersoï basin is the Arlit-In-Azawa (AIA) fault, which is related to the Pan-African orogeny with N-S trending associated with several secondary shearing faults with NNE-SSW or ENE-WSW orientations. Teloua which belongs to the Tim Mersoï sedimentary basin is an upper Triassic-lower Jurassic formation that consists mainly of medium to coarse sandstones locally intercalated with conglomerates.

There are no previous petrological-mineralogical studies conducted on the Teloua formation, particularly for studying clay minerals. Therefore, the objectives of this work are to study the mineralogical-chemical evolution of clays with depth, and to characterize the changes that are related to late fluid flows along the AIA fault in the Teloua formation (COMINAK mining site). Three drill holes were investigated as a function of their distance from the AIA fault, a distal drill hole (DH 1) is located at 2.45 km west of the fault (109 m thick) while two other proximal drill holes (DH 2 and DH 3) are located at approximately 0.5 km and 0.25 km west of the fault (62 m and 64 m thick) respectively. 73 samples were collected from the three drill holes including the Teloua formation (66 samples), the unconformity horizon between Teloua and the underlaying upper Permian Moradi formation (3 samples), and the top of the Moradi formation (4 samples).

XRD and SEM results indicate no significant variation in detrital mineralogy between the samples of the three drill holes. Samples of the Teloua sandstones are mainly composed of quartz, K-Feldspar, Na-Feldspar, Fe-oxides, Ti-oxides, phosphates (apatite and monazite) and zircon. Mica has been also observed in the three drill holes at different levels. High amount of analcime is present in the top of the Moradi Fm. The only difference is the presence of dolomite and calcite at the unconformity surface of Teloua-Moradi on the DH 2 and DH 3 (i.e. close to the AIA fault). The clay mineralogy related to the diagenetic evolution of the sedimentary column is similar in all drill holes. Tosudite occurred essentially in the Teloua Fm, saponite occurred at the unconformity between Teloua Fm and Moradi Fm, and dioctahedral smectite occurred at the top of Moradi Fm. Late downward circulations of fluids are evidenced from the superimposition of clay paragenesis identified only in the Teloua Fm of the proximal drill holes. Superimposition of clay paragenesis is due to the partial alteration and replacement of diagenetic tosudite by kaolinite-smectite mixed layer + di-smectite at shallow depth and by only di-smectite deeper. Such a vertical transition in the mineralogy of the late clay phases is interpreted as a result of a downward infiltration of rather acidic fluids which tends to be progressively neutralized with increasing depth.

$^{40}Ar/^{39}Ar$ radiometric dating of thrust activity using synkinematic clay minerals: a case study from the Axial Zone of the Pyrenees

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Clay minerals are one of the major components of fault zones in sedimentary rocks. The radiometric dating of synkinematic illite/mica was found to be a reliable technique to provide the timing of thrusting and tectonic events. However, dating tectonic activity in the sedimentary environments is a challenging subject due to the mixing of different generations and/or different grain-size of clay minerals, superposition of multiple tectonic events and related uplift and exhumation processes.

The present study focusses on the Pyrenean orogen that is formed by the convergence of the Iberian and European plates during the Late Cretaceous to early Miocene periods. The range is well suited to study the evolution of tectonic activity because it features well exposed deformation structures and exceptionally well preserved syntectonic strata in the foreland basins. The main focus of the present study is the Pic de Port Vieux thrust (PPVT) located in the southwestern part of the Pyrenean Axial Zone. The PPVT is a secondary thrust related to the major Gavarnie thrust (GT) with a footwall comprising Upper Cretaceous limestones, and a hanging wall made of Lower-Triassic pelites and sandstones. A vertical transect in the fault hanging wall was investigated to characterize the deformation mechanism and to date the thrust activity by using the $^{40}Ar/^{39}Ar$ step-heating technique on muscovite.

Petrographic observations confirm that pressure solution and recrystallization/dissolution processes in presence of fluids are the main mechanisms that controlled the chemical/textural changes in the fault core zone. Three groups of muscovite are identified in the fault zone i.e. detrital, diagenetic and newly-formed muscovites. The detrital and diagenetic muscovites are mainly present in the damage zone, while the newly-formed muscovite is abundant in the core zone and is synkinematic to the fault activity. Different size fractions of two samples from the core and damage zones were encapsulated and dated using the $^{40}Ar/^{39}Ar$ technique. All size-fractions of the core zone sample have younger ages compared to ones from the damage zone and the ages decrease with grain-size reduction. This indicates the strong effect of deformation in the core zone that enhanced the recrystallization of younger muscovite. The finest fraction (< 0.5 µm) of the core zone sample has a plateau-like spectrum with a total gas age of 36.9 ± 0.2 Ma. This age is interpreted as the oldest age possible for the activity of the PPVT during the late Eocene (Priabonian) that coincides with the activity of the GT.

In Situ Scanning Electron Microscopy Analysis of Nanoindentation Pop-Ins in High Clay Content Shale

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Pop-ins created in micro and nano-layered natural colloidal porous composites, with relatively high clay mineral content, were mostly observed when indenting perpendicular to the depositional planes of the geological material. Pop-ins were not affected by rate of loading, however, they were almost wiped out as the shale samples were indented under elevated temperatures. Shale source rocks are naturally laminated composites of clays among other minerals, while also containing rich mixtures of organics that render the overall material difficult to characterize mechanically or physically at macro-scales in laboratories or in-situ. This work elucidates, under the large stresses of the nanoindenter tip, that a wide range of geological phenomena and failure types could be observed while the pop-ins size, frequency and their related energies could be established. While pop-ins continue to be analyzed and debated in materials science, in this study they are discussed and interpreted for the first time, using *in-situ* SEM images correlated with isolated load-depth curves and displacement-discontinuities, for this high clay content organic rich shale.

Hydromechanical properties of a commercial bentonite from Slovakia

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Bentonites are a very important part of the technical barrier system designed for a deep geological repository of the radioactive waste (DGRW). Their research for this specific kind of application is going on for more than 30 years, while some countries are already very close to the moment of turning the construction plans into reality. Other countries like Slovakia are very far from solving the problem. The research of suitable local bentonites is much more advanced than the survey of suitable sites for the DGRW. The time span between the bentonite research and its application is too long, resulting in exhausting the best bentonites for other applications probably earlier than the construction of DGRW starts. This is the destiny of the best Slovak bentonite from the Jelsovy Potok deposit. Also the very similar high-quality bentonite from the close deposit in Kopernica disappeared from the portfolio of its earlier provider. A “bentonite of Kopernica type” (BKT) is sold instead.

A range of mineralogical and geochemical analyses were carried out to test the suitability of BKT and to compare it to the bentonite K45 which was reported earlier. No big differences were found that time. Now the hydromechanical properties were studied. Suction was measured by the chilled mirror method and water retention curves were constructed for bentonite in both forms, powder or compacted to different dry densities. Swelling pressure of the compacted bentonite was also tested at relevant dry densities to create a data set for the estimate of the relation between the suction and swelling pressure. Results of the water adsorption by Enslin-Neff were compared for those bentonites, too.

Results are not such as expected according to previous analyses. BKT shows lower swelling pressure than K45. Because of the quite weak brass material used for the closed cups with compacted samples for the suction tests, bentonite could not be compacted to densities necessary for DGRW yet. New cups from hard steel should prevent the deformation of cups during compaction and swelling of high-density bentonites. For this reason, research is still going on, just preliminary results can be presented. They already show BKT is not of the same quality as K45.

Ion exchange in fougèrite: influence of crystal size and structural defects

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Fougèrite, a Fe(II)/Fe(III) layered double hydroxide that was identified twenty years ago in hydromorphic soils, is a naturally-occurring form of green rust (GR). GR layers are positively charged because of the occurrence of mixed $Fe^{2+/3+}$ valence states within the layers. The layer charge is compensated by anions in the interlayer space. These interlayer anions are exchangeable with anions present in the pore water. Where present, GR participate to the biogeochemical cycling of anions, including nutrients or pollutants, in the environment. In this study, we carried out a detailed analysis of green rust ion exchange properties, with the aim of contributing to a better understanding of the biogeochemical cycle of elements in soils. In particular, we investigated the Cl^-/SO_4^{2-} exchange mechanism on two samples having similar layer structure, but particle size distributions either in the nanometer or in the micrometer size range. Samples were characterized by a combination of chemical and physical methods, including synchrotron high-energy X-Ray scattering and synchrotron *in situ* and time-resolved X-ray diffraction. The replacement of Cl^- by SO_4^{2-} followed a 2:1 stoichiometry, and led to an increase of interlayer distances, in agreement with an anion exchange mechanism without dissolution or recrystallization. Total anion exchange capacity and Cl^-/SO_4^{2-} selectivity coefficients (K_{ex}) were inferred from modelling of aqueous chemistry data. Exchange data were adequately described by an anion exchange thermodynamic model using the Rothmund-Kornfeld convention with a K_{ex} value of 0.58 and a β value of 3 for nanometric samples and 0.14 and a β value of 5 for micrometric samples.

Elaboration of hybrid photosensitizer based on natural clays for water micropollutants photodegradation

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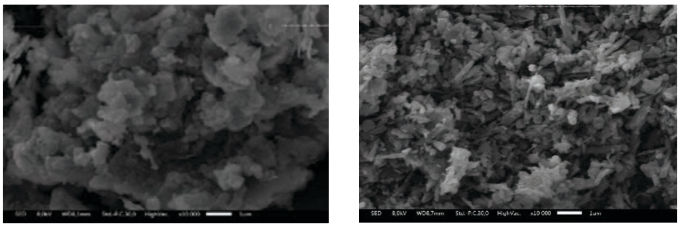
The aim of this study is to develop a new hybrid photosensitizer based on natural clays for water micropollutants photodegradation. Phenalenone (PN) was successfully incorporated to Halloysite and Kaolinite. The Characterization of obtained hybrid materials PN-Halloysite and PN-Kaolinite by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and UV-VIS Spectroscopy confirm the incorporation of Phenalenone to the clays.

The preparation of the hybrid materials was achieved by adsorption in aqueous solution in one- step procedure. After 24 h of stirring, the dispersion was centrifuged and the spectrophotometric analyze confirm that Phenalenone is adsorbed in surface with a rate of 1.7×10^{-7} mole g^{-1}. The structure of Halloysite and Kaolinite was preserved.



(a) (b)

Fig.1. SEM images (a) PN-Kaolinite; (b) PN-Halloysite.

Both Homogenous and Heterogeneous photodegradation of Phenol (micropollutant model) were conducted in an annular photoreactor with UV and visible light irradiation. The rate of the photodegradation was higher with the hybrid materials than for free PN in homogenous aqueous solution. A first order reaction with phenol is observed with UV or visible irradiation.

Efficacy of indigenous clays of Pakistan in reducing the toxicity of aflatoxin to broiler chickens

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Aflatoxin contamination in poultry feed causes aflatoxicosis. Numerous studies have shown that adding clays to the feed can reduce the bioavailability of aflatoxins to various animals. As bentonite occurs in nearly every country, using local bentonite or other smectite-rich clays for aflatoxin detoxification is a practical and economical solution in fighting aflatoxicosis. Yet, no systematic evaluation of the clays in Pakistan for mycotoxins detoxification has been conducted. The objective of this study was to evaluate the efficacy of selected indigenous bentonite and palygorskite clays of Pakistan in adsorbing aflatoxin from naturally contaminated feed.

Prior to their use as toxin binders, the mineralogy was studied through X-ray diffraction analysis. Aflatoxin B1 adsorption isotherms were established to find out their aflatoxin binding capacity in vitro. The controlled shed feeding trial comprised five different clays, dominated by smectite, smectite-vermiculite mix, super expanding smectite, palygorskite, and palygorskite-smectite mix, applied at two levels (1 and 2%) with positive and negative controls; the toxin feed had 250 µg kg^{-1} contamination level. The trial was replicated thrice having 10 birds each. Broiler birds were reared for three weeks on experimental feed after initial brooding on clean feed. The birds were slaughtered at fifth week and body weight gain, feed intake, internal organs (heart, liver, and spleen) weight and morphology was recorded.

Supplementation of clays in clean feed improved growth and efficiency of broilers at 2% induction level, indicating no detrimental effect of clays on the birds. The aflatoxin contamination resulted in slow growth and body weight gain. Smectite dominant clays performed better in reducing aflatoxin incidence and result in statistically significant weight gain of live birds and their internal organs. The morphology and size of the liver show a detrimental effect of toxin and binders efficiency in contaminated feed. Super expanding smectites and palygorskite dominated clays couldn't induce pronounced improvement in birds' health and body weight gain. However, the smectite, palygorskite-smectite and smectite-vermiculite clays mixed feed reared birds had higher body weights and no signs of toxin were evident from their internal organs morphology and size. The toxin contaminated feed reared broilers could reach up to 1200 grams and clays addition improved body weight gain by 50-60%. Results correlated positively for body weight and internal organs weight.

Our study suggested that Pakistan's large clay reserves use in feed industry could reduce risk incidence of aflatoxin and improve growth of feed reared birds. The addition of smectite dominant clays at applied levels was enough in controlling aflatoxicosis and improving birds' growth.

Direct imaging of monolayer silicate nanosheet by aberration corrected scanning transmission electron microscopy

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Direct imaging of single atom or molecule on/inside low-dimensional nanomaterials was significantly progressed owing to the recent development of aberration corrected electron microscopy. For deeper understanding of clay-based supramolecular chemistry, direct structural imaging of silicate nanosheet and these complexes are required. Our group has reported photochemical processes of organic guest molecules self-assembled on silicate nanosheet surfaces via Coulombic interaction.[1] However, since clay minerals are typically sensitive to an electron beam irradiation, local atomic structure in clay minerals has been investigated by electron microscopic images from cross section direction, in which atom columns are parallel to the electron beam[2].

In this research, atomic-range observation of monolayer silicate nanosheet was conducted by high angle annular dark field scanning transmission electron microscopy (HAADF−STEM) for the first time. STEM measurement was conducted at an acceleration voltage of 300 kV using a FEI Titan Cubed G2. STEM samples were prepared by dropping a solution containing well-dispersed montmorillonite (KunipiaF; KUNIMINE INDUSTRIES) nanosheet (Figure) aqueous suspension onto a carbon-coated Cu grid. To understand the stability of monolayer silicate nanosheet during the electron beam irradiation, decrease of SAED (Selected Area Electron Diffraction) intensity was analyzed. As a result, SAED intensity decrease of monolayer silicate nanosheet was significantly smaller than the few-layered sample, indicating the monolayer nanosheet is relatively stable under electron beam.

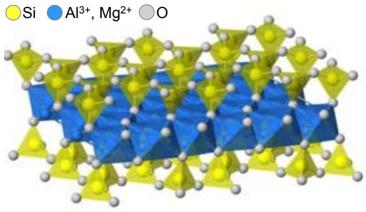

Figure Atomic structure model of montmorillonite

[1] Y. Ishida, *Pure Appl. Chem.* **2015**, *87*, 3–14. [2] T. Kogure, E. Okunishi, *J. Electron Microsc.* **2010**, *59*, 263–271.

A real-space investigation of excited energy transfer reaction in quantum dots assembly on silicate surfaces through electron tomography

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Förster Resonance Energy Transfer (FRET) is non-radiative excited energy transfer process from excited donors to lower energy acceptors via long range dipole-dipole interactions. The reaction rate constant k_{FRET} is inversely proportional to the sixth power of the donor–acceptor distance. In this work, we prepared self-assemblies composed of anionic clay nanosheets in water and quantum dots (QDs) decorated with cationic thiols via Coulombic interaction. FRET between the donor and acceptor QDs (QDs(D), QDs(A)) was investigated from the real-space distance between donors and acceptors for the first time using electron tomography[1] while FRET is generally studied by spectroscopic techniques.

Two different sized CdSe/CdS/ZnS core/shell/shell QDs were synthesized and decorated with cationic thiols ((11–mercaptoundecyl)–*N,N,N*–trimethylammmonium). The diameters of QDs(D)) and (QDs(A)) are ca. 7 nm and 9 nm, respectively. Their self-assemblies were obtained by mixing the aqueous solution of QDs and anionic clay nanosheets (Montmorillonite). Tomographic 3D images were reconstructed from tilt image series consisted of 61 HAADF–STEM images with tilt angle ranging from –64° to +56°, tilt increment of 2°. QDs(D) and QDs(A) were distinguished from reconstructed tomographic images according to their diameters and each QDs(D)–QDs(A) centre distance (R) was determined. The reaction rate constant k_{FRET} was estimated with R in a Fötster equation. Using obtained k_{FRET} values the reaction efficiency η_{FRET} of each QDs(D) was estimated to 3–51%. The average value, which can be considered as η_{FRET} of the whole domain, was 27%. This value showed good agreement with the steady state or time-resolved fluorescence spectroscopy results (28% or 25%).

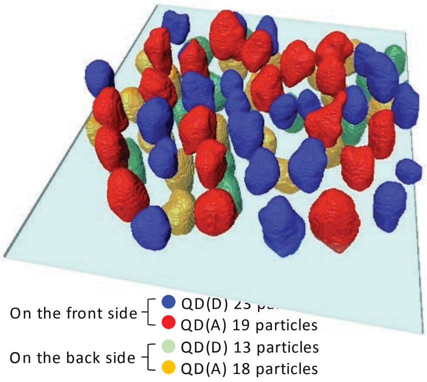

Figure A surface-rendering image (the clay nanosheet was sketched for guiding

These results suggest that electron tomography techniques can potentially be applied to investigate photochemical reaction in supramolecular assemblies through the real–space localization of the components on 2D silicate surfaces.

1) Y. Ishida, I. Akita, T. Pons, T. Yonezawa, N. Hildebrandt, *J. Phys. Chem. C*, **2017**, *121*, 28395–28402.

Clay-organic complexes of the modern steppe soils and paleosols of East European Plain of Russia in relationship with climatic parameters.

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Mineralogy, mineral surface properties, multivalent cations, microorganisms, and quality of soil organic matter mainly control the interactions between organic and mineral constituents in soils. The understanding of the degree and mechanisms of organic coverage on soil mineral surfaces is still incomplete. The properties of clay-organic complexes of the modern steppe zone soils from East European Plain of Russia in relationship with climatic parameters (rainfall, temperature, and aridity) will presented. Samples from more than 30 profiles of soils within a transect, more than 1500 km long from Lower Volga to the central European part of Russia were selected and studied by complex of modern geochemical and mineralogical methods. Studied transect include various climatic zones with a gradient in mean annual precipitation (MAP) up to 500 mm/year and average annual temperature (MAT) from 8 to 11° C. Such gradient in rainfall and temperatures allow us to receive reliable calibration of climatic parameters with soil function, weathering intensity and factors controlling soil organic carbon (SOC) storage. In additional a chronosequence approach applied to reveal the formation of organo–clay complexes of paleosols during stages of soil evolution in connection with Holocene climate variation and duration of weathering.

The bulk samples and clay fractions of modern soils and palaesols were analyzed by XRD, XRF the clay-organic-complexes by FTIR and solid-state 13C NMR spectroscopy. The clay-organic-complexes pronounced shifts of SOM quality in relationship with climatic gradients. Amounts of C-species according to 13C NMR spectra demonstrate the changes in structure of organic matter versus climate of soil formation and clay mineralogy. The organic matter of clay-organic-complexes from soils formed in a humid climate is characterized by reduce amount of alkyl C and increase of aromatic C structures with relative increase of illite. In arid conditions, the clay fraction characterized by a low content of aromatic structures and the predominance of aliphatic and relative increase of smectite content. Carbon isotope compositions (δ13C) of organic matter of clay fractions of palaeosols suggest changes of the paleovegetation, C3 or C4 type of plant, which dominated in specific periods and climatic conditions over time in steppe environment.

Acknowledgment. The Russian Foundation for Basic Research projects № 18-04-00800 has supported the work.

Soil humin and kerogen. Clay mineralogy stabilizing effect.

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The term "humin" was proposed more than 150 y.a. by J. Berzelius and G. Mulder for soil humic substances insoluble in alkaline solutions. First we present published data on humus composition of ~ 200 modern soils of different genesis and of > 100 Quaternary paleosols. The processing of data shows that content of humin in modern soils is 50±15% from soil organic matter (SOM) and thus represents an important part of SOM pool. The content of humin in Quaternary paleosols is 54±21% which is comparable with that of modern soils, so under diagenesis humin does not accumulate and is not the inert fraction of SOM, but is a subject to mineralization and transformation.

50-75 % of SOM is bound to clay minerals and develops organo-mineral complexes. As a consequence, soil clay fractions are enriched in OC. From other side our study shows that humin content in clay fractions in comparison with corresponding whole soils is considerably smaller (36±21% and 60±15 % respectively).

Solid state ^{13}C NMR spectroscopy study showed that OC of humin has relatively low humification degree (alkyls/O-alkyls 0.45±0.10 and 0.74±0.16 for whole soils). Irrespectively to soil genesis humin is aliphatic and enriched in *O*-alkyls and acetal groups. Total SOM from other hand contains more aryls and carboxyls. ^{13}C NMR spectroscopic study of SOM in soil clay fractions shows the enrichment in alkyls. Humin in clay fractions as that of whole soils is enriched in *O*-alkyls. The above findings allow to conclude that soil humin is not homogeneous and consists from at least two distinct parts: clay – bound organic C, non-hydrolyzed being chemically and physically protected and weakly decomposed plant residues stable to hydrolysis.

In studied carboniferous fossil soil (palaesols) the main carrier of OC are their clay fractions where OC content varied within 0.50-5.50%. Maximal concentrations of OC were observed in case of kaolinite composition of clays. Most of it exists as aryls (aromatic C). Humin part of OC in these palaeosols represents 0-55% of SOM and also clearly depends on clay mineralogy being maximal in case of palygorskite and minimal – for kaolinite.

OC content in carboniferous montmorillonitic lacustrine "black mud" is 1.4 %, and 74 % of it is non-hydrolysable part - "kerogen". Its OC has the aquatic (sapropel) precursor. ^{13}C NMR spectroscopic study of kerogen showed the principal difference between it and terrestrial humin: in OC of kerogen alkyl groups absolutely dominate.

We suppose that both nature of organic matter and mineral matrix effect the quantity and quality of stabilized fossil organic matter.

Research is supported by Russian Foundation for Basic Research, Project № 18-04-00800.

Preliminary results of the IBL (International Bentonite Longevity) project

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Kunimine Industries Company (KIC)'s Tsukinuno (NW Japan) sub-surface bentonite mine is a source of Miocene age Na- (at depth in the mine) and Ca-bentonite (near-surface). The site is ideal for studying processes of direct relevance to safety cases (SC) for radioactive waste repositories which utilise bentonite as part of their multi-barrier safety systems (i.e. buffer, backfill and tunnel and borehole plugs and seals). The International Bentonite Longevity (IBL) project focusses on studying long-term, safety-relevant processes, including:
Saturation state – natural saturation states of bentonite in differing environments (on the surface and at varying depths underground, under dry and wet host rock conditions) for comparison with current SC assumptions (based on short-term, laboratory and underground rock laboratory tests)
Bentonite density changes (swelling and heave) - due to exposure to groundwaters
Bentonite water interaction processes with fresh and deeper groundwater chemistries – for both surface and deep groundwater chemistries, including changes in cation exchange capacity (CEC) and exchangeable cation composition (EC) across thin and thick bentonite beds
Bentonite erosion – both under repository-relevant conditions at depth in the tunnels where water conducting features contact the bentonite and under extreme conditions such as erosion from surface-water processes
Bentonite reaction - with mudstone and siltstone host rocks
Bentonite sampling/analytical development – novel sampling/analytical approaches are explored
Stakeholder communications – use of 'real' examples to explain repository safety concepts

The 31 bentonite layers in the Tsukinuno mine, varying in thickness from a few cm to ca. 7 m, are providing information of direct relevance to the long-term behaviour of bentonite at physical (bentonite thickness, lithostatic pressures, groundwater chemistries etc) and temporal (from decades to millions of years) scales of relevance to the repository buffer, backfill and plug/seal clays. The IBL project has just started and this presentation will provide an overview of the first sampling campaign and analytical results along, with the ongoing and planned work in the project.

Evaluation of the geotechnical properties of clay soils of Astana using GIS-technology

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The actual problem for today is the method of determining the bearing capacity of foundations in clay soils. The territory of Astana due to the rather complex engineering-geological conditions, which is confirmed by a large variety of bedding relatively weak clay soils top of the base, but at the same time supporting the soil layers are sufficiently robust [1]. The paper analyzes the experience of the design and construction of pile foundations in clay soils using GIS-technology.

For example: Zhusupbekov A.Zh.; Alibekova N.T.; Abilmazhenov T.; Morev I.; Zhagpar A.; Iwasaki Y.; Mimura M. The modern approach to research of geotechnical properties of soils / Proceedings of the 14th Asian Regional Conference on Soil Mechanics and Geotechnical Engineering, Hong Kong, China, (**2011**)., P.482

Dating supergene kaolinites by electron paramagnetic resonance spectroscopy: what have we learned from the latest studies?

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Since early studies in the 70's (discovery of radiation-induced defects in kaolinite using electron paramagnetic resonance spectroscopy), it was shown that kaolinite can be used as a natural dosimeter on a geological time scale, allowing tracing of past transfers of radioelements (Allard et al., 2018a and reference therein) or dating of laterites (Balan et al., 2005; Allard et al., 2018b; Mathian et al., 2019). In complement to other secondary minerals such as some Mn-oxides and Fe oxy(hydrox)ides, dating of kaolinite from laterites, that represent 1/3 of emerged continents area, participates to an increasingly detailed understanding of evolution of continental surfaces.

First, we present recent advances in the methodology that is based upon artificial irradiations to simulate the effect of natural ionizing radiations on kaolinite. Improvement in dosimetry data-fitting (Mathian et al., 2019) provides more accurate paleodose (dose experienced since the formation of the mineral) and age. This also requires that several corrections of the dose rate related, e.g., to spatial distribution of uranium or degree of aperture of decay chains can be achieved. The main advantages and limitations of the kaolinite dating approach, when compared to other relevant dating methods for tropical weathering surfaces, will be presented.

In a second part, a selection of several contrasting examples of kaolinite dating in shallow continental sediments, Fe-duricrusts and loose horizons of laterites from the Amazon Basin will be shown. Measured ages of dominant periods of kaolinite formation reach the lower Miocene. Discussion will point to stratigraphy correlation, profile genesis (generations of kaolinite, weathering fronts), and forcing by main geodynamic or paleoclimatic events.

Allard T.; Beaufort D.; Mathian M.; Uri F.; Brun E.; Quirt D.(**2018a**). J. Geochem. Explor. 188, 340-349.

Allard T.; Gautheron C.; Bressan Riffel S.; Balan E.; Fernandes Soares B.; Pinna-Jamme R.; Derycke A.; Morin G.; Taitson Bueno G.; do Nascimento N. (**2018b**) Chem. Geol., 479, 136-150.

Balan E.; Allard T.; Fristch E.; Selo M.; Falguères C.; Chabaux F.; Pierret M.C.; Calas G. (**2005**) Geochim. Cosmochim. Acta 69(9), 2193-2204.

Mathian M.; Aufort J.; Braun J.J.; Riotte J.; Selo M.; Balan E., Fritsch E.; Bhattacharya S.; Allard T. (**2019**) Gondwana Res., 69, 89-105.

Modelling sulfide fluxes and corrosion rates of copper canisters in a KBS-3 repository using a Donnan equilibrium approach.

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Spent nuclear fuel is planned to be disposed in geological repositories at Olkiluoto, Finland and at Forsmark, Sweden using the KBS-3 multi-barrier design. According to this design the spent fuel will be stored in copper canisters which will be emplaced in vertical deposition holes excavated at the base of a deposition tunnel. Surrounding the copper canisters is a buffer of swelling bentonite. After emplacement the deposition tunnel will be backfilled with swelling clay.

Recently, more attention has been paid to the role of accessory minerals in the bentonite, in particular to the role of gypsum and soluble organic matter. Following the re-saturation of the backfilled tunnel/deposition holes with groundwater, gypsum and organic matter will dissolve, releasing calcium and sulphate and dissolved organic material into the pore water. Sulphate and organic matter constitute potential electron acceptors and donors, respectively, that could sustain microbial populations in low density zones of the bentonite or along the interface zone between backfilled tunnel/deposition holes and the rock. Bacterial reduction of sulphate to sulfide is of particular concern as sulfide is a well-known corrodant to copper.

We used a modified version of the high performance reactive transport code PFLOTRAN (www.pflotran.org) to study the effects of mineral reactions, multi-component diffusion and bacterial activity and the resulting corrosion rates. Diffusion through the bentonite buffer was simulated with an explicit treatment of electrical double layers. The effect of electrical double layers was implemented by assuming Donnan equilibrium between pore waters in the free porosity, unaffected by surface charge, and Donnan water representing the diffuse layer of excess cations balancing the mineral surface charge.

Simulations show that the flux of electron donors limits the rate of bacterial activity. A comparison of simulations involving conventional ion exchange with simulations using a Donnan equilibrium approach reveals that computed sulfide fluxes through the bentonite, and thus copper corrosion rates, differ strongly if the predominant electron donor is negatively charged, if there are major differences in D_p between free and Donnan porosities, and in strongly compacted bentonites with low free porosity.

Synthesis optimization and structural characterization of MAl_4 layered double hydroxides with M = Co(II), Ni(II), and Zn(II)

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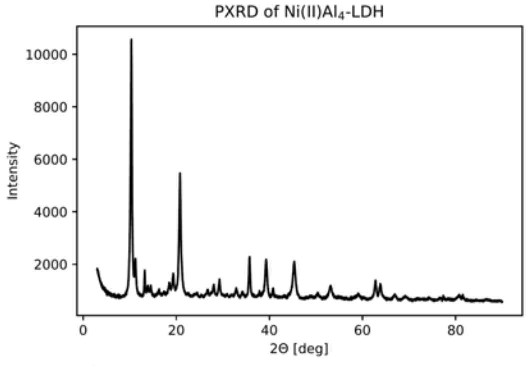
Layered double hydroxides (LDHs) find widespread applications as catalyst materials, energy materials and materials for environmental remediation due to their versatile chemistry and ability for ion-exchange. Two classes of LDHs are known, the “hydrotalcite-type” and the “aluminum hydroxide-type”. The hydrotalcite-type, which has been studied extensively, is derived from layered divalent metal substitution of M(II) with M(III) giving the general formula $[M(II)_{1-x}M(III)_x(OH)_2A_y{\cdot}nH_2O]$, where the anion, A, balances the excess charge in the cation layer. The aluminum hydroxide type is much less studied and consists of $Al(OH)_3$ sheets where one third of the Al-sites are vacant. This allows for intercalation of M(I) or M(II) into the vacant sites giving the idealized formula $[M(II)Al_4(OH)_{12}A_x{\cdot}3H_2O]$ for divalent cations. The anions occupy the $M(II)Al_4(OH)_{12}$-interlayers and balances the excess positive charge. These LDHs can be synthesized by hydrothermal treatment of a mixture of solid gibbsite or bayerite and a highly concentrated solution of the M(II) cations. Obtaining pure samples without remaining starting materials or formation of side products such as aluminum oxyhydroxides is challenging [1]. We have studied the intercalation of Co(II), Ni(II), and Zn(II) into the $Al(OH)_3$ polymorph bayerite with either NO_3^- or SO_4^{2-} as anions, using different M(II) concentrations and temperatures for the hydrothermal treatment to understand how the synthesis conditions control the sample purity. The products were characterized by multiple experimental techniques for studying both the bulk phase and the atomic level structure including PXRD, TGA, ICP-OES, SEM, and solid-state NMR spectroscopy. The interplay between the methods allows us to gain valuable insight into the synthesis of $M(II)Al_4$-LDHs.



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NMF in kaolinite: Intercalation kinetics by Near-Infrared spectroscopy

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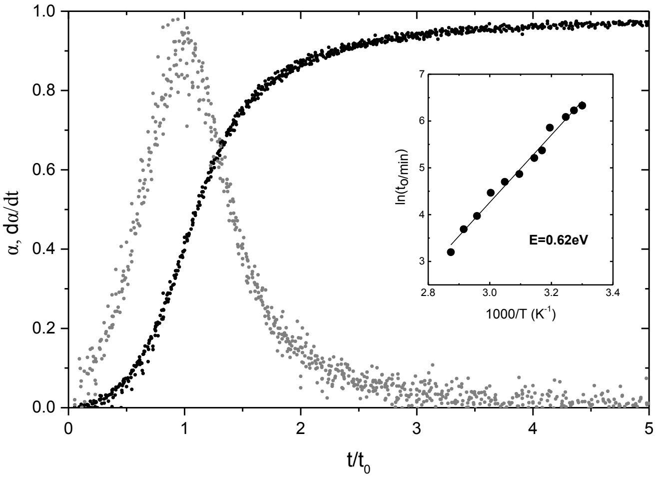
The interaction of N-methylformamide (NMF) with kaolinite is a model intercalation reaction, relevant to the synthesis of new hybrid materials by self assembly. Such reactions are typically studied *ex situ* by XRD, owing to the expansion of the interlayer. In the present study we employ non-invasive FT-near infrared spectroscopy to study in real-time and as a function of temperature the intercalation of NMF in low-defect kaolinite, KGa-1b.

Thick, opaque slurries of kaolinite/NMF are introduced into a small glass reactor (~5ml), which is hermetically attached to the Y-type optical fiber probe of the FT-NIR spectrometer. The tip of the probe with the reaction cell attached to it is then immersed in a thermostatic bath (20-80 °C). High-quality spectra can be collected with a maximum time resolution of ~60s over very long times (>100h). Proxies of the intercalation reaction, such as the 2vNH band at ~6700 cm^{-1} of the intercalated NMF, can be extracted from the spectral time series and studied as a function of time and temperature (see Fig.). Finally, the non-monotonic effect of H_2O concentration on the kinetics of the intercalation is demonstrated.



(left) Reaction progress (α) and rate (dα/dt) of the intercalation of anhydrous NMF in KGa-1b (1ml/1g), monitored by the integrated intensity of the 2vNH mode of intercalated NMF, normalized by its value at infinite time. Data obtained at 12 different temperatures in the 30-80 °C range, exhibit excellent time-temperature superposition when normalized by t_o, the time of max(dα/dt). Activation energy E_a was estimated to be 0.62±0.01 eV (14.3±0.2 Kcal/mol, 60±1 kJ/mol, see inset).

This work was supported by project "Advanced Materials and Devices" (MIS 5002409) of TPCI-NHRF, funded by the Operational Program "Competitiveness, Entrepreneurship and Innovation" and co-financed by Greece and the European Union.

Ionic adsorption on the (010) and (110) edge surfaces of kaolinite: Molecular dynamics simulation with updated ClayFF potential

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Clays are the major mineral component in shales and largely responsible for their chemical and physical properties. In particular, they play an important role in controlling the retention, distribution, and transport of radionuclides of naturally occurring radioactive materials (NORMs) in the related to shale oil and gas exploration, which is of significant environmental concern (Yethiraj and Striolo, 2013).

Kaolinite is one of the most abundant clay minerals in shale formations. Here we address the adsorption of NORM cations on various kaolinite surfaces, taking advantage of the most recent parametrization (Pouvreau et al., 2017; 2019) of the ClayFF force field (Cygan et al., 2004), which now allows to accurately represent not only the basal surfaces, but also various edge surfaces of clay particles. Sr^{2+} and Ba^{2+} are selected as proxies of NORM cations, and their adsorption properties are compared with those of Na^{+}, commonly present in shale fluid.

NORM cations are shown to preferentially sorb as fully hydrated complexes on the basal surfaces of kaolinite, but inner-sphere (IS) complexation on the edges is also significant. There are two main types of IS complexation sites on the (010) and (110) edge surfaces of kaolinite: Al-vacancy and Si-vacancy. The stability of the surface binding is dependent on the cation's ionic radius, hydration energy, charge, number of interacting surface hydroxyls, and the presence of competing cations in solution. Adsorption free energy calculations show no significant difference between adsorption mechanisms of Sr^{2+} and Ba^{2+} on the neutral kaolinite surfaces. Hexagonal sites of the siloxane (001) surface demonstrate the highest affinity for cation adsorption, but once they are saturated the edge adsorption sites continue to contribute to NORM cation immobilization. Na^{+} can successfully compete with NORM ions for surface adsorption sites.

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Sodium deactivation of Brazilian bentonite varieties

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This study investigated the influence of cation type on the sodium deactivation of Brazilian bentonite varieties. The main reason is that different companies have reported loose of bentonites properties after some months of storage. Four bentonite clays were studied, including three polycationic or mixed bentonites and one magnesium bentonite. Swelling and the main exchangeable cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) were the main evaluation parameters in this study. Periodic washes of the activated bentonites were performed based on the hypothesis that a possible desorption of the cations (primarily Na^+) could cause the deactivation. Sodium activation was monitored using Powder X-ray diffraction (XRD) measurements, reduction of 001 reflection from ~ 15 Å to ~ 12 Å, and an increase in swelling. Sodium deactivation was observed and monitored via a decrease in swelling. Positive and negative effects, caused by the proportions of the cations and the dominance of one of them were emphasized by the set of cationically different samples applied in this study, which helped to answer some of our questions regarding what causes or accelerates deactivation. The lowest swelling values were attributed to higher Mg^{2+} values. The results showed the strong influence of Mg^{2+} on the deactivation process.

Stabilization/solidification of lead (Pb) and zinc (Zn) contaminated marine clay using halloysite nanotubes

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Remediation methods for soils contaminated with heavy metals are urgently needed to prevent severe widespread pollution of the surrounding environment and groundwater. Stabilization/solidification (S/S) is a commonly used technique for remediation of heavy metal contaminated soils. In this study, S/S technique was tested on marine clay contaminated with lead (Pb) and zinc (Zn) using two types of halloysite nanotubes [Matauri Bay (MB) and Dragonite (DG)]. The selective use of halloysite nanotubes to improve the engineering properties of contaminated clay can be a novel approach considering their potential as pollutants adsorbents for remediation of contaminated soils. To this end, an extensive laboratory-testing matrix was developed to investigate the effects of MB and DG contents (2, 4, 6, and 8% by mass of dry clay) as well as Pb and Zn concentrations (0.5, 1, and 2% by mass of dry clay) on the engineering properties of the tested clay, including Atterberg limits, compaction, unconfined compressive strength (UCS), elastic modulus, and flexural strength (FS). The effects of MB and DG contents and curing time on the strength properties of the stabilized clay were also evaluated. Furthermore, X-ray diffraction (XRF), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), and nitrogen-based Brunauer-Emmett-Teller (N_2-BET) tests were conducted to understand the mechanisms controlling the changes in macro-properties of the stabilized clay. The results show that the UCS and FS increase with increasing MB and DG contents and curing time. After 14 days of curing, the UCS values of the stabilized clays are approximately 2.3 – 5.7 times those of the untreated clay. The N_2-BET test results show that the specific surface area reduces notably after MB and DG stabilization. The FESEM analysis reveals that the stabilization process modified the porous network of the clay as the pores of the clay were filled by the halloysite nanoparticles. The level of Pb and Zn concentrations were found to have minimal influence on the engineering properties and microstructural characteristics of the stabilized clay. The findings suggest that the S/S treatment with MB and DG halloysite nanotubes additives showed excellent performance in improving the engineering properties of the contaminated marine clay.

An approach to geological interpretation using uranium and thorium isotopes in kaolinitic clays

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The association of phyllosillycates in continental sedimentary deposits can provide important insights about the paleoclimate and weathering conditions where they formed. However, the formation of rocks involves through mixing of different kinds of phyllosillicates, a fact that makes difficult the interpretation of their study. To the best of our knowledge, no exploration has been made on the potential of uranium and thorium isotope ratios to provide further insight on the evolution of kaolinites since their formation. For this the aim of this work were: a) establishing the chemical fractionation of uranium and thorium using tandem quadrupole ICP-MS/MS, b) testing the possibilities of the analyses of uranium and thorium isotopes in kaolin samples, c) to apply those results to the evolution of kaolinitic clays after their formation.

The studied kaolin materials were sampled in six different outcrops located in the easternmost part of the Iberian Range (NE Spain), the so-called Maestrazgo Basin. This basin was originated during one of the most active stages of the Late Jurassic-Early Cretaceous rifting process. The typology of samples including one sample from the Lower Cretaceous (Barremian) Fuentespalda karst bauxite deposit (Teruel); a lateritic claystone from the Barremian Artoles Fm; two samples belong to the Barremian Camarillas (red claystone and medium to coarse white creamy sandstone) and two black claystones from the Albian Escucha Fm near Ariño and Estercuel (Teruel), respectively.

The radiochemical method proposed was applied to certified reference samples in order test uranium and thorium fractionation throughout the procedure. We determined the isotope ratios $^{238}U/^{235}U$, $^{238}U/^{234}U$, $^{232}Th/^{230}Th$ and the U and Th concentrations (which are determined through the isotope ratios 238/236 and 232/229, respectively).

Bauxite is composed mainly of kaolin minerals with hematites as minor and trace of anatase and chlorite; WMV36AR<2µm is composed of kaolinite, with minor amount of illite and calcite and traces of quartz and feldspar; WMV36AC <2µm is mainly composed of kaolin minerals, illite and traces of anatase, quartz and feldspar; and those of the Escucha Fm are containing kaolin minerals with organic matter, vermiculite, pyrite, minor quartz and illite, and traces of calcite, gypsum and goethite.

The isotopes analysis indicated the following: a) laterites suffered strong lixiviation; b) the bauxite shows a possible descalcification; and c) clays with high organic matter contents reflect typical U accumulation indicating a possible reduction (anoxic) environment.

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This research was funded by the Spanish Ministerio de Educación y Ciencia (CGL2013-46169-C2-2-P) and the contract of Domingo Martín granted by the V Plan Propio de Investigación de la Universidad de Sevilla.

Na-Ca-K cation selectivity in reduced iron-bearing clay minerals and implications to low-salinity water flooding

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Clay minerals can play a significant role during oil production from a conventional reservoir, because they exhibit a structural variety which will induce different physical and chemical behavior during oil production processes. Some of these behaviors are the swelling ability, especially for smectites, but also other kinds of characteristics, such as the ability to exchange cations on external surface areas, and in the interlayer space, the ability to absorb organic matter due to net charges, as well as to flocculate and disperse in porous media (fines migration).

All these should be taken into account during an enhanced oil recovery method, such as low-salinity water flooding, where injected water is of lower salinity than that originally in the reservoir, with very low divalent cation content. This low-salinity water usually consists of NaCl in a concentration of 5000 ppm. The main functioning mechanisms involved for this process are multi-ion exchange, local pH increase, fines migration, double layer expansion, all associated with clay minerals, and leading to wettability changes from mixed-wet to more water-wet. However, none of the above methods conclusively explain low salinity enhanced oil recovery.

One factor that is least examined is the presence and possible influence of iron (Fe) in some clay minerals such as nontronite, Na- montmorillonite, or chlorites that can be found in sandstone reservoirs. As iron is a redox-active element, the redox state of iron can affect the behavior of clay minerals, i.e. cation exchange capacity (CEC) which will increase in a nontronite after reduction of its Fe_{str}. Conceptually, a sandstone reservoir should be in a reduced state just prior to production and any intervention, such as waterflooding, can cause a shift towards more oxidizing conditions, if not total oxidation. So, in order to understand better the underpinning mechanisms for low-salinity water flooding it is essential to examine and compare how Fe-bearing clay minerals behaving in these two different redox states.

For this project, contact angle measurements on clay films are taken for oxidized and reduced clay minerals, using crude oil. Also, the cation exchange series of these clay minerals is studied under reduced conditions for Na, Ca and K. Furthermore, FTIR is used for oxidized clay minerals, with different interlayer cations, and aged in carboxylates in order to examine again the effects on oil adsorption in the presence of different cations on the hydration profile. Future work will assess the corresponding reduced clay minerals.

Imogolite as a sorbent phase for pharmaceutical products microextraction in water

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On the last years, new analytical methodologies have been developed for the determination and removal of emerging contaminants, among them, the microextraction methods have been widely used due to their improvements in reduction of time, costs and environmental pollution [1].

Among the adsorbents for microextraction in solid phase, there is a wide range of commercial products such as C18 and Oasis® HLB, between others. In the present work, the use of imogolite nanomineral as a solid phase adsorbent for the microextraction of some emerging contaminants is proposed for the first time. Imogolite nanomineral is a nanotube that can be obtained from clays from glassy volcanic ash soils or can be synthetized [2,3]. An advantage of the imogolite as adsorbent is the versatility in its synthesis, which allows the generation of modifications in its structure, inside and/or the outside of the nanotubes.

The present research presents the adsorption behavior of three pharmaceutical products, belonging to different chemical families: gemfibrozil, ibuprofen and 17β-estradiol (anti-cholesterol, non-steroidal anti-inflammatory and steroid hormone, respectively). These compounds can be found among the most consumed pharmaceutical products in the world [4].

Studies of adsorption in batch were carried out, using 10 mL standard solutions of concentrations from 100 to 500 µg/L in distilled water for each compound at pH=7. Ten milligrams of imogolite previously sifted at 75 microns was added and the solution was stirred at a 1250 rpm in a magnetic stirrer for 30 min. The remaining solution was evaluated by fluorimetry. After 5 min stirrer, a reduction of 30% of the contaminants concentration in the solution was achieved, obtaining a maximum of adsorption at 15 min. Currently, a multivariate optimization adsorption process for each compound, as well as, the effect of the imogolite functionalization in the adsorption capacity of the compounds studied is been developing.

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Conducting sepiolite-halloysite multicomponent nanoarchitectures for electrochemical devices applications

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Sepiolite and palygorskite attract increasing interest as nanoplatforms for the stabilization of a large variety of nanoparticles profiting for the large external surface area offered by these fibrous clays (Aranda & Ruiz-Hitzky, 2018). In this context, water dispersions of sepiolite incorporating carbon nanotubes (Fernandes & Ruiz-Hitzky, 2014) or graphene nanoplatelets (Ruiz-Hitzky et al., 2016) were submitted to sonomechanical treatments to produce stable suspensions that can be processed in diverse ways for producing conducting materials of interest in diverse applications. In this communication we will introduce recent results that show that this strategy of synthesis could be further extended to produce the co-assembly of sepiolite and halloysite nanotubes (HNT) in water producing also highly homogeneous and stable suspensions from which it is possible to cast films of variable sepiolite:HNT composition. Moreover, their co-assembly with graphene nanoplatelets and/or carbon nanotubes produces electrically conductive inorganic materials that can be processed as films or as foams. The additional incorporation of biopolymers, such as chitosan, improved the mechanical properties of the resulting conducting bionanocomposite films and foams. The possibility of loading the HNT with bioactive species (Lvov & Abdullaley, 2013) opens the way to the production of versatile multicomponent nanoarchitectured materials of interest for diverse applications. For instance, glucose oxidase enzyme was loaded in the HNT lumen renders materials acting as active components of electrochemical devices such as active phase in biosensors and as 3D bioanode in biofuel cells. These results in bioelectrocatalysis represent an incipient development that could be extended to other fields.

Acknowledgements: MINECO, Spain (MAT2015-71117-R & IJCI-2015-23886), and University of Palermo, Italy (“PERFEST” grants).

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Silica-layered double hydroxide nanostructured materials

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Clay minerals and related solids, such as layered double hydroxides (LDH), are typically used as building-blocks in the development of a large variety of nanostructured materials from typical polymer-clay nanocomposites to diverse nanoarchitectured materials involving their assembly to nanoparticles (NP), such as magnetite, silica, titania, etc. To produce this last type of nanoarchitectures, the use of organoclays in combination with sol-gel approaches has proved to be a very convenient methodology as their organic-inorganic interface facilitates the association and stabilization of alkoxysilanes and metal alkoxides, in which the controlled hydrolysis and polycondensation of the alkoxide can take place (Aranda et al., 2018). Thus, in the case of layered silicates the presence of the alkoxysilanes in the interlayer region facilitates the delamination of the clay reaching the formation for instance of silica-clay nanocomposites (Letaïef and Ruiz-Hitzky, 2003). In this communication we will introduce recent results showing the application for the first time of this procedure to LDH as a way to produce nanostructured materials. In this way, various LDH (Mg-Al, Fe-Ni, Ni-Co-Fe) were co-precipitated in presence of sodium dodecylsulphate (SDS) leading to LDH where the presence of interlayer dodecylsulphate anions procures a convenient organophilic interface for the incorporation of tetrametoxyortosilicate (TMOS). TMOS was further hydrolyzed by adding a small amount of water starting a polycondensation process that through a sol-gel transition gives rise to a silica matrix, resulting in LDH-DS/SiO_2 intermediates in which the layer stacking of the LDH is loss. The removal of organic matter and consolidation of the polysiloxane matrix is achieved by heating at 400 ºC, avoiding the irreversible transformation of the LDH in oxide phases. In the resulting solids the LDH structure can be reconstructed by treatment with salt solutions confirming the presence of delaminated LDH associated to SiO_2 NP. The obtained nanoarchitectures show relatively high specific surface areas which is of potential interest for diverse applications, such as in biomedicine, catalysis or energy storage. Furthermore, the resulting nanoarchitectures containing silica nanoparticles could be further functionalized by treatment with organosilanes, which could afford multifunctionality to the final materials.

Acknowledgements: financial support from MINECO, Spain (MAT2015-71117-R project) and the Algerian Ministry of Higher Education and Scientific Research (P.N.E. 2016-2017 Program).

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Ligand specific suppression of hydrogen peroxide generation in ultraviolet irradiated titanium dioxide

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The growing use of nano titanium dioxide (TiO_2) in various consumer products has accelerated its introduction into terrestrial environments, although regulations for its use vary among countries. While past research has heavily focused on its aquatic toxicity, the impact of TiO_2 on terrestrial organisms, including soil biota, has not been extensively documented. One of major factors of TiO_2 toxicity is photochemically induced ROS (e.g., H_2O_2) production. In soils and sediments, pore waters contain common ligands like phosphate and nitrate. Several researchers have previously concluded that ligands can either hinder or enhance the ability of TiO_2 to degrade organic contaminants. However, the effects of ligands on photochemically induced ROS production by TiO_2 have not been clearly understood. The objective of this study is to assess the effect of phosphate and nitrate on UV-irradiated (λ: 320-400 nm) TiO_2.

Accordingly, environmentally relevant concentrations of the ligands (0, 50, 100 µM) and pH values (4 and 8) were used to monitor the production of H_2O_2 by UV-irradiated TiO_2. Kinetic experiments were conducted from 0-100 min., and the concentrations of H_2O_2 and ligands were determined using a homovanillic acid based fluorometric method and spectrophotometry, respectively.

In the absence of ligands at pH 4, H_2O_2 production followed a logarithmic growth rate of $y = 4.1648\ln(x) – 0.4389$ ($R^2 = 0.9456$). H_2O_2 reached 18.67 µM after 100 min. At 50 µM P, H_2O_2 grew at a rate of $y = 1.7428\ln(x) + 0.9248$ ($R^2 = 0.9704$) and reached 8.72 µM after 100 min while at 100 µM P, the H_2O_2 generation rate was $y = 0.8224\ln(x) + 0.8542$ ($R^2 = 0.6727$), and H_2O_2 reached 5.35 µM after 100 min. Conversely, at 50 µM NO_3^-, H_2O_2 was produced at a rate of $y = 4.2494\ln(x) + 1.0968$ ($R^2 = 0.9612$) and reached 23.15 µM after 100 min while at 100 µM NO_3^-, H_2O_2 generation followed a growth rate of $y = 4.2258\ln(x) – 0.272$ ($R^2 = 0.9536$) and reached 20.28 µM after 100 min.

Preliminary assessment at acidic conditions suggests that an increase in phosphate loading level on TiO_2 more effectively suppresses H_2O_2 production during UV irradiation than any loading level of nitrate. The effects of ligand concentration and specific and non-specific adsorption of the ligands on H_2O_2 production by TiO_2 will be discussed.

Mineralogical and morphological characterization of different size fractions of Na- saturated Illite du Puy

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Argillaceous rocks (Opalinus, Boom and Callovo-Oxfordian Clays) are often considered as host formations for the storage of radioactive wastes. Hence, understanding the migration of water and solutes in these complex natural systems is of a great interest. The diffusion/adsorption processes in these rocks are mainly controlled by its clay fraction which is often dominated by illitic-clay minerals. For these reasons, different studies used Na-saturated Illite du Puy (Na-IDP) to design a “single-phase” porous medium with only inter-particle porosity. In literature, the common methods used to purify natural IDP normally leave a significant content of mineralogical impurities in final Na-IDP. Indeed, some authors reported that 7% of kaolinite (Poinssot et al., 1999), or 12% of sanidine (Bradbury and Baeyens, 2009), or 20% of illite/smectite (rich in illite) interstratified minerals (Altmann et al., 2015) could remain in the final Na-IDP samples. Such a variation in the final composition of Na-IDP raises the question regarding how and to which extent these residual mineralogical impurities affect the results of diffusion/adsorption experiments obtained using a porous clayey medium made of Na-IDP particles.

In this study, we applied a method initially developed for soil samples (Hubert et al., 2012) to purify natural IDP. This method involves classical decarbonation and Na-saturation of the bulk samples, followed by the extraction of different particle size fractions: <0.02 µm, 0.02-0.05 µm, 0.05-0.1 µm, 0.1-0.2 µm, and the >0.2 µm. Physico-chemical characterization techniques are applied on each size fraction separately to analyse potential variation in mineralogy and intrinsic particle properties (morphology, CEC). Results obtained using (i) qualitative and/or quantitative XRD-modelling of experimental patterns, (ii) morphology and chemical analysis obtained with SEM-EDS, (iii) N_2-BET measurement for the external specific surface area, and (iiii) CEC measurement at pH 7, will be presented. The motivation for using this methodology is to concentrate illite particles in one or two size fractions and to exclude associated impurities including smectitic layers in a different size fraction. By doing so, such a methodology is expected to provide a material with well-constrained particles’ crystal chemistry and morphology suitable for diffusion/adsorption experiments.

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Supercritical solvothermal flow synthesis of nanominerals

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The specific properties of supercritical fluids are exploited for more than 35 years to develop breakthrough technologies, especially in the field of the preparation of advanced materials, from organics to inorganics through carbon-based materials. This technology of material processing is continuous, fast, sustainable and scalable and gives access to high quality nanostructured materials with unique physico-chemical properties, meaning which can not be obtained with other synthetic methods.

After a brief introduction to the supercritical solvothermal flow synthesis, a focus will be proposed on the advanced tools, which are today available to process nanostructured materials, while allowing understanding and improving the control of their formation. Then the preparation of advanced nanominerals in supercritical solvothermal conditions will be discussed with a chemist prospective. The chemistry accessible with this synthetic method will be described offering the opportunity to prepare different families of materials as oxides, metals, nitrides, etc, with unique properties.

In the last 3 years, we have opened a new field for the supercritical solvothermal flow synthesis: the continuous production of synthetic phyllosilicates and ionosilicates. The proof of concept was made with the synthesis in few tens of seconds of talc in a continuous millifluidic process. Very interestingly, this synthetic talc exhibits unique properties as its hydrophilicity knowing that naturel talc is hydrophobic. Adding ethanol to water, meaning switching from supercritical hydrothermal to supercritical solvothermal conditions, brought unexpected results. Depending on the water/ethanol ratio of the solvent, three different minerals adopting an octahedral brucitic sheet can be obtained: i) without Si-tetrahedral sheet (O), ii) associated with one Si-tetrahedral sheet (T-O) or iii) intercalated between two Si-tetrahedral sheets (T-O-T). The supercritical hydrothermal flow synthesis has also been extended to the ultrafast preparation of inominerals, the xonotlite and the tobermorite, two calcium silicates with interesting properties for the cimentitious industry. Especially, it is important to underline that the tobermorite is obtained under thermodynamically metastable conditions.

The benefits of the sub- and supercritical continuous solvothermal route include not only better performances for advanced applications but also environmental issues associated with the synthesis process. This will be emphasized with the studies performed using LCA approaches.

Characterization of (natural, acid activated and Ce-Al_{13}/pillared) Darbandikhan clay and their efficiency for the removal of Methyl orange as a model anionic dye

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Natural clay from Darbandikhan, Iraq, was investigated as potential adsorber material for the clarification of industrial wastes. The clay was evaluated in its natural form, after acid activation, and after pillaring as adsorbent for the adsorption of methyl orange as a model anionic dye adsorbate. The effect of different clay treatments was investigated using XRF, XRD, FTIR, TG/DTA, and N_2 gas adsorption analyzer.

A 12% increase of the silica content was observed by the action of acid activation. The microporosity has increased significantly by introducing the pillars to the clay as denoted by N_2 adsorption-desorption experiments. The natural clay exhibits no detectable adsorption capacity towards methyl orange. Both, acid activation and pillaring resulted in a significant increase in adsorption capacity (75.0 and 596.5 mg. g^{-1}) respectively. The increase in the removal efficiency by the pillared clay could be explained by catalytic reaction in addition to the adsorption mechanism. The time required for equilibrium adsorption was 100 and 180 minutes for the acid activated and the pillared clay respectively. The adsorption favored acidic pH for the anionic dye (MO). The adsorption process was found to follow pseudo second-order kinetics. The rate constants k_2 for the acid activated clay were between (0.0191 to 0.0234 g mg^{-1} min^{-1}) in the temperature range of 20 - 50°C, respectively. These values were much higher than those of the pillared clay (4.5 $x10^{-4}$ to 2.4 $x10^{-3}$). The activation energies 5.9 and 40.1 kJ mol^{-1} were obtained for the adsorption of MO on ADC and PILDC which are characteristic of physical adsorption.

The adsorption isotherms (Langmuir and Freundlich) were fitted well to the experimental data. The specific surface area of the natural clay was very low (22.39 m^2. g^{-1}) compared to high-class adsorber materials. This value has increased to 53.2 m^2. g^{-1} by the pillaring process. Nevertheless, because of its local availability the activated materials may be useful for the cleaning of local industrial waste waters.

Isolation of solid organic matter from complex clay matrices

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Clay formations (e.g. Boom Clay (BC), Ypresian Clays (YC), Callovo-Oxfordian (COx), Opalinus (OPA), etc.) are one of the environments widely studied worldwide for constructing future Deep Geological Repositories (DGR) for high level radioactive wastes. In this type of facilities clay formations are recognized as natural barriers due to their low permeability and their capacity to ensure delay and attenuation of the release [1, 2].

Solid Organic Matter (SOM) is common in reducing clay rocks, with contents up to 5% (TOC content of the total rock) in the case of Boom Clay formation [3]. SOM can be divided in insoluble solid organic matter (known as kerogen) as soluble solid organic matter (e.g. humates, fulvates, etc.). Formations as BC and YC are enriched in immature organic matter, meaning there is still a large fraction which is not kerogen type (compared to OPA/COx formations). Immature organic matter is highly reactive and expected to affect RadioNuclide (RN) transport of strongly hydrolyzing RN. SOM has been subject of several studies during the last century. There are several processes to isolate SOM from the main rock matrix allowing its characterization; the most common being the acid treatment with HF and/or HCl [4]. Nevertheless, this process may involve the alteration of its structure and therefore could lose representativeness. The focus of our recent research is the optimization of the extraction method used to isolate kerogen by a process that attacks as less as possible the material structure, but with high purity and recovery levels. This contribution presents our preliminary isolation results and a comparison with an already extracted kerogen obtained by the method described in [4].

Preliminary experiences have been done with strongly oxidized BC samples, following a simple open-system method (acid treatment done under atmospheric conditions). Our results indicate that this system produces a low kerogen recovery with high ash content and with the likely formation of secondary minerals (i.e. neofluorides) due to the acid treatment. An accurate isolation experiment is currently on-going in a closed inert system with fresh BC samples, i.e. non-oxidized, to avoid any possible oxidation of the organic matter and the concomitant alteration of kerogen. The definition of an extraction protocol and the evaluation of the influence of this extraction protocol on BC SOM is the main target of this research. This work will increase the confidence on the assessment of this important rock-forming components and will help the generation of more comprehensive models.

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Sorption of molybdates and tungstates on modified smectites

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Smectites have been recognized as low-cost, easily available mineral sorbents of heavy metals and other organic and inorganic compounds polluting water. By gaining an understanding of the sorption mechanism of molybdenum and tungsten on mineral sorbents it will make it possible to determine methods of their effective removal from aqueous solutions and subsequent management. The aim of this work was to determine the sorption mechanism and to identify reaction products formed on the surface of smectite and organo-smectite after sorption of molybdates (Mo) and tungstates (W). Smectites are frequently modified to generate the negative charge of the surface. The main objective of the study was to investigate and compare the features of Na-montmorillonite (Na-M), montmorillonite modified with dodecyl trimethyl ammonium bromide (DDTMA-M), and montmorillonite modified didodecyl dimethyl ammonium bromide (DDDDMA-M) before and after sorption experiments. The material after sorption was studied by X-ray diffraction (XRD), infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The best sorbent for removal of Mo(VI) and W(VI) was DDTMA-M, which adsorbed 388 mmol Mo(VI) and 537 mmol W(VI)/kg. It is presumed that the most probable mechanism of sorption of Mo(VI) and W(VI) corresponds to the process of crystallization of inorganic salts on the surface and in the interlayer space of montmorillonite. XRD results confirmed the presence of new crystalline phases and infrared spectroscopy showed the presence of Mo-O and W-O bonds. The presence of bands in these specific ranges of wave numbers (about 830 cm^{-1}, 940 cm^{-1}) indicates the adsorbing of polymeric forms to organo-montmorillonite. XPS analysis confirmed the presence of Mo(VI) and W(VI) in samples in the forms of Mo_2O_5, MoO_3, WO_3 and WO_2. SEM analysis confirmed that molybdenum and tungsten can be present in the salt type. Clusters in the form of crystallites or covers on the surface of montmorillonite were associated with the crystallization of inorganic-organic salts - alkylammonium molybdates and tungstates.

This research was financed by the National Science Centre, Poland Grant No. 2014/13/N/ST10/04945 and supported by the Foundation for Polish Science (FNP).

Mineralogical changes related to a fault zone: La Barquilla fault zone, Salamanca, Spain

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Faults zones architecture includes core and damage zones. Core fault zone accommodates most of slip and fault rocks are intensively developed. Deformation damage decreases progressively into the country rock, but structural criteria to define the damage zone width is a matter of debate. We have explored mineralogical variations across a regional NE-SW tardi-Variscan structure in the Iberian Massif: La Barquilla fault zone. Interestingly a continuous cross-section shows the fault core and damage zones developed into different lithologies: sandy slates and biotitic granite (Díez Fernandez et al. 2013).

Samples were collected in the core zone and across the N and S damage zones, affecting biotitic granitoid and slates respectively. Mineralogical characterization was conducted by X-ray powder diffraction. Particle morphology and textural relationships were established by using scanning electron microscopy (SEM). VNIR-SWIR spectra were acquired using an ASD FieldSpec 4 Standard-Res Spectroradiometer in the 350–2500 nm spectral range. Both, laboratory and field spectra have been acquired.

Non-damaged slates are composed mainly by quartz, chlorite and mica, while granites show quartz, feldspars and phyllosilicates, mainly mica and minor kaolinite and chlorite. The core zone concentrates slip, and breccias, cataclasites, ultracataclasites and fault gouges have been identified. In the damage zone the protolith is clearly recognized, and second-order structures dominate, like minor fractures and veins. In the whole fault zone variable proportions of chorite/smectite mixed-layers are found. Besides the proportion of the mixed-layer and the proportion of swelling layers in the mixed-layer is higher in the core than in the damage zone. Mixed-layers were not found in non-damaged rocks and could be related to the circulation of hydrothermal fluids through the fault zone. Moreover mixed-layer phase can be identified by VNIR-SWIR spectra analysis, and second derivate of the spectral curves allow to discriminate core and damage zone. As a conclusion mineral *fingerprints* has to be included on fault zone architecture research.

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Particle-scale simulation of clay compression

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Particle-scale simulations are a useful tool to advance the understanding of clay behaviour. Amongst others, Ebrahimi et al. (2014) successfully used Molecular Dynamics (MD) to model montmorillonite particles. Ebrahimi et al. idealized the clay platelets to be ellipsoids and used the Gay-Berne (GB) potential, which includes the contribution of both van der Waals and electrostatic components, to describe inter-particle interactions (Gay and Berne, 1981). Ebrahimi et al. considered only one clay mineral and did not consider the influence of pore-fluid chemistry (salt concentration, pH) on the interactions.

This contribution develops upon this earlier work and considers kaolinite. The open source MD software LAMMPS (Plimpton, 1995) was used. Simulations were carried out on a virtual sample containing randomly oriented ellipsoidal kaolinite particles assuming a 1mM potassium chloride (KCl) solution at alkaline pH (=8). The GB potential parameters were calibrated by considering DLVO theory and parameters documented by Liu (2015) and Gupta (2011). The system was firstly equilibrated by performing constant energy and temperature controlled simulations. Then the sample was subject to isotropic compression to $100\ kPa$. Following a discussion on the choice of simulation methodology, the contribution analyses the material fabric. Macroscopic observations of the system (Figure 1) at $100\ kPa$ show that the prevailing particle arrangement is face-face with formation of stacks containing several particles. The maximum repulsive forces associated with the face-face interactions are larger than the maximum edge-edge interaction forces. However, the rate of decay of the repulsive force is higher for the face to face case than for the edge to edge case.

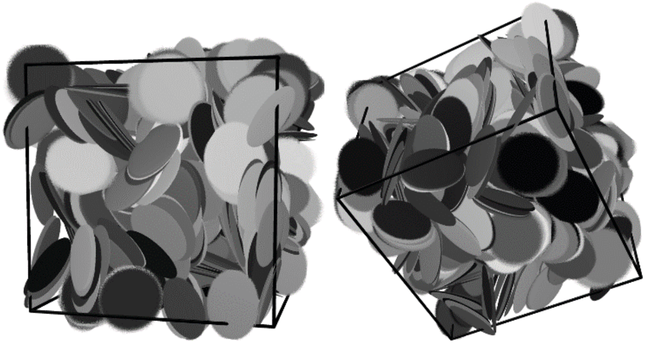

Figure 1. Particle arrangement after isotropic compression on kaolinite at pH=8 in a 1mM KCl electrolyte

Carbon paste electrode modified with cobalt-impregnated pillared smectite for analytical detection of glucose

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Glucose detection is of great importance in diabetes control, food industry and bioprocess monitoring [1]. In recent years, non-enzymatic glucose sensors (NEGS) have been widely studied. NEGS based on nanostructured transition metal oxides supported on graphene, carbon nanotube and ordered mesoporous silica based-materials have been studied due to their low cost, easiness of synthesis and high electroactivity [2].

In this work aluminum pillared clay (AP) with well-defined porous structure was chosen as the supporting material for cobalt oxides. The incorporation of cobalt oxides in pillared clay was performed using the incipient wetness impregnation method (CoAP) followed by heat treatment at 450 °C. Carbon paste electrode (CPE) modified with CoAP (CP-CoAP) was prepared in order for CoAP to be tested as a novel glucose sensing material. The CP-CoAP was prepared by mixing CoAP, carbon black (CB) with paraffin oil and packed into the hollow Teflon tube. Cyclic voltammetry was employed to evaluate the performance of CP-CoAP in NaOH solution with and without glucose. Bare CPE (CP-CB) and CPE modified with AP (CP-AP) were also tested.

There were no peaks observed for CP-CB and CP-AP neither in NaOH solution, nor in glucose containing solution. On the other hand, cyclovoltammogram (CV) of CP-CoAP in this supporting electrolyte exhibited well-defined peaks that can be attributed to oxidation/reduction cobalt oxide/hydroxide species [3]. Therefore, successful incorporation of cobalt into the AP was proven. The addition of glucose to NaOH solution resulted in the appearance of anodic peak corresponding to the oxidation of glucose. The CV of CP-CoAP at different concentrations of glucose showed that glucose oxidation peak current was directly proportional to glucose concentration. In this manner the possibility of applying carbon paste electrode containing cobalt impregnated aluminium pillared smectite for the analytical detection of glucose was confirmed.

Acknowledgment: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, (Project No. III 45001)

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Effect of ionic strength on the molecular aggregation of cationic dye in colloidal dispersions with montmorillonite particles

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The formation of dye molecular aggregates at colloidal particle interface is a complex phenomenon including different processes. It results in significant changes in spectral and photophysical properties of dyes. Although the study of various parameters on this phenomenon has been the subject of numerous scientific articles, some details of the course of dye molecular aggregation have not yet been explained. Describing the processes involved in this phenomenon is essential to understand the principles of dye/clay mineral interaction. It is also important for the purpose of investigating the possibilities of using organic dyes as molecular sensors for the characterization of colloidal particles.

In this work, the effect of ionic strength on rhodamine 123 (R123) molecular aggregation in colloidal dispersions of montmorillonite (Mt) was investigated. The ionic strength was altered by changing the concentration of an inert electrolyte ($NaNO_3$). Measurements of dye aggregation kinetics were realized using the combination of a stopped-flow device and the UV-Vis spectrophotometer equipped with a diode array detector. Subsequently, the decomposition of the spectral data matrix in a visible range by chemometric method resulted in spectral and concentration profiles of R123 monomers and aggregates. Parameters of R123 aggregation kinetics were estimated using a non-linear regression analysis of the concentration profiles of the respective dye species.

The interaction of R123 cations with Mt particles led to a formation of oblique J-aggregates of the dye over reaction time. The mechanism of their formation was described by two parallel processes, both of which proceeded by first-order reaction kinetics but differ in their rate constants. The amount of R123 cations participating in molecular aggregation slightly increased with the ionic strength. Significant effect of electrolyte concentration on the rate constants was observed: increasing the ionic strength increased the rate of the processes involved in dye molecular aggregation. However, the variation of the rate constant did not follow the equation describing the kinetic salt effect. In addition, a linear dependence of the rate constant on the reciprocal value of Debye length indicates, that diffusion processes in the colloidal system play a significant role during the formation of dye molecular aggregates.

Acknowledgement: The present work was supported by the Slovak Research and Development Agency (APVV-15-0347), the VEGA grant agency (1/0278/16, 2/0141/17) and Comenius University in Bratislava (UK/331/2018).

Spectroscopic study of organo-smectites and cationic laser dye hybrid systems

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Organoclays based on quaternary tetraoctylphosphonium (TOP^+) and tetraoctylammonium (TOA^+) cations and their hybrid systems with rhodamine 6G (R6G) were investigated by means of various spectroscopic methods, with the aim to study the influence of the amount and type of the organic cations on dye molecular aggregation and interactions within systems.

Organoclays were prepared from Sumecton saponite (Sap) and Kunipia montmorillonite (Mt) and TOP^+ or TOA^+ cations in the amounts equal to 25, 50, 75, 100% of the cation exchange capacity of the smectite. The infrared spectra in the middle (MIR) and near-infrared (NIR) regions displayed the absorption bands assigned to the C-H vibrations of both the surfactants with the shape of the bands depending on the type of the organic cation. The intensity of the bands within each series increased with the content of an organic phase. The presence of R6G was clearly detectable in MIR spectra based on the bands assigned to C=O and C-H vibrations of aromatic rings or CH_3- groups, respectively. The appearance of a new band, invisible in a pure dye spectrum, could be attributed to the interactions of the dye cations with smectites surface via hydrogen bonding. The UV/VIS absorption and fluorescence spectra provided information on the R6G species formed within the systems. UV/VIS spectra of both Sap/R6G and Mt/R6G exhibited bathochromic shifts and the formation of H- and J-aggregates. The increase in dye concentration induced a decrease in absorbance of the main absorption band centered at ~ 535 nm and enlarging the contribution of the bands at shorter (H-band) and longer (J-band) wavelengths. A predominant contribution of H-aggregates was detected in the spectra of Mt/R6G due to higher layer charge of Mt on contrary to the Sap. The presence of surfactants reduced the tendency of the dye cations to self-associate and promoted the formation of fluorescent J-type aggregates. The emission spectrum of R6G incorporated in organoclays caused a bathochromic shift, the extent of which depended on the composition of a sample. The increase in the dye amount caused the shift of an emission band to longer wavelengths (J-bands) that was further shifted in the presence of surfactants.

The authors acknowledge financial support from the Slovak Grant Agency VEGA (project No. 2/0132/13), Slovak Research and Development Agency (project Nos. APVV-15-0741 and APVV-15-0347).

New constraints on Early Mars weathering conditions from an experimental approach on rock simulants

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A denser CO_2 atmosphere and higher temperatures than present-day condition are frequently invoked as prevailing conditions for the formation of part of the ancient hydrous mineralogical associations present at the surface of Mars. The weathering conditions are of particular interest to better understand and constraint the weathering processes of the early martian crust.

For this purpose, weathering experiments on martian rock simulants and individual martian mineral analogs were performed at low temperature (45°C) under an anoxic CO_2 atmosphere (1 atm.) during 6 months.

The solution properties and thermodynamic calculations, as well as mass-balance calculations, allowed determining some constraints on the weathering conditions. Experimental solutions display prevailing acidic conditions in the 4.8 - 6.5 pH range. The Eh-pH conditions (Eh in the -14 - 213mV range) suggest conditions favorable to the formation of ferric minerals despite an anoxic CO_2 atmosphere. The mass-balance calculations show that the weathering trend under a CO_2 atmosphere involves leaching of alkali and alkaline Earth elements (Mg, Ca, Na, and K) and an enrichment of the solid phases in Al, Fe, and Si.

The characterization of weathering products using HRTEM observations, EDX analysis, and electron diffraction evidenced amorphous Si-rich and Si-Al-Fe materials on the surface of primary minerals in experiments on martian rock simulants. Al-rich clay minerals were also observed in experiments on pyroxenes. The MIR spectrum of <1 µm fraction evidenced meaningfully carbonates ions only in experiments involving olivine (Fo65), however the infrared feature suggests amorphous carbonates.

The geochemical partitioning appears very similar with those observed in weathering profiles under actual Earth atmosphere. All the results strongly suggest conditions unfavorable for crystalline carbonate formation on Early Mars despite the dense CO_2 atmosphere and show an enrichment of the weathering products in Si, Al, and Fe.

Experimental evidence of the metastability of nontronite

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The stability and the fate of clay minerals, and especially smectite, in function of time appear to be a crucial issue due to the ubiquity of these minerals in natural systems and their use in many applications, notably in waste storage. For this purpose, an experimental approach based on the hydrothermal synthesis of clay minerals at different times was performed. Two series of iron-rich smectite ($[Si_{4-x}\ {}^{[4]}Fe(III)_x]\ {}^{[6]}Fe(III)_2\ O_{10}(OH)_2\ Na_x$ - Na-nontronite) were synthesized at two pH (near 12 and 13) from 1 day to several months at 150°C. XRD, FTIR, and HRTEM data of the synthesized products confirmed the formation of Na-nontronite for the short time duration experiments. However, the disappearance of Na-nontronite and the concomitant formation of aegirine were observed with increasing time of synthesis. The pH also influences clearly the rate of the reactions. After two months for the experiments at highest pH, Na-nontronite had totally disappeared and aegirine and hematite were the only crystalline phases observed. For all the experiments, the chemical compositions of solutions were overtime far from the thermodynamic stability field of nontronite, but very close to that of the aegirine-hematite equilibrium suggesting that the formation of the smectite depends on kinetic reasons.

All the data converge and suggest that the formation of Na-nontronite at the earlier stage of the experiments is likely due to specific thermodynamic properties linked to the nanoscale particle size of these crystallized smectite. When they reach a critical size, Na-nontronite dissolves, leading to the formation of the stable assemblage aegirine and hematite.

Clay Mineralogy of the K/P transition in Tremp Group (Tremp basin, South Pyrenees)

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The mineralogical composition of lutites and marls of the KP transition in a detailed section (15 m) including the top of the Lower Red Unit and the bottom of the Vallcebre units of the Tremp Group was studied, and the evolutions of significant parameters of the weathering evolution from Lower to Upper Red Unit of this group in the Tremp basin found in a previous paper in the whole basin is considered.

Agreement is found for (illite + chlorite)/(kaolinite+ smectite) and smectite/ kaolinite ratios between the studied section and the trend for the whole basin (decrease and increase respectively) in Red Units (Lower and Upper). No significant increase was recognized for the FWHM values of 001 reflection of ethilenglycol solvated illite, from top Lower Red Unit to bottom Vallcebre unit, concurring with no significant negative difference between Lower and Upper Red Unit in the whole basin.

The evolution for (illite + chlorite)/(kaolinite+ smectite) was considered in similar units of south Pyrenees as indicative of relative warming and aridification. The increase in smectite/ kaolinite ratio, was also recognized during the Upper Cretaceous–Lower Paleocene of the Aix-en-Provence basin by other authors and related to alternating seasons with pronounced dry seasons.

Crystallite size evolution of mullite in whiteware triaxial porceains made from two different kaolin raw materials

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Triaxial porcelains were produced from two whiteware blends made with two different kaolins B and M (made respectively of "high crystallinity" kaolinite and of a finer halloysitic kaolin with "low crystallinity" kaolinite) with different firing cycles (fast/slow) in the temperature range 1270 – 1340 ºC. The X Ray diffraction mullite microstructure was studied from 110 and 001 reflections using the Voigt function method, and microstructural evolution of mullite crystals was studied by optical and electron microscopy.

Greater range of values and greater significant differences for mean 001 mullite crystallite sizes of mullite compared to 110 crystallite sizes were found in the studied porcelains at higher firing temperature.

Microstructural differences of mullite crystallite sizes can be recognized between porcelains obtained with different kaolin and also in porcelains obtained with different firing conditions.

The influence of the flux of the triaxial composition to promote mullite crystallite growth has been shown by comparing the studied crystallite sizes with that found in the firing of a reference kaolin

The results obtained showed clear and positive significant positive differences of crystallite sizes for 110 reflections between porcelains from blends with M or B kaolin and also for slow/fast fired porcelains. Positive differences were also found for mean widths of prismatic faces at the same temperature and speed of firing, but this agreement is not general.

Differences for 001 reflections were also significant positive in slow firing (not significant at 1320ºC), but in fast firing the differences are significant positive at 1270 and 1300ºC but not at higher temperatures. Positive significant differences for 001 crystallite in agreement with significant differences for mean lengths of mullite prisms, but also exceptions were found.

The mentioned exceptions must be explained because there is not a single crystallite size distribution but a mixture of distributions (corresponding to primary and secondary mullite) with different mean values.

Studying the interaction of halloysite nanotubes with nucleotides and nucleic acids

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An extensive literature exist about the binding of RNA, DNA and their components by clays, and a possible role of clays as catalysts in prebiotic RNA synthesis and the origin of life was even hypothesized. Clay minerals have been proposed as possible DNA delivery vectors because of their well-known ability to bind and protect DNA from degradation and even to transfect microorganism cells in soil. Halloysite belongs to clay minerals of kaolinite group and occurs as natural nanotubes of up to 1 µm length, the outer diameter of about 50 nm and the inner diameter of 10-15 nm. DNA-binding properties of halloysite remain the least studied among all the clay varieties. Halloysite nanotubes constitute a clay mineral with unique properties because of their oppositely charged surface and lumen both of which can be used for binding different preparations, making halloysite a promising sorbent or drug and cosmetic carrier. They can be further modified in order to change their charge, lumen size or colloid stability.

The binding experiment was performed in distilled water (pH 5.2-5.4). The reaction mixture included a nucleotide species (DNA, polyAU, UMP Na_2, ADP Na_3, dATP Na, AMP, uridine, ATP Mg), halloysite (in the final concentration of 1.5 mg/ml) and optionally $MgCl_2$ (10 mM). A set of $MgCl_2$ concentrations was tested to optimize DNA binding and release by the nanotubes.

HNTs bound nucleotides only slightly (AMP and ATP were best adsorbed (up to 10% of initial NP quantity)) and did not bind uridine. Some NP such as AMP and ATP were bound by HNTs both in the presence and absence of $MgCl_2$. Longer molecules such as DNA and polyAU were significantly bound by halloysite only when $MgCl_2$ was present. It was proposed that cations can form bridges between the phosphate groups of DNA and the negatively charged silica layer on the clay surface. However, a possibility that small negatively charged molecules can also penetrate inside positively charged halloysite nanotube lumen cannot be ruled out, because such species as AMP were bound by halloysite with equal effectiveness both in the absence and presence of Mg^{2+}. Z-potential measurements demonstrated that all studied substances were bound by halloysite. The modification of the nanotube surface with DNA was confirmed by a difference in adhesion forces between pristine and DNA covered HNTs, measured using AFM, and also was visualized using TEM.

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University. This work was partially funded by the subsidy allocated to the Kazan Federal University for the state assignment in the sphere of scientific activities (project 16.2822.2017/4.6) and RFBR according to the research project № 18-29-25057.

Adsorption of emerging contaminants on derived clay materials

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Pharmaceuticals, personal care products and some pesticides are frequently detected in surface water, ground waters and wastewaters because their extensive use in a wide range of human activities. These compounds are known as emerging contaminants (ECs) and their removal receives special attention because of their potential impact on the environment and human health [1]. The technologies investigated include those based on conventional systems (chlorine, biological treatments), membranes, adsorption, advanced oxidation processes or electrochemical systems [2]. Clays and derived-clay material have demonstrated a high adsorption capacity for different contaminant and have attracted much attention owing to their high cation exchange, swelling properties, and high surface areas.

In the current work, we have focused the attention on the adsorption properties of several commercial clays, organoclays and derived-clay materials, studying their adsorption performance for different emerging pollutants. Ibuprofen (IBP), acetaminophen (ACE) and tetracycline (TC) were selected as pharmaceutical targets while atrazine (AZ) was chosen as pesticide EC. The kinetic adsorption tests were performed at 20ºC with 20 mg/L of contaminant and a clay concentration of 250 mg/L. The higher q_e (45 mg/g) were achieved for ibuprofen adsorption with an organo-sepiolite. It is noteworthy that the nature and chemical properties of the ECs were binding in the adsorption process. While IBP was removed successfully from the water, the other ECs selected, all being nitrogen compounds, showed a poor adsorption, even the q_e for AZ was lower than 0.3 mg/g.

The adsorption performance of IBP was studied in more detail. The kinetic data was fitted to different models, comparing the adsorption rate. Further, the adsorption isotherms were also carried out at different temperatures (20-80 ºC) and different initial concentrations (5-80 mg/L). These data were also fitted to different models, stablishing the main adsorption parameters.

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Macroscopic identification of a bacterium found in Algerian palygorskite

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Bacteria are the most abundant forms of life we know on our planet that can be able to survive in a variety of habitats, from hot to cold springs, from soils to sedimentary rocks and in living organisms. In this work, we evaluated the effect of bacteria in clays. The clay selected is a Tertiary sedimentary palygorskite-rich sample, located near the town of El Ghoufi (East Algeria) [1,2] with a fibrous microstructure and rich in many elements (eg, Si, Al, Mg, Fe, Na, K, Ca). This fibrous clay (Pal) has been characterized and applied in previous works as adsorbent for retention of pesticides [2,3] and pharmaceuticals products[4]. We have chosen raw and purified palygorskite (Si Pal, Pur Pal) [1,2]. The average mineralogical formula of Pur Pal is as follows: $(Si_{7.88}Al_{0.12})\ O_{20}\ (Mg_{1.69}\ Al_{1.71}\ Fe_{0.43})\ (OH)_2\ (K_{0.06}\ Ca_{0.05}\ Na_{0.15})\ (OH_2)_4.4H_2O$ [3]. In a test tube, 1 gram of palygorskite is mixed with 9 mL of NaCl. Then, 1 mL of this suspension is placed in a Petri dish containing a thiosulfate-citrate-bile salts-sucrose agar, TCBS agar is highly selective for the isolation of *V. cholerae* and *V. parahaemolyticus* as well as other species of vibrio culture medium. The Petri dish is then placed in an autoclave at a temperature of 30 °C for several days. The macroscopic results show that after 20 days of incubation of petri dishes containing palygorskite in a TCBS culture medium, the appearance of colonies show a yellow color, with a thickness of 15 mm, as well as a curved shape and a regular contour. Following these preliminary results, more efficient techniques will be used to identify the bacterial strain.

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Hydrothermal treatment of natural Algerian palygorskite to produce LTA zeolite

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In the present study, zeolite LTA is synthesized using natural Algerian fibrous clay [1] named palygorskite as a precursor material. The synthesis essentially consists of two steps; at first, preactivation of Pal to get X-ray amorphous product and hydrothermal reaction of activated Pal with aqueous alkali and sodium aluminate. For this purpose, 1g of Pal is activated using HCl solution. The obtained solid is dried and then mixed with NaOH solution, stirred with solid/liquid ratio of the clay and alkaline solution is 1g/20mL and 5g of $NaAl_2O_3$ with 20mL of deionized water. The mixture is stirred 3h. The obtained gel solution is fitted in an autoclave which is kept in a conventional oven (6, 18 and 24h). The synthesized products are washed with deionized water, and then dried at 80°C and 24h. The samples were characterized by X-Ray diffractometry and scanning electron microscopy. The synthesized zeolite product (LTA) showed a high purity.

This approach of using palygorskite to synthesize LTA zeolite may be a more economical method of production with environmental benefits.

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Neptunium (V), uranium (VI), cesium (I) and strontium (II) uptake by various natural filtration and non-filtration sorbents

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As a result of the operating nuclear fuel cycle, thousands of tons of radioactive waste with various compositions are produced annually in Russia. Over the past 50 years, many countries are actively developing modern approaches to solve the problem of highly radioactive waste, which is planned to be buried in deep geological repositories. Also there is a problem of ensuring the safety of nuclear legacy objects: isolation and reclamation of millions of tons of medium- and low-level activity waste located in near-surface storage facilities, decommissioning of reservoirs with liquid radioactive waste and complex engineered objects.

This study is devoted to the sorption properties of natural filtration and non-filtration sorbents at various pH parameters, as well as the study of the mechanisms of sorption and the transformation of the structure of minerals in alkaline and acidic conditions. The following natural sorbents with sorption capability were selected: diatomite from the Inzenskoe deposit (Ulyanovsk region, Russia); glauconite from the Karinskoe deposit (Chelyabinsk region, Russia); zeolite from Sokernitskoye deposit (Ukraine); shungite of the Zazhoginsky deposit (rep. Karelia, Russia). Data on sorption from different clays were used for comparison characteristics: bentonites (Kutch, India and 10th Khutor deposit, Russia) (Semenkova et al., 2018; Parneev et al., 2017) and kaolin (Aldrich) (Semenkova et al., 2018). Sorption experiments were performed with ^{239}Np(V), ^{233}U(VI), ^{137}Cs(I) and ^{90}Sr(II) in the solution with 0.01 M $NaClO_4$ ionic strengths and pH values from 2 to 10 adjusted by the addition of dilute $HClO_4$ or NaOH.

The study was supported by the Russian Science Foundation, project № 18-77-00015

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Resonance energy transfer between dye molecules in hybrid films of a layered silicate including the effect of dye surface concentration

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Rhodamine 6G (R6G) and Oxazine 4 (Ox4), considered a "Förster Resonance Energy Transfer" (FRET) pair due to the significant overlap between the fluorescence spectrum of R6G (as energy donor, ED) and the absorption band of Ox4 (as energy acceptor, EA), were intercalated into an expandable layered silicate, saponite (Sap). Several films with different dyes/Sap loadings were prepared with the aim of studying the energy transfer process between both the dyes at variable concentrations in the solids. As the dye loading increased in the films, the FRET efficiency between ED (R6G) and EA (Ox4) also increased, up to a loading of 1 % of cation exchange capacity (CEC), at which FRET efficiency attained maximal values. Above this value, fluorescence was significantly quenched, probably due to the presence of molecular aggregates of the dyes. The exception was the emission signal of a new blue-shifted R6G species, which seemed neither to be quenched by the H-aggregates nor to take part in the FRET process. A theoretical model for the calculation of FRET efficiency was proposed for hybrid solid materials. The method was based on calculated probability density functions of the intermolecular distances in the solids, which were determined for each dyes/Sap ratio. The mean FRET efficiency was defined as the integral of the inner product of two functions: probability density function for a respective dyes/Sap ratio, and the FRET efficiency between R6G and Ox4 molecules, as the function of intermolecular distances. The theoretical results were compared with FRET efficiencies determined experimentally using steady-state and time-resolved fluorescence spectroscopy. Considering the very high sensitivity of the FRET efficiency to the intermolecular distances between ED and EA, the theoretical model could predict experimental data reasonably well for the films with low dye loading (< 1% CEC). At higher dye loading, the dye aggregation or the formation of the luminescent rhodamine 6G species with blue-shifted bands, which did not participate in FRET, made the theoretical prediction more complicated.

Acknowledgement: The present study was supported by the Slovak Research and Development Agency under contract No. APVV-15-0347 and VEGA grant agency (1/0278/16, 2/0141/17).

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Removal of emerging pollutants in aqueous phase by CWPO and photo-assisted CWPO with Fe-TiO_2 delaminated clays

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Emerging pollutants (EPs) are defined as synthetic or naturally occurring chemicals that have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects, often not well known. Nowadays, more than 700 emerging pollutants, their metabolites and transformation products, are listed as present in aquatic environments [1]. They can be released from specific pollution sources like urban or industrial areas but usually they come from diffuse sources. Among the more than 20 classes of EPs referring their origin reported, pharmaceuticals (urban, stock farming), pesticides (agriculture), disinfection by-products (urban or industrial), wood preservation and industrial chemicals can be found. So, the presence of these substances with very high potential impact on aquatic life and human health must be avoided.

Among the different methods in study for EPs removal, advanced oxidation processes (AOPs) can provide useful solutions working under near-ambient conditions. Catalytic wet peroxide oxidation (CWPO) is one of the most widely AOPs used, heterogeneous version of the homogeneous Fenton system, achieving high degradation rates while drastically reduces the continuous loss of iron in the effluent that characterizes the Fenton process. In addition, photo-assisted CWPO process can improve the oxidation rate. Different catalysts can be found in the literature for CWPO of different pollutants and EPs [2] including modified clays [3]. Recently, delaminated clays with mesoporous structure have been prepared for different applications [4].

In this work, Fe-TiO_2 delaminated bentonites have been prepared using CTAB as surfactant. TiO_2 was incorporated from a Ti-BALDH aqueous solution and Fe was incorporated from a $FeCl_3$ aqueous solution by wet impregnation. Batch experiments for CWPO test were performed.

The amount of CTAB and TiO_2 used in the preparation of the Fe-TiO_2 delaminated clays has been tested in the CWPO and photo-assisted CWPO of acetominophene and antipyrine pollutants (initial concentration 5 mg/L). Catalysts prepared with high CTAB amount showed the best textural properties and CWPO activity. The TiO_2 loads tested (10 and 25 mmol/g clay) gave rise to materials with similar BET surface area and catalytic activity, so the lowest load is enough to obtain satisfactory catalysts. The introduction of photo-assisted processes improved the catalytic activity of the catalysts, reaching the complete removal of the pollutants in lower reaction time.

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Fe-modified kaolin as catalyst for CWPO of phenolic compounds

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Industrial activities produce considerable amounts of wastewaters contaminated by a wide diversity of organic species, many of them of recalcitrant and toxic character. Phenolic compounds are among the most representative of toxic species listed by the European Commission and the US Environmental Protection Agency (EPA) as priority pollutants since the mid-70's [1]. They are ubiquitous in the effluents from various important industries, including refineries, coking operations, coal processing, pulp mills and petrochemicals manufacturing, among others.

Among the different methods used for the removal of these pollutants advanced oxidation processes (AOPs) have been defined as those aqueous phase oxidation processes based on the use of hydroxyl radical as oxidant. Catalytic wet peroxide oxidation (CWPO) is one of the most promising AOPs based on Fenton's reagent, namely Fe^{+2} and H_2O_2. CWPO uses Fe-bearing heterogeneous catalysts based on iron but also with some other transition metals supported on different materials [2]. Kaolin has not been very used in the literature as catalytic support probably due to its less developed porous texture compared to other clays as montmorillonite. However, its textural properties can be improved upon appropriate treatment [3].

In this work, a natural kaolin from Jijel (Algeria) was subjected to successive treatments: calcination followed by acid and alkaline attack in order to improve its textural properties. Next, incorporation of iron was performed by wet impregnation of the solid. CWPO tests were conducted in a thermostated batch glass reactor at different temperatures (25-55ºC) using phenol and 4-chlorophenol as target pollutants.

Physical and chemical treatments gave rise to a material with a well-developed specific surface area with a main contribution of mesopores. Complete pollutants removal was reached regardless of the reaction temperature essayed. Around 70% TOC reduction was achieved after 4 h of reaction at 55ºC with the stoichiometric amount of H_2O_2. Iron leaching from the catalyst was below 5% of the initial iron load.

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Effects of CO_2 Pressure, Temperature and Brine Composition on the Interlayer Spacing of a Mg-exchanged Montmorillonite

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Carbon dioxide (CO_2) capture and storage, where supercritical CO_2 is injected and sealed in deep saline aquifers[1], is being considered as an effective approach of ameliorating the increase in anthropogenic CO_2 in the near environment. The mineral smectite is a primary constituent of both the aquifer and the cap rock. Smectite can expand or contract with changes in local conditions and thus has the capability to control the porosity and permeability of the aquifer. Injection of CO_2 potentially can compromise the safety and integrity of reservoirs being considered for CO_2 storage. We use a high-pressure environmental chamber (HPEC)[2] to investigate *in-situ* the effects on the layer-to-layer spacing of Mg-exchanged montmorillonite (SWy-2) by varying temperature (T), pressure (P), including the partial pressure of CO_2 [$P(CO_2)$], and activity of H_2O [$a(H_2O)$].

At $P(CO_2)$= 1bar and T = 30 °C, an increase in $MgCl_2$ brine concentration from 0.17 M to saturation results in a decrease of $d(001)$ spacing of Mg-exchanged SWy-2 from 19.17 to 15.09Å (21%). The steepest decrease is observed at brine concentrations between 1.37 and 2.75 M from 18.99 to 16.12Å (15%). An increase of $P(CO_2)$ from 1 to 500 bars at T = 30 °C shows a 1.5-2% decrease in the $d(001)$ spacing of Mg-exchanged SWy-2 at brine concentrations less than 1.37 M, whereas no change in $d(001)$ spacing is observed at greater concentrations. Increasing T from 30 to 150 °C shows a more pronounced effect on the $d(001)$ spacing of Mg-exchanged SWy-2, with a minimum of 3% decrease. The greatest decrease in $d(001)$ spacing is observed at a concentration of 2.40 M, from $d(001)$ = 17.25 to 16.02 Å (7%), occurring from 75 to 150 °C. Furthermore, it is observed that the onset of the decrease of the $d(001)$ spacing occurs at lower temperatures with increasing concentrations. This is apparent with brine concentrations of 1.71 and 2.40 M. The $d(001)$ spacing starts to decrease at 100 °C from 17.95 to 17.52 Å at 150 °C for 1.71 M, whereas the $d(001)$ spacing starts to decrease at 75 °C from 17.25 to 16.02 Å at 150 °C for 2.40 M.

The results of this study further improves our understanding of the effect of temperature, pressure, $P(CO_2)$, and brine composition and concentration, on the interlayer H_2O content of montmorillonite (SWy-2). In previous work with Na-rich brines, local conditions were shown to be important parameters affecting $a(H_2O)$ and, thus, the loss or addition of H_2O in the interlayer of montmorillonite. In conclusion, presence of montmorillonite should be considered to assess partially the safety and integrity of reservoirs being considered for CO_2 storage.

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Characterization and comparative study of anionic clays prepared by standard coprecipitation and urea methods for phosphate removal

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Layered double hydroxides (LDHs), also known as anionic clays, constituted by a stacking of positively charged sheets (brucite-like layers) separated by interlayer spaces containing solvated anions. They are represented by the general formula $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+} (A^{n-})_{x/n}\cdot m(H_2O)$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively. The value of x is equal to $M^{3+}/(M^{3+} + M^{2+})$ and A^{n-} is the intercalated anion.
The purpose of this study was to prepare MgAl-LDHs, with molar ratio of 3, by two methods (urea hydrolysis and standard coprecipitation) and to examine the effect of synthesis method on phosphate removal from aqueous solution. The obtained anionic clays were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), the specific surface area was calculated from (BET) adsorption equation. The comparative results showed that the preparation method affect the structural features and the textural properties of LDHs clays, consequently, the phosphate removal capacity of the tested clays. The experimental evidences showed that the clay synthesized by urea hydrolysis had a removal capacity of 94% for phosphates ions with the initial concentration of 100 mg L^{-1} at pH=7 and at room temperature while 85 % were uptaked by clay synthesized by coprecipitation method.

Keywords: Anionic clay; Coprécipitation, Urea hydrolysis, Phosphate; wastewater treatment.

Study of uptake mechanism for halloysite nanotubes in different cell lines

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Halloysite nanotubes (HNTs) are a natural aluminosilicate clay with a chemical formula of $Al_2Si_2O_5(OH)_4 \times nH_2O$ similar to that of kaolinite. Halloysite is positively charged in the inner lumen, which consists mostly of aluminum hydroxide, whereas the external surface, which is silicon dioxide, is negatively charged. The different surface chemistry allows the selective functionalization making possible the synthesis of several nanomaterials with hierarchical nanostructure (1, 2). The different surface chemistry enables the selective modification both of external surface and of inner lumen. The hollow tubular structure provides HNTs to play an important role in drug delivery system, but is currently unclear the mechanism by which they are internalized into living cells and what is the transport pathway. Herein, we study the *in vitro* mechanism by which fluorescent HNTs are internalized in different cells line and their internal distribution by means flow citometric analysis and fluorescence microscopy. Furthermore, as the HNTs may play an important role in biomedical applications we also evaluate the hemocompatibility.

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Gas permeation characteristics of biopolymer-modified fine-grained geomaterial

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The release of greenhouse gases from municipal solid waste landfill sites is of great concern to the environment. Control, collection, and usage of landfill gas is an energy efficient solution to mitigate this problem. Though the gas collection system requires an intermediate cover liner, the use of permanent gas barriers is not advisable. Instead, the clay-based barrier having moderate permeability is considered as an appropriate cover liner. Based on the low permeation and volume change behavior, sand-bentonite mixtures are considered as a potential barrier material. However, these mixtures undergo desiccation cracking which in turn compromise engineering performance, particularly gas permeability.

In view of the above, sand-bentonite mixtures having different micro-structure were modified using two biopolymers, guar gum and xanthan gum, in order to enhance their engineering performance. The gas permeability of virgin, as well as biopolymer-modified materials, were assessed by employing a transient gas permeability method, using nitrogen gas as a permeant. The mineralogical and micro-structural analysis of the treated soil were carried out by means of X-Ray diffraction, FTIR analysis and microscopic imaging. The results show a reduction in gas permeability with the increase in biopolymer content. This is primarily attributed to the substantial reduction in micro-cracks and formation of hydrogel in the sand-bentonite mixtures upon treatment with the biopolymer.

Clays and clay minerals in ceramics: engineering properties of textured materials

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Texture in polycrystalline ceramics results from a nonuniform distribution of grain orientations in the sintered material. It leads to anisotropy onto the properties of the material and can be the source of a significant improvement in physical properties. The degree of property improvement depends on the strength and type of texture, as well as on the degree of anisotropy in the single crystal properties.

Clay ceramics is a group of important engineering ceramics that can be textured by a few different shaping methods. Specific orientations are mainly based on the anisotropic morphology of phyllosilicate platelets, which have been widely used as a template or seed in the fabrication of highly textured clay ceramics.

In general, specific shaping methods can lead to anisotropic green compacts that undergo anisotropic thermal transformations during the thermal process. The most important ones are densification and recrystallization phenomena that are accentuated in specific directions.

Kinetic data obtained from thermal transformations show that reaction mechanisms are dominated by oriented mullite crystallization processes, followed by strongly anisotropic grain growth since topotactic transformations at phyllosilicate faces and along alumina arrangements occur. Large mullite crystals are mainly oriented in plane of layers and toward specific directions.

The degree of preferential crystallite orientation is usually quantified by means of three-dimensional crystallographic data that are well correlated to the engineering properties of the fired materials. In oriented clay ceramics, the mechanical properties are highly improved since both rupture strength and toughness are increased leading to common ceramics that are less susceptible to damage.

Such result has been also observed in many published studies devoted to texture in different clay ceramics used for a large range of applications. They all evidence the role of phase preferential orientations in the improvement of properties in use.

The redox state exchanges between Fe and Mn distribution in chlorites and fluid in the magmatic-hydrothermal system of Borralha, Portugal

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Fe,Mn-chlorite $(Al_{2.69}Fe^{3+}_{0.02}Fe^{2+}_{7.54}\mathbf{Mn}_{1.08}Mg_{0.62})(Si_{5.31}Al_{2.68})_4O_{10}(OH)_8$ and Fe-chlorite $(Al_{3.01}\mathbf{Fe^{3+}}_{0.25}\ \mathbf{Fe^{2+}}_{7.95}Mn_{0.26}Mg_{0.19})(Si_{5.44}Al_{2.56})_4O_{10}(OH)_8$ were identified join to scheelite ($CaWO_4$) and wolframite ($Fe,MnWO_4$) in the magmatic-hydrothermal system of Borralha, Portugal (Bobos et al. 2018). In the first case, $[WO_4]^{2-}$ combined preferentially with Ca^{2+} to form scheelite, favoring the incorporation of Mn^{2+} into the Fe,Mn-chlorite structure. In the second case, Mn^{2+} is partitioned primarily to Mn-bearing wolframite and Fe^{2+} enriched the chlorite composition, occurring as Fe-chlorite. Both mineral assemblages were found in equilibrium stability with the fluid.

The importance of the Mn/Fe ratio in chlorite minerals emphasized the importance of the Mn/Fe ratio of the mineralizing fluid as the main factor controlling either chlorite or wolframite composition. The Mn/Fe and Fe/Mn ratio (6.3 to 34.12) in coexisting chlorites vary with the redox state exchange between fluid and mineral. The Mn/(Fe+Mn) ratio ranges from 0.12 to 0.16 in Fe,Mn-chlorite and Fe/(Fe + Mn) ratios 0.86 and 0.97.

The amount of Fe^{3+} is lesser 0.02 in Fe,Mn-chlorite and 0.25 in Fe-chlorite, being related to fO_2. Also, the fO_2 was controlled by the assemblage Fe,Mn-chlorite – scheelite and Fe-chlorite – hubnerite/ferberite ratio. The Fe/(Fe+Mn) ratio of Fe-chlorite was also correlated with the hubnerite/ferberite ratio in wolframite.

Fe-oxidation state of chlorite minerals was evaluated by stoichiometry and X-photoelectron spectroscopy (XPS), where the released H^+ per oxidized Fe(II) reacted with the apical oxygens forming water at the crystallite edges. Also, the chlorite dehydroxylation measured by differential termal analysis occured at about 600 ^{o}C. The $Fe^{3+}/\sum Fe$ ratio calculated on the basis of XPS ranging from 0.04 to 0.07 in Fe,Mn-chlorite and from 0.10 to 0.15 in Fe-chlorite. Equilibrium temperatures and $X(Fe^{3+})Chl$ was calculated at low and high temperature.

Crystal growth of NH_4-illite in the hydrothermal system of Harghita Bãi (Eastern Carpathians) deduced from crystal thickness distributions and light (B and Li) isotopic composition

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Crystal growth of NH_4-illite (NH_4-I) was deduced from the shapes of crystal thickness distributions (CTDs). Coarse (<2 µm) and fine (<0.2 µm) clay fractions of NH_4-illite-smectite (I-S) interstratified structures (R1, R2, and R3-type ordering) were collected from the argillized andesite rocks. The percentage of smectite interlayers generally decreases with increasing depth in the deposit. This decrease in smectite content is related to the increase in degree of fracturing in the breccia structure and corresponds to a general increase in mean illite crystal thickness. The samples (30) were saturated with Li^+ and aqueous solutions of PVP-10 to remove swelling and then analyzed by X-ray diffraction. The profiles for the mean crystallite thickness (T_{mean}) and crystallite thickness distribution (CTD) of NH_4-I crystallites were determined by the Bertaut-Warren-Averbach method using the MudMaster computer code. The T_{mean} of NH_4-I ranges from 3.4 to 7.8 nm. The CTD shapes of NH_4-I fundamental particles are asymptotic and lognormal. The crystal-growth mechanism for NH_4-I samples was simulated using the Galoper code. Reaction pathways for NH_4-I crystal nucleation and growth could be determined for each sample by plotting their CTD parameters on alpha vs. ß^2 diagram constructed using Galoper. This analysis shows that NH_4-I crystals underwent simultaneous nucleation and growth, followed by surface-controlled growth without simultaneous nucleation.

The $\delta^{11}B$ isotope compositions decreased from –12.6 ± 0.8‰ to –16.9 ± 0.2‰ during nucleation and growth, reaching as low as –22.4 ± 0.9‰ (end member NH_4-I), where nucleation ceased and growth became surface/supply-controlled. There is no isotopic difference between coarse (2.0 – 0.2 µm) and fine (<0.2 µm) fractions in the NH_4-I-S samples (%S >10%), but the temperature changed during this growth and different $\delta^{11}B$ values obtained may reflect a different temperature with a constant fluid composition. Small differences in $\delta^{11}B$ from –19.2 ± 0.9 ‰ to -22.4 ± 0.9 ‰ are observed between coarse (2.0 – 0.2 µm) and fine (<0.2 µm) size fractions, which formed at a high temperature based on higher % illite. Surface/supply-controlled growth and the lighter $\delta^{11}B$ values measured in the youngest crystals support an influx of ^{10}B-enriched fluid. The isotopic variations support dissolution/precipitation as the mechanism of smectite tobelitization, where the isotopic trends show a significant decrease of the $\delta^{11}B$ from –12.4 ± 0.8 ‰ to –22.4 ± 0.9 ‰. Different δ^7Li isotopic values were measured between coarse and fine clay size fractions of the NH_4-I clays. The positive isotopic range values obtained on the <0.2 µm clay fractions of NH_4-I-S clays suggest that the first nucleated fine clay fractions derived from magmatic fluids. Later, growth of NH_4-I-S was associated with a fluid of distinctly light Li-isotopic composition.

Hybrid systems based on layered silicate and cyanine dyes prepared by LBL method for studying FRET phenomenon

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Nanofabrication of hybrid materials into well-defined architectures is essential for the next generation of miniaturized devices. One of the methods used for the formation of hybrid materials with layered structures is layer-by-layer (LBL) deposition. This procedure is suitable for the construction of thin hybrid films at a molecular level achieving materials withwell-defined structures and compositions.

LBL multilayer assemblies based on two cyanine dyes – 3,3′-diethyl-oxocyanine (OxCy) and 3,3′-diethyl-2,2′-thiacyanine (ThCy), synthetic layered silicate saponite Sumecton (Sap), and polycationic electrolyte poly(diallyldimethylammonium chloride) (PDDA) were synthesized and characterized by absorption and fluorescence spectroscopies.

With an increasing number of layers, a slight suppression of the dimerization of the ThCy was observed regardless the type of the film. Different behaviour was observed for OxCy. There was no change in the aggregation in the films based on a single OxCy dye only. However, a slight suppression of the dimerisation was observed for this dye in the films containing both the dye components.

Complex films composed of alternating layers of the two dyes were made mainly for the purpose of investigating photophysical phenomenon of fluorescence resonance energy transfer (FRET). The effects of the concentration of dye molecules as well as the number of deposited layers in the assembly on FRET efficiency were proved.

The results obtained can be useful as a basis for further investigation of hybrid materials in order to achive the utilization and controlled manipulation of light energy.

Acknowledgments

The present study was supported by the Slovak Research and Development Agency under contract No. APVV-15-0347. Support from the VEGA grant agency (grants 1/0278/16 and 2/0156/17) is also acknowledged with gratitude.

Sediment clay minerals as longterm sink for hydrophobic organic chemicals?

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Sediments are an environmental compartment affected by numerous interactions. They are deposited on adjacent land areas (e.g., alluvial soils), which can be highly productive sites for plant production. Besides an increase of fertility, the flooding of these sites can lead to their contamination in densely populated or industrial areas. The input of persistent organic pollutants (POPs) respectively hydrophobic organic chemicals (HOCs) (e.g., polychlorinated dibenzo-p-dioxins and –furans [PCDD/F], polychlorinated biphenyls [PCBs], hexachlorobenzene [HCB]) can result in an extensive contamination of soils and thus in cultivation restrictions. For the risk assessment and management of contaminated flooding sites, the biological availability and accessibility of pollutants is of vital importance, which is significantly controlled by sorption and remobilization processes.

For HOCs, the soil organic matter is of particular relevance for sorption processes. Nevertheless, sorption occurs as well to natural mineral constituents such as clay minerals, as shown by here presented results of sorption studies focusing on HOC–mineral interactions. Due to their high stability and common occurrence, mineral fractions, especially clay minerals, could be of special relevance for the long-term storage of HOCs in soils and sediments.

The contribution gives an overview on results from adsorption experiments with HCB and different sediment fractions from different sites of the Rivers Rhine and Elbe. Amongst others, results show variations in the HCB adsorption, which cannot be explained by organic matter.

Based on further results on HCB adsorption to defined mineral fractions, open questions regarding HOC–mineral interactions are discussed with the aim to deduce further experiments in order to enhance the understanding of processes, especially with regard to sequestration of pollutants, their remobilization and bioavailability.

Hybrid organic-inorganic nanotubes selectively adsorb some organic pollutants from aqueous phases

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Methylimogolite nanotubes (NTs, chemical composition $(OH)_3Al_2O_3SiCH_3$) were synthesized according to ref. 1. Powders XRD analysis and N_2 sorption isotherms at 77 K showed that, in powder form, the NTs arrange into bundles with pseudo-hexagonal geometry, have a Specific Surface Area of 615 $m^2\ g^{-1}$and an inner pore diameter of 2.0 nm. The NTs were dispersed in water: zeta-potential measurement showed that the NTs are positively charged in the low pH range, with a point of zero charge at pH = 8.8 (2), very close to that of inorganic, fully hydrophilic imogolite NTs ($(OH)_3Al_2O_3SiOH$) and of transition aluminas (3). The positive charge of the outer surface is due to the protonation of outer Al(OH)Al groups: $Al(OH)Al + H^+ = Al(OH_2)^+Al$. Adsorption of MCPA (2-methyl-4-chlorophenoxyacetic acid), ethanol, bromobenzene, tiophene and diclhoromethane was studied by means of SAXS (Small Angle X-rays Scattering). SAXS measurements show that MCPA is unable to enter the NTs pores, in agreement with its size, but the other (smaller) molecules are able to. In order to verify the type of interaction with the NTs, adsorption/desorption isotherms of MCPA and of dichloromethane were measured at room temperature at different pH values. It was shown that MCPA, which dissociates in water, mainly adsorbs at the outer surface of NTs, due to electrostatic interaction with the positively charged surface of NTs. The interaction of NTs with CH_2Cl_2, instead, was more complex, as the molecule likely interacts with both the inner surface of NTs, lined with $–CH_3$ groups and accessible to CH_2Cl_2, but also with the outer surface of NTs, which, being positively charged, is able to polarize Cl atoms. The polar outer surface and the hydrophobic inner one, makes the NTs potentially useful for selective adsorption of molecules from aqueous phase.

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Mineralogical and petrographic characterisations of a granite weathering profile from South Brazil

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The transport properties of rocks and geomaterials are strongly affected by their microstructure which leads to different weathering processes. Understanding these processes is primordial in being able to predict in long-time scales the transformation of rocks or geomaterials and the rate of porosity formation. The development of porosity allows on one hand water flow or water holding capacity, and, on the other, rock weathering which are both key parameters of production or sustainability of soils and durability of materials. Weathering induces progressive changes in rock mineralogy and pore space geometry through the circulation of water in cracks. It is then of most importance to study the co-evolution of the porosity with the mineralogy during the weathering.

The case study proposed here is a granodiorite weathering profile from South Brazil (30° 09' 66" S; 51° 03' 15" W), located at 25 km of Porto Alegre in the Rio Grande do Sul State. The rock is mainly composed of K-feldspars phenocrysts, quartz, plagioclases and micas minerals. Although it evolves in subtropical conditions, the profile does not present a strong chemical alteration (low argilization) but a strong physical alteration. Indeed, the weathering profile is a thick saprock and saprolite (about 15 m) that are overlaid by a 3-4 m deep soil. We proposed here to study the co-evolution of the mineralogy along with the porosity during weathering as key elements to establish the weathering processes which are at the origin of the formation of this atypical weathering profile.

For this purpose, changes in mineralogy with weathering were investigated after extraction of different fraction sizes (< 2 µm, 2-20 µm, 20-50 µm, 50-200 µm and 200-2000 µm) by X-Ray Diffraction and chemical (X-Ray fluorescence) analyses. Petrographic observations (optical microscopy, Scanning Electron Microscopy associated to EDS microanalyses) are also performed. As the size of the cracks in crystalline rocks span over several orders of magnitude (< 1 µm – 1 mm), the determination of the spatial distribution of the porosity (macrocracks and microcracks) was performed using the original approach of ^{14}C-PMMA (PolyMethylMethAcrylate) method, including autoradiography. This method is based on the total impregnation of connected pore space of materials with ^{14}C-labelled resin that allows detecting the connected crack network using autoradiography with a spatial resolution of crack aperture lower than 1 µm.

The first results have shown an increase of the porosity during weathering as well as the formation of secondary minerals such as clays minerals which are infilling the cracks and pores of the rock. Clay minerals are essentially vermiculites, smectites and kaolinites, mainly resulting from the alteration of micas (biotites) and feldspars.

Compositional and Technological characterisation of 2nd-5th c. AD ceramic bowls in south-western Austria

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Sherds of decorated grey bowls are very common on 2nd to 5th c. AD Roman sites in south-western and wider region of Austria (known as *Noricum*). The bowls are typically around 20 cm in diameter, and seem to have been handmade and wheel finished. Their functionality is ambiguous: either they were used for cooking – but very few bases, that would confirm this hypothesis, have been found –, or they were used for serving, as suggested by their surface decoration. Due to their abundance and homogeneous appearance, these bowls hold a significant potential for studying the manufacturing traditions in 2nd to 5th c. AD western *Noricum*, in particular the organisation of pottery production as well as trade and exchange networks between the communities that used these ceramics.

A total of 50 sherds have been selected from two contemporary sites at *Municipium Claudium Aguntum* and Lavant, which were located in south-western *Noricum*. The sites were situated within 10 km from each other, and interconnected by a road. The study of the imported ceramics, including African Red Slip Ware and amphorae, has indicated that these two settlements had differing histories during Late Antiquity (the 4th and 5th c. AD). The activity at Lavant seems to have increased, whereas the settlement at *Aguntum* declined gradually.

As part of a larger project, which focuses on pottery regions, we have analysed the 50 sherds of grey bowls in detail, with the aim of reconstructing aspects of their production technology and raw materials. These grey bowls show a high level of macroscopic homogeneity. Therefore, we have examined their petrographic and chemical composition (using PGAA and NAA), in order to detect changes in potters' selection of raw materials and technology over time. Our results indicate that there are several compositional groups among the sherds, suggesting that pottery production was organised at a small-scale. We have also compared these groups with established reference groups from known production sites in the region, enabling us to map trade and exchange networks in which the communities in western *Noricum* participated during the 2nd - 5th c. AD.

Acknowledgements: the detailed compositional study was financed by the Transnational Access to the instruments of the Budapest Neutron Centre within the Integrated Platform for the European Research Infrastructure ON Cultural Heritage (IPERION-CH) project (IPERION-CH Grant Agreement Number: 654028). C.I. acknowledges support of the Romanian Ministry of Education and Ministry of Research through the UEFISCDI/CNCS project PN-III-P4-ID-PCE-2016-0229.

Nanomaterial based on interaction of ethambutol with palygorskite as a tuberculostatic medicine

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Tuberculosis is a bacterial infection caused by a germ called Mycobacterium tuberculosis. This disease is the second cause of death in the world from an infectious disease, affecting one third of the world's population and it is estimated that it produced 10.4 million new cases in 2016 and 1.7 million deaths. Over 90% of tuberculosis cases occur in low- and middle-income countries. High morbidity and mortality rates make also the development of effective tuberculosis treatments an important global health priority. The currently recommended treatment for new cases of tuberculosis consists on a six-month regimen of four first-line drugs (isoniazid, rifampicin, ethambutol and pyrazinamide). However, two factors determine a poor adherence to the therapy: its long-term duration and polymedication. As a result of the low patient compliance, multidrug-resistant tuberculosis increases globally, requiring longer and more expensive treatments (WHO, 2018). The design and development of new modified drug delivery systems arises as a good strategy to reduce the frequency of drug administration, increasing compliance and reducing resistant tuberculosis incidence. The use of clay minerals, like palygorskite, as carriers for these systems appears as a low cost and biocompatible alternative (Aguzzi et al., 2007).

With these premises, aim of this work was the computational study of the adsorption of ethambutol drug in the channel of the palygorskite clay by molecular modeling methodologies, as a first step in the development of a modified release system based on the drug-clay mineral interactions (Figure 1).

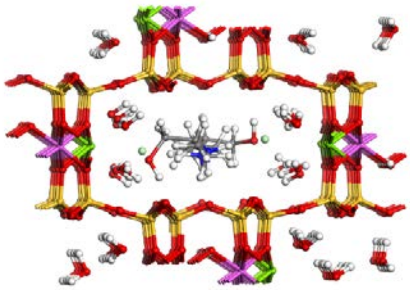

Figure 3. Adsorption complex formed by the ethambutol dihydrochloride and palygorskite.

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Coupled hydrology, chemistry, and mechanics of fine-grained soils and sedimentary rocks

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A recurrent theme in the use of the subsurface for water, energy, or carbon mitigation is the importance of fine-grained soils and sedimentary rocks. Fine-grained rocks are used as caprocks, host rocks, and source rocks in a range of low-carbon energy technologies including carbon capture and storage, high-level radioactive waste storage, and shale hydrocarbon extraction. Fine-grained soils play an equally outsized role in agriculture and soil carbon storage. This importance of clay-rich media derives largely from their distinct hydrologic and mechanical properties (ultra-low permeability, swelling-shrinking, and cracking). These properties are of singular importance in controlling fluid flow in the subsurface (where fine-grained rocks constitute roughly two-thirds of the sedimentary rock mass), yet they remain a sparsely charted frontier research area in groundwater hydrology.

Here, we review existing data on the hydrologic and mechanical properties of fined grained soils and sedimentary rocks. We show that these properties are controlled by chemo-mechanical-chemical couplings at two key scales: a nanoscale defined by the aggregation and swelling of clay (nano)particles and a mesoscale defined by the assemblage of larger grains. We present recent advances in modeling the distinct properties of clay-rich media on these two length scales using molecular dynamics (MD) and computational fluid dynamics (CFD) simulations. In particular, we present our development of a novel CFD approach that can capture the co-existence of coarse grains, macropores, and microporous clay and the ability of the clay matrix to swell, shrink, and deform in response to fluid chemistry and hydrology. We also briefly present our progress towards using MD simulations of clay particles suspended in bulk liquid water to derive constitutive relations describing the stress-porosity, porosity-permeability, and porosity-rheology relations of the microporous clay matrix as a function of pore water chemistry.

Clay minerals in cultural heritage, how to teach a wide panel of materials and issues?

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Clay minerals are widely present in cultural heritage. They are the first building material of humanity of which archaeological sites are the witness. Man has used earth to build the first cities of his settlement as the city in the Indus Valley, and to decorate ancient cave paintings to fine art. Clay minerals are also the first medium for writing, symbol of the knowledge transmission through the cuneiform tablets, thousands of which being conserved in the Louvre museum. Plasticity of clays and their variable properties when they are baked offer also an extraordinary field of production of ceramics from the Antiquities to Modern time; Clays are also colour: in archaeology and art history, among the traditional inorganic pigments, iron oxides and earth are considered for their archaeological evidence and their uses as a coloured matter, or preparation support. In architecture and masonry, clays minerals are also present within the stones. Their swelling properties lead to local stresses, initiate propagation of micro cracks; where, at the macro scale, important scaling may occur. Some stone replacement or specific conservation treatments need therefore to be practiced. For all these applications, clay minerals in cultural heritage is a specific research field gathering pluridisciplinary teams to lead national and international projects. Teaching such a multi-scale approach is unusual in clay science and conservation scientists in museums and building heritage organized a specific course "clays in cultural heritage" at the international master in clay science in Poitiers University. The course proposes to present an overview of conservation issues on built heritage as well as cultural heritage in museum dealing with clay minerals. How is identified this heritage, and what are its uses and conditions of conservation? Based on practical projects, practices and examples, this course is the opportunity to show: The know-how of clays and ceramics, from the origin of the raw material, and evolution of ceramic techniques through the ages; the unfired clays artifacts and their conservation challenge: as the Mesopotamian clay tablets; The pigments and their chemical composition, structural and chromatic properties; the specific properties of clays used for conservation purposes on object and building as cleaning or desalination purposes; A multiscale approach of the earthen material from capillary cohesion between clays and grains to build buildings for millennia; the impacts of hydric and hygric deformations that can cause heavy damages on buildings (flaking, cracking of withdrawal, etc...); And finally, the ways to conserve and restore this extremely rich heritage. The submitted **oral** presentation proposes to expose the implemented teaching approach illustrated by research and practical examples in relation with the different issues linking clay minerals to cultural heritage and how they are presented.

Effect of wetting and drying cycles on compacted silt from Loire’s Levee: evolution of permeability and 3D textural analyses with X-Ray tomography

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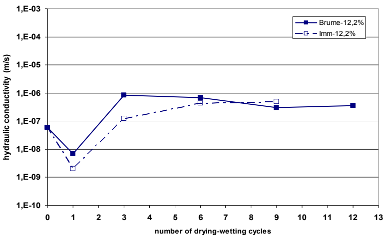
River’s levees are submitted to wetting and drying cycles during seasonal floods. Levees built with compacted sands are particularly sensitive to theses cycles because of the porosity and capillarity mechanisms that favour the ingress of water deep into the structure.

In order to quantify the influence of such cycles on the mechanical properties of compacted sands, we perform controlled wetting and drying cycles in laboratory. The material is a natural soil coming from a Loire’s Levee near Tours (France). The soil is a brown silt with 21% of 80µm, 8% of 2µm, a very low plasticity index (w_L = 26%, methylen blue test = 0,68 g/100g), an optimal moisture content w_{OPN} = 11% and an optimal dry density r_{dOPN} = 19,49 kN/m^3. The sample has been pressed at the optimum in a special mould to form a core of 20 mm long in 15 mm in diameter. This core is maintained in a plastic tube and was submitted to wetting period of few hours simulating seepage, followed by a period of drying of one week minimum, the two constitute one cycle. 12 cycles have been performed. At the end of each period, the sample is analyzed by X-Ray tomography with a voxel resolution of 7.5 µm. Comparison between both 3D images and 2D sections of successive cycles allows changes in porosity, conductivity and sand-grain structure to be characterized.

The accumulation of wetting and drying cycles on a compacted soil modify the conductivity (figure 1). While the hydraulic conductivity decreases after the first cycle, its value increases strongly and stabilizes at 10^6 m.s^{-1} for the following cycles. Correlatively, the porosity changes after the second cycle with the development of large voids (figure 2). That can explain this increase in permeability. The rearrangement of the particles can be seen since the first cycle.

These results indicate that wetting and drying cycles affect the structure and therefore the permeability of compacted sands. That has consequences on stability over time of levees. Aging affects the initial performance of compacted soils. The loss of performance depends on the type of soil, the intensity of drying, the initial density/water content and the number of cycles.



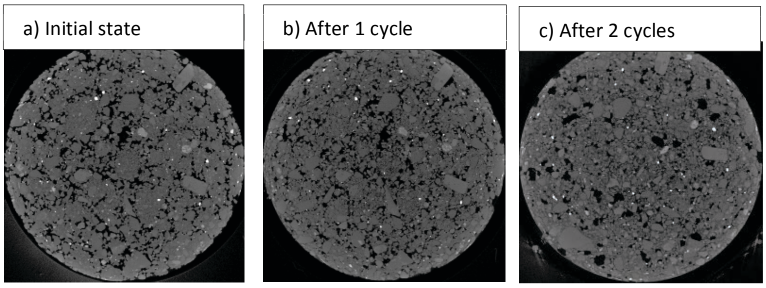

a) Initial state
b) After 1 cycle
c) After 2 cycles

Figure 1 : permeability evolution of a compacted silt after drying and wetting cycles

Figure 2 : X-Ray tomography picture of the same compacted silt after 0, 1, 2 drying and wetting cycles

Raw and amphoteric surfactant-modified Laponites®: application in the field of competitive adsorption of Cs and Sr

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Effluents contaminated by radionuclides are mostly derived from nuclear energy production. It is well known that clay minerals are suitable compounds for the long-time storage of radionuclides (Montoya et al., 2018) but less attention has been paid to their use to remove radionuclides from contaminated water (Abdel Rahman et al., 2011). The aim of this study is to develop new adsorbents, starting from Laponite® and an amphoteric surfactant, able to adsorb Sr and Cs and to compare their properties to those of raw Laponite®. X-Ray diffraction, Infrared as well as ^{29}Si and ^{1}H solid state nuclear magnetic resonance spectroscopies as well as kinetic and isotherm adsorption tests were conducted in order to characterize the structure and determine the adsorption capacities of Sr(II) and Cs(I) alone or in competition onto the different adsorbents. It was shown that Sr(II) is adsorbed through cation exchange onto the different adsorbents, the highest adsorption capacity was noticed onto Laponite®. Adsorption of Cs(I) was weak onto the raw Laponite®, whereas the adsorption capacity was improved in the case of the intercalated Laponite®. These trends were observed both for the adsorption of each radionuclide alone or in competition. The adsorption capacities in competition were systematically lower than that of each radionuclide alone. Desorption experiments of Cs(I) and Sr(II) were performed in order to check the stability of the adsorbates. Cs(I) was mostly released (from 40 to 70%) in every tested saline solution. However, the release was higher in Na(I) solution than in Ca(II) and pure water solutions. The divalent Sr(II) was in the same way more released in Ca(II) solutions in comparison with Na(I) and pure water, but the released percentage is lower (i.e. 1 to 30 %) than that of Cs(I).

With these results, it can be concluded that these new adsorbents based on Laponite® are good candidates for the decontamination of liquid effluents containing radionuclides. Studies are underway to improve the capacity of the new functionalised media.

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The Onset of Osmotic Swelling in 2:1 Layered Silicates

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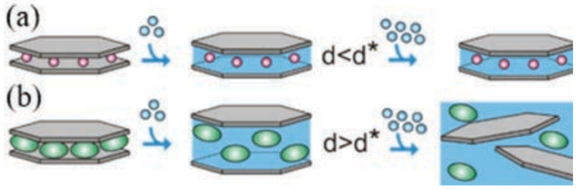

Figure 1 : Schematic explanation for the onset of osmotic swelling of organo-layered silicate: At a critical d-spacing entropic contributions to the total energy reverse the interactions between adjacent layers from cohesion to repulsion. (a) At higher layer charges, hydration enthalpy is insufficient to achieve the threshold d-spacing. (b) By amending hydration by a steric pressure of a bulky organic, but yet hydrophilic, interlayer cation even vermiculite-type high layer charges can be utterly delaminated.

The combination of chemical and physical properties of various layered materials allows for the assembly of ordered heterostructures with tailored optical and electronic properties.[1] Synthetic Na-hectorite belongs to a handful of layered compounds that show the long-known[2] but rare phenomenon of osmotic swelling. Contrary to liquid-phase exfoliation typically applied e.g. with graphene[3] that applies brute force sonication, osmotic swelling is a thermodynamically allowed process. It allows for an utter and most gentle delamination preserving the aspect ratio inherent in the tactoid diameter of the starting material. For Na-hectorite, nanosheets with 1 nm thickness and a median diameter of 20 µm are obtained simply by immersing the as synthesized material into deionized water. Due to the large aspect ratio even very dilute suspensions (< 1 vol%) are not isotropic but rather nematic.[4] Like reported for titanate nanosheets,[5] dilute aqueous dispersions of Na-hectorite nanosheets adopt a cofacial arrangement due to strong electrostatic repulsion and exhibit structural colours. In this nematic state adjacent silicate layers are not only held in a coherent cofacial geometry but are also separated to long distances which are determined by the clay content and typically exceed 50 nm. This allows for easy diffusion of polymer chains into the spacious galleries between adjacent layers. Simply by mixing the aqueous nematic clay dispersions with polymer solutions perfectly homogeneous nanocomposites can be obtained.

Despite this eminent technological importance of osmotic swelling, a fundamental understanding of this facile delamination process is lacking. Empirically, for clay minerals a maximum charge of x=0.5 per formula unit has been established.[6] We proposed a mechanism for the osmotic swelling being based on transitional entropy (Figure 1)[7] that can be extended into the regime of vermiculite-type layered silicate by the choice of appropriate organo-cations.[8]

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Synthesis and application of hectorite interalated nanoparticles

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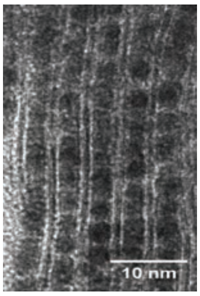

Figure 1: TEM micrograph of 3.5 nm Pd particles intercalated into Na-hectorite.

Highly active catalysts require large accessible surface areas as provided by nanoparticles and little defects in particular in photocatalysis. Molecular capping agents mostly applied to stabilize and to suppress Ostwald ripening severely limit the accessible temperature range of the catalysis. Moreover, reduction of defect concentration by annealing is also hampered. Heterogeneous supports allow for higher temperatures. Nanoparticle mobility on external surfaces is, however, high and sintering with concomitant loss of activity is frequently encountered.

In this context, clay minerals offer the possibility of enclosing nanoparticles between two charged surfaces which will slow down nanoparticle mobility while still giving access to a large portion of the surface area of the catalyst. Several groups have produced clay-supported nanoparticles by ion-exchange followed by precipitation or reduction occurring supposedly in the interlayer space [1,2]. The drawback of this *in situ* synthesis routes are obvious: The volume of nanoparticles that can be produced this way is limited by the cation exchange capacity and typically amounts to as little as e.g. one 3 nm Pd-particle per 1200 nm^2. For natural clay minerals with a diameter in the range of this length scale this leaves one worrying whether these few particles are indeed trapped in the interlayer space or whether they rather nucleate at the edge sites.

Synthetic Na-hectorite $[Na_{0.5}]^{inter}[Mg_{2.5}\,Li_{0.5}\,]^{oct}[Si_4]^{tet}O_{10}F_2$ can be repulsively delaminated by osmotic swelling. Due to the large diameter of the layers (20 µm) nematic phases are produced where adjacent layers are separated > 50 nm at 2 wt% [3-7]. This allows for the first time to intercalate pre-made nanoparticles between silicate layers without kinetic hinderence (Figure 1). This allows to apply published standard protocols for nanoparticle synthesis giving access to numerous compositions, sizes, or shapes.[8] Intercalation between the adjacent layers in the nematic phase, however, requires a positive surface charge which can easily be obtained by the right choice of capping ligand. By controlling the absolute value of the zetapotential, the number of positively charged nanoparticles ("pseudo-cations") needed for complete ion-exchange can be controlled. This way microporous hybrid materials are obtained with a very high loading of nanoparticles (e.g. 2 g Pd /g of hectorite) which are, however, held in place by sandwiching between the silicate layers, which in turn gives access to reactive sites. For instance, a catalyst consisting of Palladium particles and hectorite exhibits high performance in high temperature gas phase oxidation reactions. Fe_2O_3, CuO, Cu_2O, ZnO or CeO_2 intercalates offer potential to selective oxidation, reforming reactions or photocatalysis.

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Thermo-poro-mechanics under adsorption capturing the anomalous thermal pressurization of water in clay

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When saturated clay is heated in undrained conditions, one observes a thermal pressurization of the interstitial water. Following usual poromechanics, the pore fluid pressurization is expected to be proportional to the difference of thermal expansion between the fluid (α_b) and the solid (α_s) with a multiplicative factor involving the poromechanical properties of the medium, drained and undrained bulk modulus (K and K_u), undrained Biot modulus (M), and porosity (ϕ):

$$\left.\frac{\partial P_b}{\partial T}\right|_{\sigma,\phi\rho_b} = \frac{KM\phi}{K_u}(\alpha_b - \alpha_s)$$

Applied to water in clay, usual poromechanics significantly underestimates actual pressurization. This anomaly is often attributed to the strong water confinement in the micropores of clay. In this work, we revisit thermo-poro-mechanics to account for the effects of confinement. Existing theories of poromechanics extended to adsorption are not adapted to the case of water pressurization in clays, for three reasons: 1- most formulations are isothermal, 2- Gibbs-Duhem relation is generally assumed for the confined fluid, which turns out to be particularly wrong for water in clay, 3- the exchanges of fluid between the micro- and macro-pores proves essential, which requires a double porosity formulation. In this work, we develop a new formulation of poromechanics that addresses those three issues. Relaxing the assumption about Gibbs-Duhem relation turns out to be conceptually challenging since it requires to fully re-derive the poromechanics from the fundamentals of the confined fluid, by introducing 6 fluid properties instead of 3 for a conventional fluid. Application of the new theory provides good estimates of the anomalous thermal pressurization of water in clay, provided that the 2W state is considered for confined water. The main source of the anomaly is little intuitive: it arises from the mismatch between the thermal expansion at constant bulk pressure and at constant confined pressure.

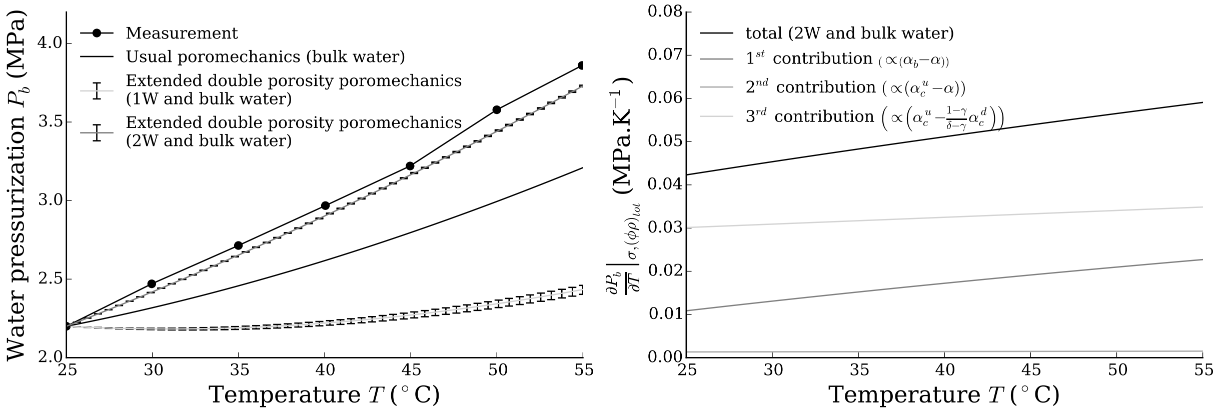

Fig. 1: (left) experimental and estimated pressurization, (right) contributions to the thermal pressurization coefficient

Impact of multiple redox cycles on the reactivity and structure of iron-bearing clay minerals

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Fe can be substituted into the clay mineral structure[1], and structural Fe in its reduced state (Fe^{2+}) is able to reductively degrade a range of organic contaminants[2]. Because the oxidation state of structural Fe can be repeatedly altered without causing significant loss of Fe from the clay mineral framework, clay mineral Fe could act as a renewable source of reduction equivalents for the long-term natural attenuation of pollution. However, other studies showed that clay minerals can be irreversibly altered by recurrent redox cycling[3]. Interestingly, marked differences in Fe reduction extents and reversibility of structural alterations have been observed for chemically (dithionite) and microbially reduced clay minerals[4], as well as for clay minerals with low and high Fe content[5]. Here, we will systematically investigate the impact of *multiple* cycles of reduction and oxidation on the structure and reactivity of Fe-bearing clay minerals.

We subjected clay minerals of different Fe contents (high: NAu-1; low: SWy-3) to three cycles of reduction and oxidation (the latter using hydrogen peroxide). We have been studying the effect of reduction via three different reduction pathways: (i) chemical reduction by dithionite, (ii) microbial reduction using a commonly found electron shuttling compound (electrochemically reduced form of AQDS (2,6-anthrahydroquinone disulfonate)) as a proxy, and (iii) microbially mediated abiotic reduction with aqueous Fe(II). The latter has only recently been described and is of particular interest due to its environmental relevance and potential to produce a variety of secondary Fe-containing precipitates[5]. The resulting clay mineral structural changes are being monitored using Mössbauer spectroscopy (clay mineral reduction extent, identity of neo-formed precipitates), X-ray diffraction (clay mineral and precipitate identity), and electron microscopy (morphology of clay minerals and precipitates). To test the reactivity of the clay mineral Fe(II), we are monitoring the reductive degradation of probe compound 3-chloronitrobenzene and analysing the reaction kinetics. Our preliminary kinetic results from dithionite-reduced NAu-1 with high (75%) and low (25%) reduction extent suggest a decrease in reactivity of clay mineral Fe with increased redox-cycling. This effect was more pronounced with higher extents of reduction and we are currently investigating the concurrent alterations of the clay mineral structure and collecting data on Fe(II) and AH_2QDS-reduced NAu-1.

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Formation of organic-inorganic hybrids having a talc-like structure: influence of the synthesis parameters

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Organic-inorganic hybrids with talc-like structure (TLH) can be synthetized by a one-step process [1]. In this case, the organic chains are covalently linked to the silicon atoms of the tetrahedral sheets and are pending in the interlayer space and at the surface. This sol-gel synthesis is performed at room temperature during 24 h using organotrialkoxysilane ($RSi(OR')_3$), as silicon source, where R represent the organic chain and R' ethoxy or methoxy groups. The final material has the following formula: $Mg_3(RSi)_4O_8(OH)_2$. The objective of this project is to study the influence of several parameters (such as pH, presence of water, duration of synthesis, solvent type) on the condensation degree of the hybrid material. The silica environment of the different samples has been studied by ^{29}Si solid-state NMR [2]. For TLH, T^1, T^2 and T^3 sites are expected (Fig. 1). T^3 sites correspond to $RSi(OM)_3$ groups where silica is covalently bonded to three Si or Mg, and represents the highest degree of condensation. T^1 and T^2 sites correspond to the presence of defects in the structure and/or border sites. This study has shown that the addition of water to the synthesis medium leads to organic-inorganic hybrids with a low condensation degree (T^3 sites ratio below 20%), while a high condensation degree (around 60%) could be obtained for syntheses carried out in absence of water. Moreover, in presence of water, the addition of a base seems to further decrease the condensation degree. The stirring duration plays also a role; syntheses carried out during 5 days show indeed a higher amount of T^3 sites when compared to those performed during 24h. Apparently, the solvent choice does not influence the condensation of the formed TLH. These results open the possibility to synthetize hybrids with a tunable condensation degree changing only the amount of water in the synthesis medium.

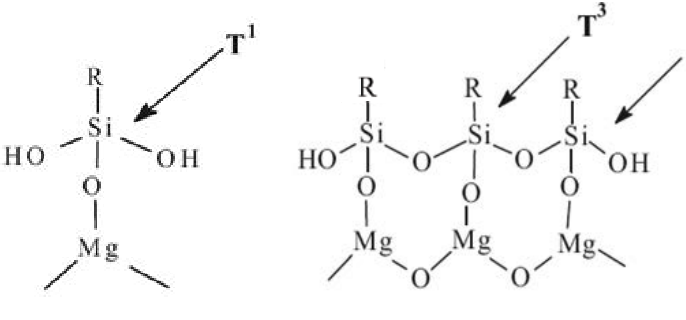

Fig. 2 : Different T sites of silica

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On the mechanism of molecular aggregation of dyes in colloidal dispersions of clay minerals. The effect of temperature

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Metachromasia represents the phenomenon of molecular aggregation of dyes resulting in significant changes in optical and spectral properties. This phenomenon is very important in the design of hybrid materials based on metachromatic dyes. Another potential use of metachromatic dyes could be probing the surface properties of clay mineral particles. Metachromatic dyes can sensitively reflect the structure of the molecular assemblies in which they are involved. The sandwich or head-tail assemblies representing H- and J-aggregates, respectively, can be easily identified by absorption spectroscopy in visible (vis) region.

The objective of this work was to shed more light on the mechanism of molecular aggregation of rhodamine 123 (R123) in montmorillonite (Mt) dispersions. Vis spectroscopy was used to see the conversion of R123 monomers into molecular aggregates over time. The spectra were rapidly sampled using a diode-array detector. More than 12,000 spectra, each with a relevant wavelength range, were analyzed chemometrically. The calculated spectra were interpreted with an exciton model. The concentration profiles were analyzed to find the mechanism and basic parameters of the reaction kinetics of dye molecular aggregation.

The oblique aggregates formed from monomers were the main reaction product. A reaction intermediate, by the spectral properties related to the H-dimer, was also identified, but its concentration remained relatively low and approximately unchanged in the course of the reaction. The larger aggregates were formed as a 4th component only in a few reaction systems. The main reaction could be described by two parallel processes of different reaction rates. The extent and the rates of molecular aggregation increased with the reaction temperature (T). The kinetics was too slow to be controlled by a free diffusion of R123 molecules, and the interaction with the surfaces of colloidal particles must have been involved in the process. On the other hand, the T effect did not follow an Arrhenius kinetics. The linear relationship between the rate constants and T indicates the mechanism may include particle diffusion processes, as described by equations of Einstein and Smoluchovski. The mechanism will be explained in detail.

Acknowledgement: The present study was supported by the Slovak Research and Development Agency under contract No. APVV-15-0347 and VEGA grant agency (1/0278/16, 2/0141/17).

Baranyaiová T.; Bujdák J. (**2018**) Clay Clay Miner, 66, 114–126.

Clays from Antarctica Dry Valleys provide analogues for clays formed under cold, dry conditions on Mars

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Cold, xeric conditions in the Antarctica Dry Valleys (ADV) provide an analogue for the Martian surface[1]. Liquid water is largely unstable[2], yet, life fluorishes[3]. We are analyzing the near-surface clays and other minerals that formed by water activity at a transient salt pond. Aqueous alteration and clay formation in cold, dry ADV conditions sheds light on the martian geochemical history, and in particular, on formation of the currently observed phyllosilicates, sulfates, and poorly crystalline phases (e.g.[4]).

We use samples collected in 1980, and compare sample fractions: bulk material, finely-crushed particles prepared in 1983[5], and ground aliquots prepared in 2018[6]. Visible/near-infrared (VNIR) spectra were collected under ambient conditions with an ASD spectrometer (SETI Institute), bidirectional and FTIR spectra were collected under dry conditions (RELAB, Brown University) as in[6]. Major and trace elements of the sediments are compared with the VNIR spectral features in order to track aqueous processes.

We compare spectral features by sample depth, measurement conditions, and grain size. Highly variable H_2O bands for different sample moisture environments suggest the presence of salts and poorly crystalline material. In contrast, gypsum-rich sediments (8-15 cm depth) vary little with environment. Broad bands at 2.2 µm (sediments from 0-4 and 20-24 cm depths) are attributed to poorly crystalline aluminosilicates. A narrower band at 2.2 µm, brighter reflectance, and changes in chemistry for the 4-7 cm depth sample are consistent with a phyllosilicate such as montmorillonite. This horizon exhibits elevated abundance of Al_2O_3 and other elements (except Si), perhaps indicating a sediment layer undergoing active alteration to form crystalline clays. We are evaluating the samples at this evaporite setting that contain montmorillonite or other phyllosilicates rather than the more common poorly crystalline aluminosilicates in order to understand factors controlling near-surface clay formation in this cold, water-limited region.

Formation of a chemically-active clay layer at an ADV transient brine pond provides an analogue for clay formation under cold, dry conditions on Mars. We postulate that chemical reaction in transient liquid water enabled formation of phyllosillicates in near-surface sediments that may have a higher moisture content than surface sediments. Clay-water interactions in the ADV are investigated here to provide insights into aqueous alteration and climate on ancient Mars that governed formation of similar minerals including phyllosilicates, poorly crystalline phases, sulfates, and chloride.

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The role of silver-bentonite in sorbing long-lived anionic radioactive species

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Clays play an important role in handling of nuclear waste. By removing cations and anions either through ion exchange, adsorption and precipitation, or all these combined, they can act as natural decontaminating agents of numerous pollutants.

In this study, Ag-bentonite is prepared and characterized, and their iodide and chloride sorption is measured in batch experiments. The kinetics, equilibrium time, sorption isotherms, and the d(001) basal spacing of Ag- bentonite are determined.

Silver cation exchanged bentonite is prepared from Ca-betonite. The modified bentonite was examined with XRF and XRD. The silver content is $6x10^{-4}$ mol g^{-1}, so 75 % of the cation exchange capacity is exchanged by silver ions. Iodide and chloride sorption was examined in batch experiments using ^{131}I and ^{36}Cl radionuclides as tracers. Ag-bentonite can sorb chloride and iodide anions from sodium chloride, potassium and sodium iodide solutions. The sorbed quantity of the halogenide ions is 67%, 57% and 73 % of the silver ion quantity of silver-bentonite, respectively. The sorption is fast, an equilibrium is reached after some minutes. The sorption in equilibrium can be mathematically evaluated by Langmuir equation. Potassium ions decrease the sorption of iodide as a results of the supposed montmorillonite-illite transformation. The sorbed amount of chloride ions decreases as the temperature increases suggesting an exothermic surface precipitation process, while in the case of iodide sorption the dissolution of AgI was observed under the high concentration of non-radioactive iodide ions. The sorption is rather influenced by the concentration than the light. The d(001) basal spacing of Ag-montmorillonite was determined with X-ray diffraction (XRD). The diffractograms show the presence of AgI, therefore halogenide ions sorb in the interlayer phase.

These results show that Ag- modified bentonite could play an important role in the treatment of radioactive waste disposals.

Acknowledgments:
This study was financed by by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008.
The work was supported by the Hungarian National Research, Development, and Innovation Office (NKFIH K 120265).

Products and mechanism study in acid-palygorskite reactions

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Two chemical composition slightly different palygorskites from Guanshan clay deposit, P. R. China were selected to be leached in HCl acid. One is magnesium rich and the other is aluminum rich and more common. The detail chemical composition could be derived in reference (Cai et al., 2007). The products formed in the acid leaching were studied using XRD, DR-UV-Vis- NIR spectroscopy, FTIR, AFM, TEM etc. The morphological observation using both TEM and AFM showed that the fibers of palygorskite changed dramatically when it experienced long-time leaching, the shapes of palygorskite grains were micro-platforms on some single fiber, hill-locks on the fibers, loose grains, dumbbells etc. The surface of palygorskite grains was smooth and flat when it only leached at a short time, such as several hours. Then surface changed into stepped micro-plat form or dumbbell like, and the loose lump of products formed nearby. The XRD of products suggested that the palygorskite content decreased but the content of silica increased with the increase of leaching time. The broad silica peak between 20 to 28 º/2q was present and increasing its intensity suggested the content of product was increasing in its amounts. However, the 110 diffraction lines was relative sharp and its intensity slightly decreased suggested the skeleton of playgorskite was preserved as well as the remaining of other main peaks but resolution of peaks deteriorated. Both FTIR and DR-Vis-NIR spectra suggested the precipitation of silica and the leaching of Mg and Fe etc. soluble cation. Selectively leaching resulted in discongruity dissolution and leave the skeleton preserved behind which constructed by tetrahedron sheets. The vibration from silica become an intense peak centered at 3417 and 1635 cm^{-1} in the FTIR and the dismissing of vibrations from octahedral cations, such as 3616 (Al_2OH), 3580 (Mg_2OH or AlMgOH), 3552 ($MgFe^{3+}OH$) from aluminum-rich palygorskites, as well as the vibrations 3686 (Mg_3OH), 3614 (Al_2OH), 3581 (Mg_2OH) cm^{-1} etc. from magnesium rich palygorskites. Furthermore, two vibrations centered at 611-621 and 470 cm-1 were assigned to vibration normal and parallel to SiO_6 sheets, respectively. These vibrations become main ones in lower bands suggested the SiO_6 hexagonal units was preserved even though the bonds among them were partially broken. As well as the FTIR, DR-Vis-NIR spectra suggested identical vibration changes from OH vibration of octahedral cations during the leaching. For example, the disappearance of vibrations of Mg_3OH, Al_2OH and Mg_2OH occurred after longtime leaching. Leaching experiments suggested that the dissolution of palygorskites was constrained by two mechanisms. For whole process, it was layer by layer dissolution and in short durations was leaching process. For leaching process, chemical compositions constrained the leaching process and partially affected the products, even though the final products were identical silica. The magnesium rich palygorskite was easier leached than aluminum richer ones, and it was a good candidate for silica preparation.

ACKNOWLEDGMENTS: This study was funded by the National Natural Science Fund Project (Project Number: 41672037).

Catalytic performances of Ni-containing smectites

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The dry reforming of biogas (CO_2 + CH_4) is used to produce synthesis gas (CO + H_2) that is of major interest for several purposes in industrial chemistry such as Fischer–Tropsch process for biofuel production. Ni-based catalysts such as NiO-Al_2O_3 doped with 0.5 % Rh is an active and stable catalyst for this reaction. The objective of this work is to study the catalytic activity of Ni-bearing clay minerals obtained from nickel lateritic ores from Niquelândia in Brazil (State of Goias). The Ni phyllosilicates are Ni/Mg smectites with a NiO content of about 23 %. The mineralogy and the crystallochemistry of the clay minerals are characterized using X-Ray diffraction and FTIR spectroscopy respectively. Prior to any catalyst analyses the clay fraction of the lateritic ore is extracted to concentrate the smectites and remove primary minerals (quartz, pyroxenes) or impurities. The clay minerals of the Ni ores were identified as trioctahedral smectites of the stevensite group. Due to similar ionic charge and ionic radius, Ni provided by the weathering of Ni-bearing ultramafic rocks (peridotites) can substitute Mg in the octahedral sites of the stevensite that is observed by typical Ni_3OH stretching band at 3628 cm^{-1} and $MgNi_2OH$ band at 3650 cm^{-1} (MIR). To evidence the impact of structural or exchangeable Ni the clays were saturated either with Mg or with Ni. The catalyst activity of the Ni smectites was estimated following the conversion of a synthetic biogas containing 50 vol% CH_4 and 50 vol% CO_2 into H_2 and CO at 800°C. Before performing the catalytic test, the samples are reduced at 700°C for 1 h under H_2 flow (5% H_2 + 95% Ar). The catalytic performances of the clay minerals were compared to the behavior of the reference 0.5 % Rh/NiO-Al_2O_3 catalyst.

Despite the absence of Rh, the preliminary results showed that the catalyst activity of the Ni-bearing smectites from natural origin was significant compared to the reference Rh/NiO-Al_2O_3 catalyst. This activity is higher with the clay minerals saturated with Ni compared to those saturated with Mg. These results support the hypothesis that both structural and exchangeable Ni plays a role in the conversion CH_4 and CO_2 into H_2 and CO. However the precise contribution of structural or exchangeable Ni has to be precise as well as the thermal stability of the clays compared to alumina derived catalyst.

On the tunability of micro/nanoparticulates of ibuprofen/layered double hydroxides dry-powders for targeting pulmonary delivery

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Inhalation aerosols defined by dry powders with mesoporous features, large surface area and small mass density permitted the highly efficient delivery of the pulmonary inhaled therapeutics into the systemic circulation. This work presents the dry-powders of ibuprofen/layered double hydroxides (Ibu/LDHs) as a novel drug delivery system with micro/nanoparticulates characteristics (see Fig. 1) that are suitable for the pulmonary delivery. The micromorphology characteristics of MgAlLDHs [1] (e.g. micro/nano particles/inter-particles sizes, mesoporous features, BET surface area) and Mg/Al molar ratios were optimized to control the amounts of Ibu that is released by Ibu/LDHs dry-powders. Results point that the heterostructuring between Ibu and LDHs can be manipulated such way to sustain a slow, fast or fast/slow delivery of the drug.

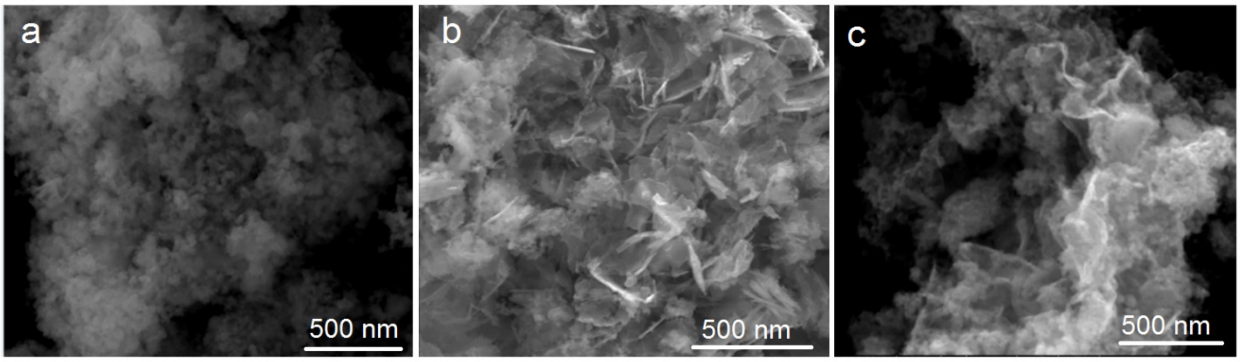

Fig. 1. Representative SEM images of micro/nanoparticulates characteristics of a) Ibu/MgAlLDH$_1$, b) Ibu/MgAlLDH$_2$, c) Ibu/MgAlLDH$_3$.

The facile and versatile strategies to develop Ibu/LDHs heterostructures as dry powders with controlled morphologies might be important in the conformal fabrications and applications of the efficient pulmonary delivery therapeutics and specifically for achieving better therapeutic action and bioavailability of Ibu at low dose.

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Mixed oxides obtained from Au/ZnCuLDH nanostructures with plasmonic photocatalytic response under simulated solar light

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Plasmonic structures have allowed the realization of numerous applications such as sensing, imaging, theranostics, photocatalysis and energy harvesting. The synthesis of plasmonic heterostructures with well-defined stoichiometry and intimacy between constituent components remains a substantial challenge [1]. We describe in this study the homogeneous mixtures of Au/ZnO/CuO/$ZnAl_2O_4$ fabricated by the thermal transformation of ZnCuAlLDHs reconstructed in the aqueous solution of Au(III) acetate. The formation of Au/ZnO/CuO/$ZnAl_2O_4$ was assessed by transmission electron microscopy (TEM), powder X-ray diffraction (XRD) and UV-Vis analysis (UV-Vis) while the thermal transformation of Au/ZnCuLDHs was followed by TG/DTG/DTA analysis coupled with infrared analyze (FTIR). We have found that a synergistic effect between constituent components is essential to promote the plasmonic photocatalytic response of Au/ZnO/CuO/$ZnAl_2O_4$ and to establish the catalysts performance for degrading pollutant compounds from water under solar light irradiation. Results point that the plasmonic response of Au/ZnO/CuO/$ZnAl_2O_4$ can be modulated as a function of Zn/Cu molar ratio in ZnCuAlLDH. This study offers new knowledge for the rational design of complex plasmonic heterostructures for applications in environmental cleanup by using solar light.

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On a variety of clay matrices of prehistoric pottery from the megalithic cemetery of Petit-Chasseur site (Sion, Western Switzerland) – the tool to investigate cultural identities?

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Pottery is of high importance in archaeology because once produced it is virtually indestructible and is often found in great quantities at archaeological sites. Thus, it readily serves as a chronological marker allowing scholars to investigate important aspects of ancient populations such as cultural identity, economy, religious beliefs, technological know-how, object circulation, and movements of people. The last few decades saw the application of various analytical techniques into the study of archaeological ceramics, which has continuously enhanced the accuracy of material characterization. Hence, the use of natural sciences in archaeology made an impressive research impact serving nowadays as invaluable tool in the study of specific traits of past societies.

Current research on the pottery from the Petit-Chasseur site allowed one to address the problematics of cultural identity of prehistoric societies that had erected the megalithic funerary monuments during the 3rd millennium BC. The cemetery is located in the middle of the Upper Rhône valley that was formed by the glacial and riverine erosion in the Western Alps. To some extent, the Rhône river separates the Helvetic and Penninic nappes dividing the valley in two. Peculiar lithology typical for the above-mentioned tectonic units has likely generated clay-rich sediments whose mineral composition may significantly differ.

In this contribution we present a variety of ceramic compositions of the pottery from the Petit-Chasseur site, putting an accent to the make-up of clayey matrix. Its characterization, performed by X-ray diffraction and Scanning electron microscopy, revealed the use of different clay-rich sources to produce vessels which, in a way, have analogue typological and stylistic features. Moreover, the pottery that belongs to particular material culture and that was recovered from the same collective grave was shown to have been manufactured using various clay raw-materials. In brief, the evidences from the Petit-Chasseur cemetery permit a question to be posed on whether the utilization of diverse plastic materials was a deliberate economic and/or social choice or is rather related to the raw-material availability in the Upper Rhône valley. The study of ceramic grave goods from the Petit-Chasseur site revealed its potential in identifying and defining the cultural identity of prehistoric communities that dwelled in this part of Switzerland during the 3rd millennium BC.

Selective adsorption of keratin onto halloysite nanotubes: colloidal stability, thermodynamics and applications

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Recently, hybrid nanomaterials with tunable functionalities were obtained by the combination of proteins and halloysite nanotubes. As evidenced in a recent review,[1] the nature of interactions between the Halloysite surfaces and the biomacromolecules is crucial to confer specific properties to the corresponding hybrids. Here, we investigated the adsorption process of keratin onto halloysite nanotubes with the aim to discriminate the driving forces between the two components. In this regards, electrostatic, colloidal and thermodynamic aspects of the keratin/Halloysite mixtures at variable pH were studied. Preliminary studies on the keratin solutions at variable pH were conducted by means of z-potential and UV-vis spectroscopy measurements. The obtained data allowed us to determine the isoelectric point (pH = 4) of the protein and the peculiar dependence of the keratin surface charge on the pH of the solvent medium. As expected, z-potential experiments at pH =4 evidenced that the addition of Halloysite does not alter the keratin surface charge ruling out the presence of electrostatic interactions between the protein and the nanotubes. Above the isoelectric point, the z-potential of the mixtures showed a decreasing trend with the Halloysite/keratin ratio as a consequence of the attractive interactions between the protein (negatively charged) and the halloysite inner surface (positively charged). According to these results, the aqueous colloidal stability of keratin/Halloysite mixtures was enhanced in alkaline conditions (pH =8) as demonstrated by the sedimentation kinetics. As concerns the thermodynamics, calorimetric measurements highlighted that the adsorption process of keratin onto Halloysite surfaces is exothermic (DHads > 0). The heat generated by the keratin adsorption was affected by the pH conditions. Above the keratin isoelectric point, we estimated larger DHads values because of the stronger keratin/ Halloysite interactions driven by attractive forces. Finally, the keratin/Halloysite mixtures were tested to develop a novel protocol for hair treatment. The reinforcing action of the keratin/Halloysite systems was estimated by morphological and mechanical investigations of the treated hair samples. In addition, the protection efficiency of the treatment was explored by monitoring the tensile performances of the hair samples after their exposure under UV radiation.

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Nontronite as natural source and growth template for (nano)maghemite [γ-Fe_2O_3] and (nano)wüstite [$Fe_{1-x}O$]

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Nontronites are iron-rich dioctahedral smectites that serve as a natural source of nanomaghemite and nanowüstite, which are industrial minerals widely used to develop biomedicine and semiconductor applications. The integration of various bulk analytical techniques and computational calculations to study the structure of nontronites show that their contents of tetrahedral Fe^{3+} surpass theoretical values. Consequently, the microstructure of nontronite has only been partially understood. Three nontronites (NAu-1 and NAu-2 from South Australia) and NG-1 (Högen Hagen, Germany) were studied as received using high-resolution techniques, namely, High-Resolution Scanning and Transmission Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (HRSEM and HRTEM-EDS), and Electron Spin Resonance Spectroscopy (ESR). Nontronite surfaces contained abundant nanodomains (predominantly ≤ 2-nm in diameter), homogeneously distributed, mostly circular in shape, discrete, crystalline, and composed by a single phase. Nanodomains were found invariably associated to nontronite surfaces, mostly embedded although loosely bound at times. Noteworthy were nanodomains showing non-round contours, a signature of halted growth. However, nanodomain abundance related to the tetrahedral Fe (or unit cell formulae). If theoretical contents of tetrahedral Fe in nontronite were higher (NAu-2, NG-1) then the nanodomains were found to be less abundant and more heterogeneous in size and shape. Acquired Miller diffraction indexes for Fe nanodomains confirmed the presence of maghemite [γ-Fe_2O_3] and wüstite [$Fe_{1-x}O$]. Most remarkably, wüstite, a highly-reduced mineral remained stable under oxic conditions, so the small size of wüstite and its interactions with nontronite surfaces inhibited the oxidation of structural Fe by atmospheric oxygen. Finally, we speculate that mineral microregions containing nanomaghemite and nanowüstite may form a Fe mixed valence system showing electronic and magnetic properties resembling those characteristic of Fe(II)-Fe(III) minerals.

Cervini-Silva J; Palacios E; Gomez-Vidales V (**2018**) Appl.Clay Sci., 156, 178-186.

Methane production and carbon assimilation in nontronite at 25 °C

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Methane (CH_4) is a clean source of energy, thus current large-scale efforts aim to produce this hydrocarbon. Little is known on how the surface reactivity of clays contributes to the *in situ* production of CH_4. This paper reports on the natural production of CH_4 after reacting four nontronites, iron-rich dioctahedral smectites [Fe_2O_3 *ca.* 30% and Al_2O_3 < 12%], against bicarbonate under strict, free-oxygen conditions at 25 °C. The analytical techniques used included X-ray fluorescence, X-ray diffraction, elemental analysis, gas chromatography, high-resolution scanning and transmission electron microscopy, and energy dispersive X-ray spectroscopy, and nano-diffraction. The production of CH_4 reached 5700 ppbv. By way of comparison, registered concentrations for CH_4 in the aqueous nontronite dispersions surpassed the average concentration of CH_4 in the Earth´s atmosphere (1.774 ppbv), and the planetary budget of CH_4 for the Mars surface (10-250 ppbv). Fitting functions for the production of CH_4 were calculated. The highest production of CH_4 was registered in dispersions containing nontronites with lower contents of Fe (%Fe). The cumulative production of CH_4 (ΣCH_4 after 60 d) varying with %Fe according to: $y = -171.5(x) + 7348$, $r^2 = 0.98$ ($n = 4$). Increases in proton activity favored the production of CH_4, *in lieu* with the notion that corrosion of highly-reduced, Fe nanodomains that occur naturally on nontronite surfaces render protons that hydrogenate carbon centres. Meanwhile, bicarbonate acted not as spectator anion, for which it acted as carbon source. On the other hand, microscopic observations identified the presence of biosignatures in nontronite, denoting asexual and sexual reproduction of bacterial iron-oxidizers, proper of a lithotrophic environment. In summary, both CH_4 production and carbon assimilation were best explained because the reduction of carbonate by labile, highly-reactive Fe nanodomains present in nontronite.

Cervini-Sillva J et al. (**2019**) Appl. Clay Sci., XXX, XXX–XXX.

Formation of new organic-inorganic hybrid materials having a lamellar structure by sol-gel process

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The aim of this work is to prepare organic-inorganic hybrids with a saponite or talc-like structure by means of the sol-gel process, an attractive way to synthesize quickly materials of high purity at room temperature (1,2,3). In a first step, the different precursors (metallic salts, magnesium chloride or nitrate, and aluminum acetylacetonate or chloride in the case of saponite-like hybrid materials) are dissolved into ethanol. The proper organo-alcoxysilane is then added to the solution as a silicon source, having a general formula R-Si(OR')3 (R corresponding to the functional group and R' a "methoxy" or "ethoxy" group), inducing the presence of an organic chain in the interlayer space and at the surface. Finally, the pH of the solution is increased up to 11 to favor the condensation steps required to form the materials. Moreover, the Si/Al molar ratio has been varied in the saponite-like hybrid samples in order to modulate their surface acidic/basic properties.

The structural properties of the materials have been characterized by using X-Ray Diffraction (XRD), Fourier-Transformed InfraRed (FTIR), and ^{29}Si and ^{27}Al Nuclear Magnetic Resonance (NMR) spectroscopies. Their thermal stability has been determined using Thermogravimetric Analyses (TGA) and high temperature XRD. To go further, specific surface area has been estimated by BET method before measuring their surface acidic/basic properties by SO_2 and NH_3 adsorption.

The first organic-inorganic saponite-like hybrids syntheses show the unexpected formation of another lamellar structure: a Layered Double Hydroxide (LDH) essentially composed of octahedral brucite-like sheets made of aluminum and magnesium (4,5). A series of samples were therefore prepared in order to gather information on the key parameters governing the formation of LDH and/or phyllosilicate-like organic-inorganic hybrids. It was shown that the type of aluminum salt plays a crucial role in the formation of the different phases and on the saponite/hydrotalcite ratio.

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Effect of clay anisotropy on the probabilistic bearing capacity of strip footing under eccentric load

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Owing to rapid urbanization and scarcity of land, structures such as bridge abutment, electrical transmission tower and building are often built on or near the edge of the sloping ground made up of clayey soil. The load bearing capacity of the foundation of such structures is always lesser than the foundations situated on the plain ground. The stability of the slope is also affected by the proximity of the structures. Many experimental as well as numerical analyses were carried out in the past to compute the bearing capacity of the foundation and also the stability of the slope. However, most of studies were related to the clayey soil slope subjected to vertical compressive loading only. Whereas, due to the structural asymmetry and lateral loads, the load coming from the superstructure becomes eccentric. Generally, the clayey soil was assumed to be isotropic. Being a highly anisotropic material, the above-mentioned assumption regarding clayey soil leads to the erroneous results. The present study considers both the effect of eccentric loading and anisotropy of clay and computes the probabilistic bearing capacity factor N_c of the strip footing of width B placed on the edge of a clayey soil slope by using lower bound finite element limit analysis in combination with non-linear programming and Monte-Carlo simulation. The randomness of the cohesive strength (C_u) of clay is modelled with the usage of random field method which is characterized by the coefficient of variation (*CoV*) and correlation length (ϑ). The correlation length in both the horizontal (ϑ_x) and vertical (ϑ_y) directions are considered to be different to consider the anisotropic behaviour of clayey soil. Figure 1 shows the one typical plot of spatial variation of cohesive strength of clay for (a) $\vartheta_x = 1$ and $\vartheta_y = 0.5$ and (b) $\vartheta_x = 1$ and $\vartheta_y = 40$. Figure 2 shows the effect of loading eccentricity and anisotropy on the bearing capacity of strip footing. Figure 2 indicates that with the consideration of loading eccentricity, the mean of N_c (μN_c) value reduces. For a particular value of *CoV* and ϑ_x it is observed that the mean value of N_c increases continuously up to a certain value of ϑ_y then it becomes constant.

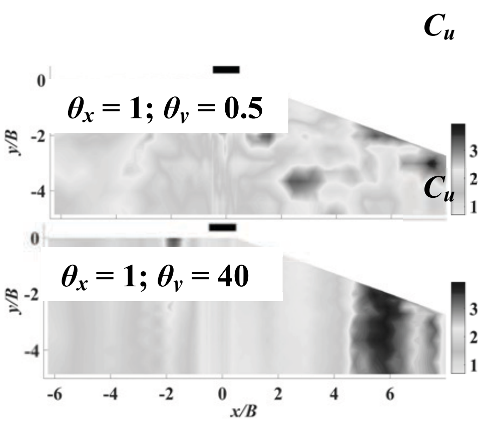

Figure. 1 Spatial distribution of C_u

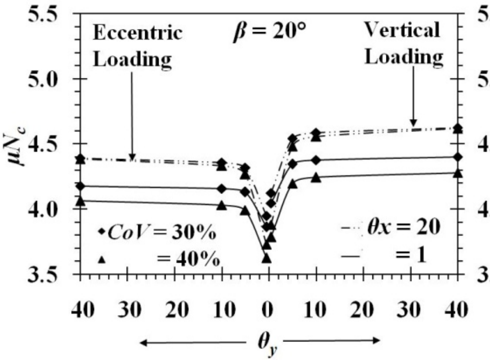

Figure. 2 Variation of μN_c with ϑ_y for vertical and eccentric loading

Mineralogical composition, firing behavior and potential use of Tunisian Clay as Raw Material in geopolymer cement

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This study aims to formulate a new and durable cement named geopolymer cement, unlike Portland cement but having similar mechanical performances, based on Tunisian clays. Tow illito-kaolinitic clay materials collected from Sejnène area (Northern Tunisia) were calcined at 700, 800 and 900 °C for two hours and activated by sodium hydroxide solution 10M. The mineral and chemical composition of the raw clays, calcinated clays and geopolymer specimens was characterized by X-ray diffraction, infrared spectroscopy and thermal analysis. The mechanical strength and water absorption of the geopolymer harded are determined subsequently. As a result, the compressive strength of geopolymer strongly depends on the calcination temperature. However, this last parameter increases with increase in calcination degree. The most suitable temperature for synthesis of geopolymer cements is obviously at 900°C, which marks the effect of calcination on the reactivity of the raw materials. The compressive strength achieved 20 MPa at this temperature. Consequently Tunisian clays show characteristics and properties allow that provide the use as raw materials for the formulation of geopolymer cement and to obtain high quality products.

Chemical and mineralogical compositions, thermal behavior and ceramic applications of the Oligo-Miocene clays from Nefza and Sejnène regions (Northwest Tunisia)

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This study aims to evaluate Tunisian clays deposits for the manufacturing of ceramic tiles for coating and construction. This study wears with the mineralogical, physical-chemical characterization, thermal analysis and technological tests of the Oligo-Miocene clays from northwestern Tunisia, precisely on the clay materials from two different sites in Nefza and Sejnène regions. These clays are affiliate with the Numidian Flysch and exposed over a large area.
As a result, these clays are essentially composed of illite and kaolinite. Smectite is present in a small amount. The associated minerals consists mainly of quartz, feldspar, calcite and dolomite. The chemical analysis indicated that the clays are composed of three major oxides SiO_2, Al_2O_3 and Fe_2O_3, with lower contents of other oxides (CaO, MgO, K_2O and Na_2O).

The firing process were mainly studied by X-ray diffraction after calcination of raw clays at temperatures ranging from 300 to 1200 ° C. The main transformations were observed firstly at 600°C by the disappearance of kaolinite and development of a disordered structure compound which is metakaolinite and secondly above 1000°C with the appearance of new crystalline phases, contributing to the densification, notably hematite, anorthite, mullite, and cristobalite.

To evaluate ceramic properties, two mixtures were prepared by dry pressing and sintering from 850 to 1150°C. Drying shrinkage, firing shrinkage, water absorption, flexural strength and color rate were also determined.

Considering to the mineralogy, chemical composition and technological tests, these clays have satisfactory characteristics and could be used for ceramics applications.

Redox conditions registrated by phyllosilicates in a thrust fault (Pic de Port Vieux fault, Pyrenees)

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Clay minerals are common minerals in fault zones, their chemical composition, crystal structure and textural arrangement are mainly controlled by burial diagenesis, tectonics activities, and interactions with fluids.

The present study focusses on the Pic de Port Vieux thrust (PPVT), a second-order thrust related to the major Gavarnie thrust located in the southwestern part of the Pyrenean Axial Zone (Spain). In the studied area, the PPVT juxtaposes Triassic pelites of the hanging wall, and Cretaceous limestone of the footwall.

The PPVT core zone is about 1 meter thick in the Triassic pelites and it is intensively foliated and characterized by the development of quartz-chlorite veins. It shows a green color, whereas the damage zone is composed of several meters of red pelites. The difference in color is related to the occurrence of hematite only in the red zone of the Triassic pelite. In the damage zone, clay minerals (chlorite and mica) are mainly inherited and are abundant in the pelite matrix with the co-existence of newly formed chlorite in veins. On the other hand, in the core zone, newly-formed chlorite and mica are synkinematic to the fault activity and related to deformation processes and fluid-rock interactions. Veins filled by chlorite are particularly abundant in the core zone and these chlorite are more Fe-rich than chlorite from veins in the damage zone (red pelites) (Abd Elmola et al. (2017).

Chlorite composition depends on the PT conditions but also on the nature of the fluid from which it precipitated. Investigation for the iron-state of the different chlorite groups is the focus of the present study. Therefore, µXANES analyses were performed on the Dispersive-EXAFS beamline of the European Synchrotron Radiation Facility (France). Chlorite from the damage zone has homogeneous composition, with XFe = $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ between 0.25 and 0.4. No distinction can be made between chlorite from the matrix and chlorite localized inside synkinematic veins. On the contrary, the iron state of chlorite from the core zone is very heterogeneous. Chlorite from the matrix is formed in more reduced conditions (XFe<0.2), whereas chlorite localized inside synkinematic veins displays higher XFe from 0.3 up to 0.5 which can be considered as moderate-to-high redox equilibrium range for chlorite. Numerical modelling (PhreeqC) is now used to propose a fluid-rock interaction scenario for the formation of this mineralogical assemblage. Besides, temperature of thrust fault activity has been evaluated using chlorite thermometry. But, the temperature calculation is highly dependant on ferric iron content; we are now able to propose more accurate temperatures.

Abd Elmola A., Charpentier D., Buatier M., Lanari P. & Monié P., 2017, Textural-chemical changes and deformation conditions registered by phyllosilicates in a fault zone (Pic de Port Vieux thrust, Pyrenees). *Applied Clay Sciences,* 144, 88-103.

New progress in $^{40}Ar/^{39}Ar$ dating technique for ultrafine minerals

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Fault chronology is one of the fundamental parts of fracture zone research, which provides time constraints for scientists to understand fracture zone activity. There are many approaches that can be used to study fault chronology. Among these, a commonly used approach is $^{40}Ar/^{39}Ar$ dating of K-bearing clay minerals such as illite and illite/montmorillonite authigenic species in fault gouges. This approach can determine the peak time and the last date of fault movement more accurately.

The $^{40}Ar/^{39}Ar$ dating approach has therefore attracted more and more attention due to its wide range of dating, abundant mineral types and high accuracy. However, because of the existence of a nuclear recoil effect during fast neutron irradiation of samples, there will be a significant deviation (usually older) between the age results obtained from $^{40}Ar/^{39}Ar$ dating of fine minerals and their true age. In general, the finer the mineral grain is, the higher the proportion of ^{39}Ar lost by nuclear recoil, and the greater the deviation of age results obtained. However, there is no defined finest mineral particle size for conventional $^{40}Ar/^{39}Ar$ dating. This defect limits the application of the $^{40}Ar/^{39}Ar$ dating approach in fault chronology. By systematic and comprehensive research, our laboratory has made breakthroughs in the research of the $^{40}Ar/^{39}Ar$ dating technique for superfine minerals. Firstly by determining the size range of mineral particles for which $^{40}Ar/^{39}Ar$ dating produces significant deviations resulting from nuclear recoil effects. Secondly, the establishment of $^{40}Ar/^{39}Ar$ dating experimental procedures for ultrafine mineral samples, including separation, classification, purity detection of neogenetic K-bearing minerals, the experimental procedure of extraction and purification of Ar gas from ultrafine mineral samples, and thirdly, studying the characteristics of Ar release from ?different grain sizes of ultrafine mineral samples, etc.

The $^{40}Ar/^{39}Ar$ dating of the reference material samples（ZBH-25 biotite and SK01 sanidine）with different grain diameters shows that the effect of nuclear recoil on $^{40}Ar/^{39}Ar$ dating results is still negligible when the sample size is fine to 300 meshes. The $^{40}Ar/^{39}Ar$ stepwise heating dating experiment of ultrafine aggregates of neogenetic K-bearing minerals with different grain diameters in tectonite samples shows that the effect of nuclear recoil on $^{40}Ar/^{39}Ar$ dating results is still negligible when the sample size is fine to 800 meshes. According to the study of Ar release characteristics and age spectra of different grain diameters samples, it was found that with the fining of grain size, the release peak of $^{40}Ar^*$ moved forward, and the age spectrum pattern also changed obviously (age plateau shortened). From maximum to minimum grain diameters, the release peak of $^{40}Ar^*$ moved forward by about 100 ℃ and the age plateau was shortened by about 3.5%. However, neither the advance of $^{40}Ar^*$ release peak nor the shortening of age plateau had any effect on the accuracy of $^{40}Ar/^{39}Ar$ dating results.

Acknowledgments: This work was supported by NSFC (41688103, 41773046, 41573049).

Mudrocks pore space storage capacities investigated by small-angle neutron scattering intensities ratio

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From the beginning of the 21th century a world global warming consideration is emerging especially focused on greenhouse gas (*i.e.* CO_2) effects and reductions. One of the main studied processes considers the injection of CO_2 into geological reservoirs such as unconventional source rock systems (the second biggest geological storage domain). These rocks are well known for their high heterogeneities and their complex fabrics due to the presence of a laminated organic/clays matrix. Their pore size distributions and their affinity for oil and CO_2 is still a matter of debate. Small Angle Neutron Scattering (SANS) is used here to localize the various components of oil as a function of source rock pore sizes.

Five unconventional source-rocks of various maturities have been analyzed by coupling XRD, SEM-EDS, HeadSpace GC, Rock-Eval pyrolysis and Raman spectrometry to assess mineral and organic heterogeneities. Quantification of all components allowed to determine 4 main phases based on their scattering length densities (SLD) : minerals, kerogen, oil and pores. Oil have been partially extracted from these source-rock using *Soxhlet* method generating another set of five samples.

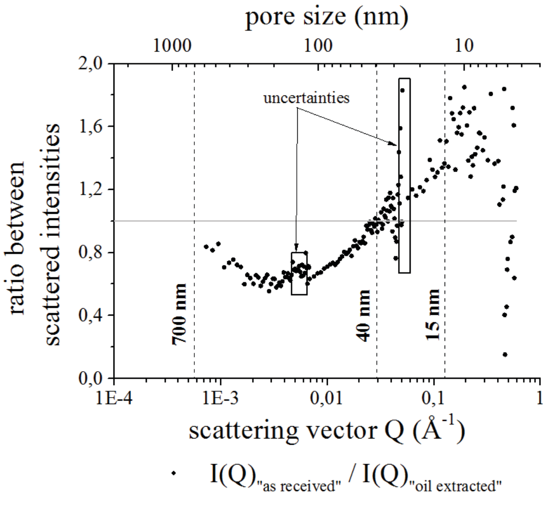

Figure 1: SANS intensities ratio of an "as received" related to an "oil extracted" sample.

The ratio of SANS intensities between the "as received" and "oil extracted" counterpart is mainly dependent on SLD contrast variation when oil is substituted by a vapor : ratio smaller than one is ascribed to substitution of high SLD oil compounds (*i.e* aromatic) whereas ratio larger than one correspond to substitution of lower SLD oil light compounds (*i.e* saturate). Such a ratio is plotted (Figure 1) as a function of wave vector *Q* that could be seen as an inverse pore size length scale. The *Q* dependence of the ratio suggests clearly that all the oil components are not equally distributed : light compounds (possibly methane, ethane, propane…) seems to be preferentially located in pores of ~10-20 nm whereas heavy compounds seems to occupy pores of 40-700 nm. Such a methodology leads to a macro- to nano- pores characterization of an heterogeneous geological media and describes affinity of such media for various fluids. It will be applied to source-rocks of various maturities and discussed for future recognition of CO_2 localization.

Nanoparticles In Hydrothermal Clays (South Kamchatka, Russia)

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The object of the study are hydrothermal clays common in the thermal fields of the Pauzhetsko-Kambalno-Koshelevo region of South Kamchatka. Hydrothermal clays are soils formed during hydrothermal processing from volcanic rocks in areas of modern volcanism. Previous studies have shown that such formations contain areas composed of mineral nanostructures. The authors refer to the nanostructure as the spatial organization of a substance composed of structural elements less than 100 nm (nanocrystals, nanoparticles, nanolayers, etc.).

Hydrothermal clays are characterized by zonal development of clay minerals. In the upper zone (up to a depth of 0.5 m), the so-called "sulfuric acid leaching" zone, kaolinite and mixed-layer formations like kaolin-smectite prevail. In the lower zone (with a capacity of 0.5-1.5 m and more) - "carbon dioxide leaching", dominated by minerals of the smectite group, mainly montmorillonite. The granulometric composition of clay samples contains from 5-8 to 28-30% nanoparticles. The mineral composition was studied with a Rigaku Ultima IV X-ray diffractometer. Nanofraction consists mainly of kaolinite (Fig. 1 a), illite, smectites (Fig. 1 b) and mixed-layer minerals kaolinite-smectite, opal, iron oxides. Studies using a scanning electron microscope (SEM LEO1450VP) have shown that the microstructures of hydrothermal clays are most often of an inherited (pseudomorphic) nature. Nanostructures have very high porosity and belong to the domain-like (Fig. 1 a), globular-lamellar, honeycomb (Fig. 1 b) and spongy types of structures. The high physicochemical activity of such clays, as well as the concentration of basic ore, alkaline and rare-earth elements in them can be explained using the data obtained.

This research was supported by Russian Foundation for Basic Research (Grants 17-05-01045a). The studies were carried out using the equipment obtained as part of the MSU Development Program.

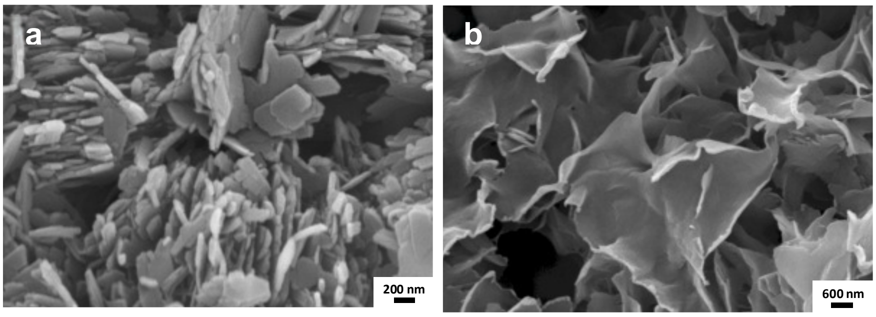

Fig. 1. SEM images of kaolinite (a) and smectite (b) in the nanostructure of hydrothermal clays.

The unique role of electron and ion microscopy in nano-clayey materials characterization

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Investigation of clayey materials, either individual nano-clay particles and/or clay fabric in nature, is difficult due to minute particle size and highly charged surfaces. Instrumentation capable of simultaneous microstructure and microchemical analyses in high resolution is essential for clay research, but historically has not been readily available. Recent developments in electron microscopy (EM, TEM, STEM and SEM) and the combination of focused ion beam and SEM (FIB/SEM) in particular, have produced very powerful and indispensable tools that may significantly facilitate clay research. In addition, *in-situ* experiments of clays in EM (TEM and SEM) and FIB/SEM can not only provide dynamic observation at high resolution, but information is crucial to understanding the natural process of clays in different environments. This paper presents unique applications of EM and FIB/SEM in clay nano-particles and fabric research/characterization in different environments as well as in 3D microstructure study.

To observe the real morphology/fabric of clayey nanoparticles in different environments, special EM sample holders have been developed for *in-situ*, high-resolution, investigative experiments in EM. Clay materials collected from different localities were purified and dispersed in de-ionized water without any dispersion agent (to avoid possible artifacts) for wet environment-cell TEM (WETEM) and Cryo-SEM observation. The *in-situ* experiments of clays in TEM, both at various hydrated states and elevated temperatures, revealed the detail of microstructure change in different environments. Conventional embedding and ultra-microtoming techniques and newer FIB methods were used for clay fabric research. Using a combined FIB/SEM technique, a series of specimens at different position (site specific) can be imaged and analyzed simutaneously. Microstructures and microchemistry of clay particles/assemblies were reconstructed and presented in 3D using modern computer software. Microstructure of clay particles at cryo-temperature using cryo-TEM and cryo-SEM were collected and compared for the first time.

With advanced instrumentation, computing technology and speed, surface 3-D topography images and 3-D tomography/microstructure can be constructed by images obtained from SEM, TEM and FIB/SEM. The novel applications of techniques for 3-D analysis of clays and the fabric promises to increase our understanding of clays in many aspects and thus improved applications. Similar techniques may also be applied to the study of other sediments, geomaterials and nanomaterials.

Provenance Study of 99MAP-P63 Core Sediments in the East China Sea

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East China Sea is known to be supplied with large amounts of sediments form Huanghe, Changjiang and various rivers in Korea. Many studies have been conducted to identify the effects of rivers and deposition process of East China Sea, but no consensus has been reached. In this study, clay minerals, rare earth elements and grain size were analyzed to study the provenance and sedimentation environment of core 99MAP-P63 in East China Sea. Clay mineral contents of 99MAP-P63 are abundant in order of illite, chlorite, kaolinite, and smectite. The provenance of 99MAP-P63 sediments using clay minerals is interpreted as the Changjiang regardless of depth. As a result of Rare Earth Elements analysis, 99MAP-P63 sediments are very similar to Chinese rivers sediments. Therefore, the provenance of 99MAP-P63 is Changjiang, and the influence of Korean river seems to be insignificant. 99MAP-P63 sediments are generally classified as sandy silt, but the top of the core is divided into sand with a sand contents of 85%. Compared with surrounding cores, sandy silt sediments are corresponded to the low stand stage when sea-level was low, and the sediments were thought to have been supplied directly through the paleo-Changjiang. Sandy sediments in uppermost of core are corresponded to transgressive stage. Although distance from estuary was increased due to sea-level rise, it was possible to supply coarse sediments due to high bottom stress, and the paleo-Changjiang sediments deposited in study area were re-deposited.

Clay Mineralogy of 420 Mud Volcano in the Beaufort Sea, Arctic

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Mud volcano (MV) is one of the methane release pathways and affects global warming. Clay minerals, a major component of mud sediments, are expected to provide important information for characterizing MV formation mechanisms, but clay mineralogy of MV has not been well known. The purpose of this study is to investigate the characteristics of 420 Mud Volcano (420 MV) in the Beaufort Sea, Arctic and surrounding marine sediments and to investigate the correlation between the composition of clay minerals and apply the formation of 420 MV. Clay minerals and grain size were analyzed for 8 box cores from 420 MV and Mackenzie trough. The relative proportions of the four major clay minerals in the Mackenzie trough are almost constant in the order of illite, chlorite, kaolinite, and smectite, regardless of the distance from the Mackenzie River. However, the grain size tends to become fining as they move away from the Mackenzie River. Comparing the clay minerals characteristics of rivers (Colville River, Kuparuk River, Sagavanirktok River, Canning River, Mackenzie River) sediments entering the Beaufort Sea in order to determine the origin of the Mackenzie trough sediments, the sediments of the Mackenzie trough are characterized mainly by the Mackenzie River with a low ratio of smectite/illite and a high ratio of kaolinite/chlorite. In 420 MV sediments, the contents of clay minerals decrease in the order of illite, kaolinite, chlorite, and smectite, and the grain size according to depth is almost constant. The content of smectite and coarse sediments is about two times higher than the reference core. No river with higher kaolinite content than chlorite exists in the Beaufort Sea, and the ratio of smectite/illite to kaolinite/chlorite is different from the reference core such as the ratio of the Mackenzie River. The higher contents of coarse sediments compared to the reference core and little variation of grain size with depth imply that 420 MV sediments are affected due to ejection by mud volcano.

Injectable Drug Delivery System with an Anionic Clay for Chemotherapy

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In the last 20 years, we have focused on new gene and drug delivery systems based on inorganic nano-vectors for chemotherapy. In the present study, an attempt has been made to design a drug-inorganic hybrid drug delivery system with high colloidal property. In order to realize such a colloidal drug, an anticancer agent (pemetrexate; PMX), was immobilized in the interlayer space of layered double hydroxide (LDH) by co-precipitation and hydrothermal methods. According to the X-ray diffraction, molecular spectroscopy and thermogravimetry analyses, the PMX molecules were stabilized inbetween the LDH sheets by electrostatic interaction, maintaining their functionality and structural integrity. From the SEM and DLS results, we found that the colloidal PMX-LDH particles were evenly dispersed with an average size of about 100 nm depending on the hydrothermal treatment conditions. Moreover, PMX-LDH exhibited superior antitumor efficacy and significant survival benefits in xenograft tumor models. It is, therefore, concluded that the present PMX-LDH colloidal particles could be a promising injectable nanomedicine for chemotherapy due to their bio-compatibility and high therapeutic effect.

A New Challenge for Boron Neutron Capture Therapy; Clay Nanovehicle Smuggles ^{10}B Clusters into Cells

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An attempt was made to apply two-dimensional anionic clays like layered double hydroxides (LDHs) as a boron delivery carrier for boron neutron capture therapy (BNCT), which needs a sufficient amount of boron in tumor cells for its successful administration. To meet this requirement, a nanohybrid (BSH-LDH), mercaptoundecahydro-closo-dodecaborate (BSH) anionic molecules in LDH, was developed as a boron delivery system. The cellular boron content upon permeation of BSH-LDH nanoparticles (42.4 μg ^{10}B/10^{6} cells) in U87 glioblastoma cell line was found to be ~ 2000 times larger than the minimum boron requirement (~ 0.02 μg ^{10}B/10^{6} cells) for BNCT, and also orders of magnitude higher than the previous results (0.2 ~ 1.5 μg ^{10}B/10^{6} cells) by those applied with other targeting strategies, and eventually resulted in excellent neutron capture efficiency even under such low dose (30 μg ^{10}B/mL) and weak irradiation (1 x 10^{12} n/cm^{2} corresponding to 20 min) condition. According to the biodistribution studies in xenograft mice model, the tumor-to-blood ratio of BSH in the BSH-LDH-treated-group was found to be 4.4-fold higher than that in the intact BSH treated one in 2 hours after drug treatment. The present BNCT combined with boron delivery system could provide a promising integrative therapeutic platform for cancer treatment.

Effect of compaction induced anisotropy on the swelling pressure development of a natural Ca-saponite

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The natural mineral deposits in the well-known Westerwald clay mining area predominantly consist of altered basaltic tuff and volcanic ashes. A recent precise characterization of the mineral deposit revealed that the altered volcanic material has been transformed into bentonites with smectite contents up to 90%. Natural calcium saponite was found to be the dominant smectite mineral in the bentonite. Saponite is a mineral of the smectite group, were Brucite (Magnesium in octahedral coordination) is the octahedral sheet of the layer.

In contrast to the lower performance of the Westerwald calcium saponite in swell index tests showing low sedimentation volume, compacted samples at medium and high dry densities developed high swelling pressures from about 5 MPa at 1.5 Mg/m^3 dry density up to 17.5 MPa at 1.84 Mg/m^3 dry density in constant volume swelling pressure tests. Therefore, Westerwald calcium saponite is actually used in briquette form (named Secursol® UHP) in the frame of applied research studies related to mining industry and underground nuclear waste repositories. In the past, usually natural bentonites with montmorillonites (Gibbsite as octahedral sheet; Aluminum in octahedral coordination) were considered to be used in these applications, for example calcium-bentonite from Bavaria (Germany) or sodium-bentonite from Wyoming (US).

The present study presents a characterization of the Westerwald calcium saponite in terms of geotechnical and physico-chemical properties. Grain size distribution, Atterberg limits, specific surface area, and cation exchange capacity are determined. Swelling pressure of compacted samples and permeability of compacted saturated samples are measured using a high pressure oedometer cell.

Main focus is on the effect of compaction density and compaction induced anisotropy on the hydromechanical behavior. For this, constant volume swelling pressure and permeability tests are performed on samples compacted parallel and perpendicular to the testing direction. The initial and final pore-size distribution is measured using mercury intrusion porosimetry.

Excavation damaged zone in Opalinus clay induced by mechanized tunneling

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For the design of a robust and economical tunnel support, the coupled hydro-mechanical interactions between the soil, grout mortar and lining system should be well understood. In this coupled system, the response of the tunnel structure against the pressure can change the stress distribution. This issue becomes more and more critical when the tunneling in over-consolidated clay rocks with the potential of swelling is in the focus. This type of clay rocks often have jointed structures with discontinuities. Due to the tunnel excavation, stress redistribution and dilation take place around the tunnel which leads to the formation of the so called Excavation Damaged Zone (EDZ) in the vicinity of the tunnel. Due to the higher permeability of clay rock in the EDZ, it acts as a preferential flow path to transport water from saturated layers to the surrounding of the tunnel in longitudinal direction. Accordingly, the degree of saturation increases with time which results in the swelling of the clay rock. Due to such swelling, the pressure that acts at the tunnel evolves with time that affects the size and shape of the EDZ, as well. Recently, mechanized tunneling is considered as an appropriate method to excavate tunnels in clay rocks with the potential of swelling (e.g. Belchen tunnel in Switzerland).

The formation of the excavation damaged zone significantly depends on the geometry of the tunnel (e.g. tunnel diameter), the method of the tunnel excavation, type of clay rock as well as the physical (i.e. bedding plane angle) and mechanical properties (i.e. K_0) of Clay rock. In this study, the time dependent variation of the size and shape of the EDZ due to mechanized tunneling in Opalinus Clay during the excavation and in long time is in the focus. Taking into account the details of mechanized tunneling, the boundary condition at the tunnel varies at different stages of the excavation that has direct influence on the shape and size of EDZ in the overconsolidated clay rock. To address this issue, a series of 2D numerical analyses have been conducted in which the constitutive parameters are calibrated in accordance with laboratory test results for Opalinus clay from literature. Afterwards, the evolution of the shape of the EDZ has been studies during the tunnel excavation. Finally, the influence of the time dependent swelling of Opalinus clay on the EDZ is investigated and the results are presented.

Rheological properties of trioctahedral smectite and sepiolite suspensions after dynamic aging at High Temperatures

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Bentonites and sepiolites are used in the formulation of drilling fluids because they form stable and viscous suspensions. However, the rheological properties of the bentonite and sepiolite fluids are affected by temperature. This study examines the influence of temperature on the rheological behavior of sepiolites (Spain and Greece) and bentonites consisting of hectorite (Hector, CA), saponite (Spain) and stevensite (Morocco). The quantitative bulk mineralogy of the samples was determined by X-Ray Diffraction (XRD) using the Rietveld approach (Autoquan® software). K-saturation followed by ethylene glycol solvation was used to determine the layer charge of the smectites (Christidis & Eberl, 2003) [1]. The dynamic aging method was applied to identify the influence of temperature on the rheological properties of the bentonites. Hence, 5% suspensions were subjected to temperatures 25 - 230°C under continuous rolling for 16 h. After cooling at room temperature, the rheological properties of the bentonite suspensions (apparent viscosity, plastic viscosity and yield point) were determined with a Grace-M3500 viscometer. The filtrate properties of the suspensions after dynamic aging were determined with an API standard filter press at room temperature.

The three bentonites contain 50% hectorite, 87% saponite and 93% stevensite respectively. The Greek and Spanish sepiolite samples contain 94% and 78 % sepiolite respectively, with the latter containing also 10% saponite. Hectorite has layer charge 0.39 e/huc, saponite 0.43 e/huc and stevensite 0.25 e/huc, i.e., they may be characterized as low charge (stevensite and hectorite) and intermediate charge (saponite). All smectites dehydroxylate at ~800°C forming enstatite. Therefore the temperatures encountered in the drilling well will not cause dehydroxylation of smectites. The rheological properties of the different bentonites and the sepiolites varied between broad limits. In addition, temperature significantly affected the rheological and filtrate properties of the suspensions. Only hectorite developed high viscosity, whereas the remaining smectites and the sepiolites did not yield acceptable drilling fluids. The hectorite suspensions displayed a pseudolastic behavior and were fitted to the Herschel Bulkley model. The apparent and plastic viscosity gradually increased with increasing temperature up to 149°C decreasing at higher temperatures. In addition, the yield point and the filtrate loss also varied between broad limits and increased with increasing temperature. The stevensite suspension developed very high viscosity at 230 °C, which decreased at high shear rates. Only hectorite might form drilling fluids with acceptable rheological properties at high temperature.

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Effect of layer charge and charge distribution on the formation of smectite-chitosan nanocomposites

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Intercalation of organic compounds in smectites yields nanocomposites which have attracted intense research interest because they are high added value materials which find novel applications in a variety of uses. Chitosan based nanocomposites display structural and functional properties which if combined with the biocompatibility and biodegradability of the biopolymer they may be of great interest in nutrition, cosmetics, water treatment, tissue engineering and drug delivery among other purposes [1]. In the present study, SAz-1 (high charge) and SWy-1 (low charge) montmorillonites, SBId-1 (low charge) beidellite and NAu-1 (high charge) nontronite obtained from the Source Clays Repository of the CMS, were selected based on their layer charge magnitude and charge distribution. The samples were classified according to the layer charge of the smectites, according to Christidis et al. (2006) [2]. Chitosan based nanocomposites were prepared with the addition of chitosan solutions to < 2μm homoionic Na^+ - smectite clay fractions to obtain nanocomposites with initial chitosan-smectite ratios of 0.25:1, 0.5:1, 1:1, 2:1, 5:1 and 10:1 respectively. The nanocomposites were examined by XRD. In addition, adsorption isotherms of the chitosan-smectite nanocomposites were prepared.

The intercalation of chitosan in the smectite interlayer was monitored by the migration of the 001 diffraction maximum towards lower angles and was characterized by decrease in the intensity of the basal reflections with increasing chitosan-clay ratio. At low chitosan loadings SAz-1 displayed highest (15.4 Å) and SWy-1 lowest d_{001} spacing (13.2 Å) with the beidellite and nontronite displaying intermediate d_{001} spacings (~15 Å). At high chitosan loadings SWy-1 displayed maximum d001-spacing (21.2 Å), whereas the intercalation in SAz-1 was barely modified (d_{001}=15.9 Å). Tetrahedral substitution led to a broad basal reflection with two diffraction maxima at 15.4 and 19 Å due to inhomogeneous chitosan intercalation in beidellite and nontronite layers, whereas homogeneous intercalation was observed for low- and high- charge montmorillonites. The XRD results are in accordance with the adsorption isotherms of chitosan on the different smectites.

Acknowledgements: E.K. thanks the State Scholarships Foundation (IKY) for the financial support through the ''Reinforcement of Postdoctoral Researchers'' (MIS 5001552) programme, OP ''Human Resources Development, Education and Lifelong Learning'', co-funded by the ESF and the Greek Public Sector.

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Surface Plasmon Resonance investigation of clay and organo-clay film formation on Au/water interface

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Hybrid organic–inorganic films are extensively studied for their potential use in a variety of advanced industrial and technological applications. Clay minerals and especially smectites, are widely used for the preparation of functional nanofilms [1] because of their excellent intrinsic properties. Functional molecules, such as alkylammonium surfactants, may be adsorbed on the clay mineral surfaces prior or subsequent to the film formation, leading to well-designed functional clay films [1].

Surface Plasmon Resonance (SPR) is a surface oriented method for the characterization of thin films and monitoring processes at metal interfaces, which has been used to investigate film formation and structural changes of clay minerals [2]. SAz-1 (high charge) and STx-1b (intermediate charge) montmorillonites obtained from the Source Clays Repository of the CMS were selected based on their layer charge and SPR was employed for the in-situ investigation of film formation from clay minerals aqueous dispersions on Au/water interface.

Both smectites adhere on the gold surfaces irreversibly producing stable clay films. Layer charge and charge distribution seems to affect the kinetics of film formation but also the total amount of clay adhered on the gold substrate. The kinetics adhesion is mainly controlled by concentration for both clays and clay film formation is dominated by the layer charge of the different clay minerals which affect the total adsorbed amount of clay on the gold substrate.

After the formation of stable clay films, hybrid organo-clay films were in-situ prepared with the introduction of alkylammonium chains in the SPR cell and their adsorption kinetics was examined. Alkylammonium molecules adsorb via ion exchange in the interlayer of clay minerals and the adsorption is controlled by the density of the clay film in full accordance with layer charge and charge localization. Therefore, a new method to construct hybrid organo-clay functional films for novel applications is proposed.

Acknowledgements: E.K. thanks the State Scholarships Foundation (IKY) for the financial support through the ''Reinforcement of Postdoctoral Researchers'' (MIS 5001552) programme, OP ''Human Resources Development, Education and Lifelong Learning'', co-funded by the ESF and the Greek Public Sector.

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Reactions on clay surfaces monitored by infrared spectroscopy

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Near-infrared spectroscopy (NIR) is a vibrational technique recording the combination and overtone modes of matter in the 12000-4000 cm^{-1} range. NIR yields the spectrum of the O-H (also, N-H, C-H) species in clays and clay-based samples without interference from the vibrations of the anhydrous part of the framework or the accessory phases that can be present in real-world samples. The extinction coefficients of the higher order modes are lower than in the mid-infrared, therefore no sample dilution is needed. NIR spectra can be acquired in the diffuse reflectance mode, non-invasively (directly or through clear glass), via optical fibers, integrating spheres, or remotely, and many sampling arrangements can easily accommodate temperature or relative humidity (H_2O, D_2O) as variables. Modern FT-NIR spectrometers offer fast acquisition (<1 min for a 100 scan spectrum), highly wavenumber accuracy (~0.1 cm^{-1}), high optical resolution (e.g. 4 cm^{-1}) and excellent long term stability (several days). NIR spectroscopy is, perhaps, the least invasive structural technique, suitable for the real-time monitoring of chemical processes of powdered samples.

The self-assembly of organics on clay surfaces is conveniently monitored because the diagnostic bands of O-H and C-H (or N-H) are observed in well distinguished spectral windows. Moreover, activity in the NIR (hence, band intensity) depends on anharmonicity which is damped when the X-H groups are involved in extensive H-bonded networks. Therefore, dangling X-H bonds are easily distinguished against the broad features of H-bonded liquids or solids, especially by 2nd derivative analysis.

This presentation introduces the field and highlights relevant research that was performed at TPCI/NHRF and dealt with the NIR monitoring of heterogeneous gas-solid, liquid-solid and solid-solid reactions on three types of clay minerals: montmorillonite, palygorskite and kaolinite.

This work was supported by project "Advanced Materials and Devices" (MIS 5002409) of TPCI-NHRF, funded by the Operational Program "Competitiveness, Entrepreneurship and Innovation" and co-financed by Greece and the European Union.

Effects of additions of organic matter or clays on carbon retention in soils

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The adsorption and retention of organic matter on clay minerals in soils is key to assessing the possibility of the sequestration of extra carbon (C) from atmospheric CO_2 in the soils. Clay minerals in soils differ from those in pure deposits, so we have studied only the clays extracted from soils by a physical method. We studied a soil rich in kaolinite and illite, one rich in smectite, and one that is rich in allophane. Dissolved organic carbon (DOC) from wheat straw was adsorbed on the clays from each of the soils without pre-treatment, and also after pre-treatments to remove, firstly, native C, and secondly, native C plus metal oxides. Following each pre-treatment, the order of adsorption of DOC was allophane>> smectite> kaolinite-illite. For each clay mineral, DOC adsorption was highest with removal of C alone and lowest with removal of both C and metal oxides. The decrease in uptake of DOC upon their removal indicates that metal oxides are strong adsorbents of DOC. The increase in DOC uptake after the removal of native organic C indicates that this occupied adsorption sites on the clay minerals.

When ^{14}C-labelled malic acid was added as a ready source of organic matter, all soils (untreated) showed a priming effect on the respiration of $CO_{2.}$ After addition of malic acid, substantially more native C was lost from the smectitic soil than from both the allophanic soil, and the kaolinitic-illitic soil, which sustained similar losses. The strong effect of priming on native C in the smectitic soil indicates that the minerals (2:1 and 1:1) offer little protection to predation of carbon by microbes, which are stimulated by the added malic acid. The lesser effect of priming on the allophanic soil, indicating protection by allophane, was expected. A similar extent of protection of organic C in the kaolinitic-illitic soil was unexpected, but consistent with strong microaggregation in this soil. Regarding prospects for sequestration of C, the results from priming suggest that simple addition of labile organic matter to soils may result in a decrease, rather than an increase, in the content of organic C. They further suggest that a high clay content (as in the smectitic soil) does not predict the capacity of a soil to retain C against predation by microbes. Furthermore, strong microaggregation helps protect organic C from predation.

Addition of (mainly kaolinitic) clay to sandy soils, often from within the profile, to cure non-wetting, led to an increase in organic C. Addition of bentonite clay to other sandy soils led to greatly increased crop growth, but addition of compost had no effect.

From the literature, organic matter in soils is closely associated with clays, but only limited areas of mineral surfaces of soils are available for the uptake of organic matter. The available surfaces are characterised as rough and may constitute micropores. The mineral surfaces are 'deserts', largely devoid of organic matter (OM).

When simply added to soils, OM may not be retained but instead provide energy for microbes to degrade native OM. World-wide, sequestration of C is most promising on sandy soils and would be aided by additions of clays, internally, or from or other (e.g. industrial) sources.

Kaolinite-Fe-TiO_2 composites as potential photocatalysts for acetylsalicylic acid removal

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Acetylsalicylic acid (ASA) can degrade in aqueous media into several potentially toxic intermediates causing environmental pollution, so its removal is mandatory. Photocatalysis is very promising for purification and degradation of pharmaceutical pollutants. In this work, a natural Brazilian kaolinite was used to synthesize a composite with $FeCl_3$ and Ti(IV) isopropoxide *via* a sol–gel route. Kaolinite (10.0 g), ethanol (200 cm^3), acetic acid (1 cm^3), and Ti(IV) isopropoxide (2.0 cm^3) were mixed at room temperature in a beaker, and stirred for 24 h. The obtained solid was dried at 100ºC for 24 h and split into four fractions: one was used as dried, and the other three were heated in air at 400, 700, and 1000ºC, respectively. The powder X-ray diffractogram and the infrared spectrum showed that kaolinite was very pure. The treatment with Ti(IV) isopropoxide and $FeCl_3$ did not produce any change in the basal spacing of clay (7.14 Å); actually, due to the difficult swelling of this clay mineral, the direct insertion of the alkoxide into the interlayer region of kaolinite was not expected. On calcination, anatase phase began to be formed at 700ºC; at 1000ºC anatase was formed, kaolinite was amorphized and finally it transformed into metakaolinite. The characteristic peaks of anatase are very close to those from kaolinite, which makes the analysis difficult. Comparison of data obtained with the material prepared in the absence of iron ions, under the same conditions, provided new insights, suggesting that the presence of iron delayed the formation of the anatase phase. The infrared absorption spectra of the sample calcined at 700ºC showed the appearance of two bands typical of Fe-O and Fe-O-Ti at 463 and 660 cm^{-1}. This suggests that functionalization occurred at the lateral silanol and aluminol groups of the kaolinite. The UV-Vis spectra of this same sample also presented some evidences of the transformation of kaolinite into metakaolinite, as a broadening of the band recorded in the region characteristic of the anatase phase, while the band at 482 nm was attributed to Fe-Fe interactions or iron substitution in the anatase structure. The degradation of ASA was studied in the presence of light using kaolinite-iron titanium catalysts calcined from 400 to 1000°C. Intermediate products formed before complete demineralization of ASA were analyzed by HPLC, infrared and UV-Vis spectroscopies. The presence of Fe ions in the catalyst proved to be essential to increase the efficiency of the catalysts. The kaolinite-Fe-TiO_2 nanocomposite promoted the interaction of the ASA molecules with the surface of the solid and the TiO_2 dispersed in the matrix promoted the generation of highly reactive OH• radicals.

Acknowledgments: FAPESP and USAL (2016/50322-2). MINECO and ERDF (MAT2016-78863-C2-R), FAPESP (2016/01501-1), CNPq (305398/2015-6). CAPES (Finance Code 001).

Multi-component reactive transport in a claystone: Insights from a ten-year alkaline in situ injection experiment

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In the 90's, early calculations based on mass balance assumptions only, and reported in Gaucher and Blanc (2006) and Savage et al. (2007), led to the conclusion that 0.2-1 m^3 of bentonite are needed to buffer the chemical perturbation created by 1 m^3 of concrete. If true, this conclusion would have been problematic for the storage concepts that rely on the properties of unaltered clay materials, and this explains why so much effort has been put in reactive transport modeling studies of the long-term evolution of clay-concrete interfaces. Recently this effort has been reviewed with a focus on large-scale simulations at the repository gallery scale (Claret et al., 2018). None of the reviewed studies considered the presence of species dependent diffusion coefficients (multi-component diffusion or MCD) and the presence of a diffuse layer in clayey and cementious materials. The consideration of MCD and of the presence of a diffuse layer is indeed computationally expansive, and few reactive transport codes are capable of handling it. Moreover, the parametrization of such a model must rely on preliminary models of relevant dataset. In this framework, a ten year *in situ* experiment has been operated in the Meuse Haute Marne Underground Research Laboratory, in which a high pH solution (pH~13.2) interacted with the Callovo-Oxfordian claystone. The complex evolution of the chemical composition of the test interval was modeled using CrunchClay (Steefel et al., 2015) in a cylindrical geometry with full consideration of MCD and presence of a diffuse layer in the claystone porosity. The modeling results gave insightful indications on the multi components diffusion and minerals reactivity in such a system, making possible to parameterize future simulations of the long term evolution of clay/cement interfaces.

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Clay polymer composites for sustained release antimicrobial wound dressings

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Chronic wound infections are a common healthcare problem and in particular when associated with leg, pressure and diabetic foot ulcers, which can lead to significant morbidity or even mortality. Many antimicrobial agents have been used to treat such wounds including antiseptics, disinfectants or topical and systemic antibiotics. Preference for these agents has declined due to concerns about antimicrobial efficacy and potential toxicity to wound tissue. Furthermore, routine use of antibiotics is seriously advised against because of the risk of accelerating bacterial resistance.

A clay-polymer based wound dressing material has been engineered and manufactured to deliver a sustained-release of an antimicrobial agent (iodine). It provides a significant advantage over comparative, commercial dressings in that release occurs over 5-7 days rather than within 24 hours. A self-stratifying process within the preparation can also allow for an effective two layered system enabling a faster or slower release surface.

The clay composite dressing was tested for *in vitro* activity against a range of common bacteria including *Staphylococcus Aureus, Escherichia Coli and Pseudomonas Aeruginosa*, and was found effective for up to 7 days. The test involved the transfer of the dressing between fresh bacteria-loaded agar Petri dishes, each after a 24 hour period - known as a passage test. The dressing also demonstrated effectiveness against two strains of hospital acquired Methicillin Resistant *Staphylococcus Aureus* (MRSA) and one strain of community acquired MRSA, which are bacteria that present an ongoing challenge to the UK's National Health Service. The extended activity offers the potential to reduce healthcare costs by providing a longer wound dressing lifetime and less disruption to wound recovery occurring during dressing changes.

The influence of clay type (Na^+ bentonite, Ca^{2+} bentonite and a synthetic hectorite 'Laponite®') on the integrity of the dressings and the nature of the time/kill studies will be presented and discussed.

3D mapping of mineralogical (XRD) data: method and applications

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Mineralogical analysis of geological materials is nowadays a common procedure. At present, this approach may render thousands of datapoints in a relatively short analytical time. The processing of this information by standard procedures is time-consuming and has well-known limitations, often related to intrinsic characteristics of natural materials. Alternative approaches were therefore tested, aiming towards a more user-friendly, fast and more intuitive solutions.

Raw data extracted from diffractogram spectra were explored by means of a conversion of 2D and 3D traditional mapping, combining mineralogical (X; Y) and stratigraphic/geological information (Z). This approach was applied to 171 files resulting from XRD analysis of bulk, insoluble residue and oriented aggregates, adding up more than 400.000 datapoints corresponding to 60 samples.

To demonstrate the advantages of the 3D mapping approach, samples belonging to two Late Jurassic epicontinental sections are used, comprising shallow-water carbonates deposited in well-differentiated settings. Fast data-processing (a few minutes) lead to single-image results, which provided new insights on syn-depositional processes occurring at each site. Bulk and insoluble residue results, dominated by calcite and quartz (respectively) were combined, allowing the identification of an overall stronger continental influence that was otherwise masked under the more marine character of some portions of the studied sections. Additionally, clear variations in clay mineral assemblage were depicted at critical times of relative changes in sea-level trend.

The proposed method offers speed, clarity, adaptability, providing single-image solutions for the representation of large datasets, with multiple applications to fields of geosciences, from outcrop to subsurface data covering recent to ancient times and settings.

Layered Double Hydroxides and their nanohybrids: characterization, biocompatibility, and biological activities

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Layered Double Hydroxides (LDH) are exciting materials to be explored in nanomedicine area as drug delivery systems. Hybrid nanoparticles comprising a carrier of bioactive species show interesting advantages: preservation of drug concentration in the body within the therapeutic range, drug delivery on a site-specific target, increase of the therapeutic drug efficiency with the administration of smaller doses, reduction of side effects, significant intensification on drug chemical stability, solubility, and penetration into cell membranes.

Main steps to address studies about biomaterials require *(i)* materials characterization by chemical, structural, thermal, spectroscopic and textural analyses among others, *(ii)* biocompatibility investigation *via* cell viability and tissue histopathology for example, and (iii) therapeutic effectiveness evaluation through *in vitro* and *in vivo* assays.

This presentation will focus on these main steps regarding studies about LDH shared in the literature and experiments conducted by our research group and collaborator laboratories. Data reported up to now point out important results and demonstrate that LDH are promising materials for health application.

Acknowledgements: Brazilian agencies Fapesp, CNPq and Capes.

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Simultaneous exfoliation and functionalization of montmorillonite clay via high speed mechanical milling

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Traditional applications of clays in the Philippines are as building material, ceramics such as pottery and whiteware, and as planting crop medium. Clays can be further utilized in one of the potential industries in the Philippines – the cosmetics industry. However, most of the raw materials utilized by local cosmetic brands are not locally resourced. Moreover, cosmetics in the Philippines is prospective with the use of naturally occurring raw materials and the continuation of clay research.

This study aimed to investigate the effect of varying the mechanical milling parameters on the exfoliation and functionalization of local montmorillonite clay samples for cosmetic application. Montmorillonite clay samples in triplicates were functionalized using 0.25% cetrimonium bromide (CTAB) as the functionalizing agent which also exhibits antimicrobial properties. Degree of exfoliation due to mechanical milling was then characterized using XRD analysis. Moreover, the samples were characterized to determine their microstructure, size distribution, and degree of exfoliation. There was a decrease in particle size.

Mineralogy of indoor dust collected from households in urban and peri-urban areas of Estarreja, and industrial Portuguese city

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This study focuses on data obtained from a pilot survey that was designed to assess the health impact of potentially toxic elements (PTEs) in household dust collected from private homes in Estarreja, a Portuguese industrial city. The study aims at assessing differences in the mineralogy of dust samples collected indoors and outdoors. A total of 21 households were recruited for the study and a self-administered questionnaire was provided to the residents. By filling the questionnaire, the participants were asked to characterize the general conditions of the physical environment of the house. Ethical approval for this study was obtained from the National Committee for Data Protection (Proc. nº 1241/2013). All participants gave written, informed consent to the study.

While composite indoor dust sample was collected from different house compartments using the High Volume Small Surface Sampler (HVS3) vacuum sampler, outdoor dusts were collected from different areas outside the house with a small brush and a plastic shovel. Qualitative and semi-quantitative mineralogical analyses were carried out by X- ray diffraction (XRD) using a Philips®/PanalyticalX'Pert-Pro MPD, Kα Cu (λ = 1,5405 Å) radiation, with 0.02º 2θ s-1 steps in goniometer speed, in order to assess the main and accessory minerals, their relative proportions, check the eventual heterogeneities, and establish the mineralogical markers.

Mineralogical phases identified include various silicates and aluminosilicates, carbonates, sulphates, oxides and hydroxides. Quartz, feldspars, phyllosilicates (mainly micas) and calcite are the main minerals, accompanied by opal C/CT, dolomite, siderite, anhydrite and graphite. Some accessory minerals, such as Fe oxides-hydroxides (hematite, lepidocrocite, goethite, and magnetite-maghemite), Ti oxides (anatase), sulphates (mainly melanterite), zeolites (clinoptilolite-heulandite), and halite are relevant discriminating phases, namely between indoors and outdoors dusts. Concerning clay fractions, indoor samples are quite homogeneous being characterized by an illite + kaolinite association, some samples showing also small amounts of smectite; on the other hand, outdoor samples are less homogeneous, showing the same basic association (than indoor) but with samples much more rich in kaolinite whereas others show an increase in smectite.

Longlived organo-clay nanocomposites formed in the atmosphere by plasma discharges

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Physico-chemical processes are assumed to control the stability of bioresistant microaggregates by adsorption of organic matter on clay minerals in the soil matrix, via charge and surface properties of clay platelets. We examine here an alternative control of the stabilization pathway of soil microaggregates linked to the incorporation into the critical zone of highly stable organo-clay nanocomposites formed in the atmosphere by plasma discharges. They are shown to be regularly produced from carbon-based aerosols mixed to mineral components. Atmospheric conditions and meteorological situations favorable to their formation are documented based on a 5-year long collect of dustfalls in a pilot region of Southern France. They are shown to consist of carbonaceous films, filaments and aggregates that have been so far confused with microplastic residues of petrochemistry materials. The precursors and their properties are documented based on SEM, HRTEM, EDS, X-Ray diffraction, Raman, infrared spectroscopy and carbon isotopes. Synthesis of similar nanocomposites by experimental setups of plasma discharges at atmospheric pressure using various carbonaceous precursors (CO_2, C_2H_2, CH_4, liquid hydrocarbon) elucidates their forming mechanisms and properties. The polymer nanocomposites are also traced within the clay matrix of microaggregates in ancient soil surfaces (hundred to a few hundred thousand years).

Based on the 5-year long collect, we establish that polymer nanocomposites presently form from charged aerosols in atmospheric conditions of enhanced ionization following volcanic explosion, hyper-velocity air blast, lightning and thunderstorms. We show the similar properties of the polymer nanocomposites encountered in present-day contexts (air, water, soils) or ancient soil surfaces and the ones synthetized by laboratory plasma. Their densely reticulated, folded and twisted, nanolamellar aliphatic matrix incorporates dispersed 2D structured nanoparticles (2D-NPs). These 2D-NPs dominantly comprise clay platelets, multi-layer graphene, metallic oxides, sulfates, phosphates, and chlorides, often embedded in an amorphous carbon-based shell. Degassing under the electron beam at 200 kev of the 2D-NPs in the present-day polymer nanocomposites contrast with the stability of the ones in ancient soils and those synthetized in the lab from fossil hydrocarbon. This reactivity reveals volatile impurities trapped within the stacked 2D-NPs. The plasma experiments illustrate how densely crumpled 2D-NPs stored for long in fossil organic pools transform under ionization by plasma discharge into highly resistant nanoplatelet assemblages due to strong interfacial interactions. Miscellaneous irradiation continuously impacting organic and mineral aerosols in the atmosphere is thus concluded to form super stable organo-clay nanocomposites that accumulate at the earth surface. Understanding their role on the long lasting sequestration of carbon-rich fractions in the critical zone and on the long-term preservation of soil memories offers a challenging route for future investigations.

Unusual clay pastes of Southern Levant Chalcolithic ceramics linking exceptional meteorological events and population dispersal

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In the southern Levant, 70% of the Late Chalcolithic sites were abandoned by 3900 year BC for 300 years. Environment and/or cultural factors have been advocated to explain this major historical phenomenon. Recent data suggest a dispersal of the populations in the neighboring regions, but do not explain the desertion of regions such as the Jordan Valley or the Galilee.

In this paper, this phenomenon is revisited through an analysis of the clay pastes of ceramic assemblages from the Southern Levant dated from the beginning of the 4th millennium BC. Diverse clay pastes of various types of vessels, originating from carbonate-rich subsurface sources (water ponds) show an unusual cementation resembling overfired products. This cementation is characterized by a dense fabric obscuring clay domains and porosity of the fine mass.

The characterization of the clay pastes has been performed by SEM-EDS of ceramics from various sites with a particular focus on this unusual cementation. All these clay pastes present uncommon components: carbonaceous domains made of polymer filaments and inclusions (metals, chlorides, sulfides/sulfates, phosphides, rare earth phosphates) in the fine mass and pure metal droplets (Fe-Cr-Ni and Fe-Cr) on coarse grains. All these components are nanostructured, showing either agglomerated ultrafine nanoparticles or a 3D-assemblage of nanofilaments. The cemented zones show high amount of the uncommon components locally merging to continuous zones, in particular elongated voids filled by nanostructured barium sulfate with sulfide inclusions. Their coarse fraction also shows the occurrence of calcite grains with degassing fine vesicles.

Based on present-day database and laboratory experiments, the nanostructured carbonaceous components with the metal and volatile nanoparticles and the degassed minerals are interpreted to have formed in the atmosphere from transformation of dust-rich aerosols by plasma discharges. Their abundance in the clay paste indicates a collect of clay sources in a period marked by enhanced dust storms and heavy lightning. The occurrence of carbonaceous and metal components in the clay materials suggests that volcanism and wildfires have jointly contributed to initiate a severe meteorological disturbance due to the massive production of ionized dust. Characteristics of the dense cemented zones trace transformation of these ionized nanoparticles when the pots where fired, i.e. condensation and precipitation during cooling of the nonvolatile components.

Composition of the ionized particles suggests that the enhanced atmospheric electrification might have severely degraded the quality of air and subsurface water resources. The inhospitable conditions would have led to desertion and dispersal of populations, except in the regions that were less affected by the degradation of environmental resources.

These first results incite to consider the potential of ceramic assemblage as archives of air/water quality to refine our perception of environmental factors on living conditions of past populations.

Waste addition in brick manufacture. Improvement of the technical qualities of bricks for use in construction and restoration work

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When restoration work is carried out on historical buildings, it is important to consider the aesthetical appearance (i.e., size, color, surface finish) and physical characteristics (mechanical strength and hydric behavior, above all) of the building materials so as to ensure the solidity and durability of the structure. Recent research on brick manufacture has focused on the possible use of raw materials that contain added waste products. When bricks of this kind are used in restoration works, the presence of waste products is not harmful if the aesthetic, physical and mechanical properties of the replacement bricks are similar to those of the originals. Moreover, the reuse of waste products in this way would be beneficial for the environment. In this work, solid bricks manufactured with a raw earth from Jun (Granada, Spain) and fired at 800, 950 and 1100 ºC were compared to others to which household glass and fly ash were added in order to find out if these waste products improve the physical properties of the bricks.

Bricks with and without waste products show almost the same mineralogy after firing. Carbonates decompose before 800 ºC and new silicates develop (gehlenite, anorthite and diopside). Phyllosilicates dehydroxylate and the proportion of quartz falls because the edges of this mineral react with the carbonates to form Ca- (and Mg-) silicates. As expected, the amount of amorphous phase is higher in bricks with added glass. The main differences between the bricks were observed in the physical tests. The bricks with fly ash have the highest water absorption values, while the bricks with glass are the least absorbent. The degree of pore interconnection decreases in all bricks as firing temperature rises, above all in those with added glass fired at 1100 ºC. The reduction of pore interconnectivity reduces the capacity of samples to dry quickly. The most porous bricks were those made with fly ash. Ultrasound tests revealed that the bricks without additives were generally the most compact, except at the highest temperature when bricks with added glass reached the highest P-waves velocity values and the total anisotropy decreased noticeably compared to the other samples and firing temperatures. The bricks made with added glass proved the most resistant to microdrilling (above all those fired at 1100 ºC), followed by the bricks without additives.

In general, the most suitable bricks for construction or restoration work are those made with added household glass.

Acknowledgements: The Research Project MAT2016-75889-R of the Spanish Government financed this work.

A general orientation distribution function for clay particles

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The preferential orientation of clay particles, owing to their lamellar shapes, has considerable impact on macroscopic properties of the porous medium such as fluids transfer in the pore network or mechanical properties of the solid. This preferred orientation associated with nanometre-sized porosity result in low permeability values having significant effect on the development of oil, gas, or water reservoirs and further explain they use as natural barrier for CO_2 capture and nuclear waste storage. Anisotropy in particle orientation is commonly studied through the analysis of the orientation distribution function (ODF). The shape of the experimental ODF is then most often approximated by considering conventional orientation distribution models (such as Gaussian, Lorentzian, Bingham/Maier-Saupe, etc …). However these analyses are restricted to a limited number of clay minerals, and/or preparation method, and/or applied to a narrow range of anisotropy. To date no conventional distribution model was shown to be appropriate for a large set of data covering different structure and organisation of clay minerals.

In this study monomineralic clay porous media were prepared on the basis of different types of clay minerals (kaolinite, mica, vermiculite, and smectite) and preparation methods (compaction, sedimentation, and centrifugation). Experimental ODF were obtained using 2D X-ray diffraction in transmission mode and by azimuthal [0, π] angular scan of the 2D scattering patterns on the 001 reflection. Analysis of orientational order parameters describing the experimental ODF evidenced a distinct signature for all types of clay minerals or preparation procedure and revealed the limitations of conventional distribution models. Based on the maximum entropy method a new distribution function is proposed which allows reproducing the whole set of data. This distribution model is based on a single variable parameter satisfactory reproducing the full shape of the experimental ODF. Finally, the obtained general ODF was successfully applied to the analysis of anisotropy in particle orientation in different natural and complex clay-rich media, i.e., a soil, a shale and a schist.

Unravelling reactive transfer of organic molecules in clays

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Understanding the mobility of organic compounds in environment constitutes a key issue in many fields, e.g. petrochemistry, water treatment, industrial wastes management… In the past decade, the reactive transport of many organic molecules has been investigated in clays in the framework of geological repositories for radioactive waste [1]. These studies aimed to quantify the diffusion and sorption properties of specific organic compounds in order to (i) identify the fundamental processes involved for ionisable sorbates, (ii) provide generic models linking transfer parameters (notably K_d values) and the chemical properties of organic molecules. An important work has been achieved for the indurated Callovo-Oxfordian clay-rich rock (COx) (east part of the Paris basin). Correlations were quantified between sorption, sorbent composition (content of clay, oxides, or natural organic matter), and the structure of sorbates (Brönsted acidity, dipolar moment) [2].

In order to challenge, validate and extend our approach, we have investigated the reactive transfer of ionisable and neutral organic compounds in the soft *tégulines* clays (east part of the Paris basin, Fig. 1). The poster will detail the overall methodology allowing the study of reactive transfer of organic molecules in clays and propose a generic model predicting the sorption properties of organics depending of the clay-materials properties and the nature of the organic molecules. Effects of the microstructural organization on sorption properties will be discussed.

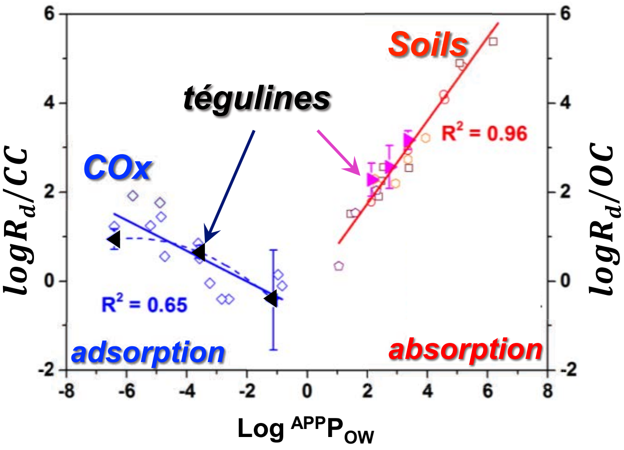

Figure 1. Sorption of organic molecules as a function of apparent octanol water partition coefficient: $^{APP}P_{OW}$. Values normalized by natural organic content (right ordinate) or clay content (left ordinate) in the sorbent.

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Effect of pressure on the adsorption on nucleotides on clays – would this favor the emergence of life on the Hadean ocean floor?

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It has been emphasized that life could actually have arisen in subsurface environments such as hydrothermal vents or subduction trenches. During the Earth infancy in the Hadean and Archean times, continents and a large proto-ocean were already present. The ocean in the early Archean had a much larger extent than at present day and high-pressure habitats (>10 MPa) covered more than 2/3 of the Archean Earth's surface. The early Ocean flooded the oceanic crust and the margins as today, as well as most of the continental crust unlike at present day. The emerged continents covered less than 1/10 of the Earth' surface. The oceanic seafloor was under a mean pressure of ca. 40 MPa. Active hydrothermal alteration of the ultramafic seafloor (komatiites) could have generated a flux of molecular hydrogen in the Hadean approximately orders of magnitude larger than at present day, and abundant magnesium- and iron-rich clay minerals. Such conditions include a source of energy, thermodynamic conditions favourable to the synthesis of the building blocks of life and metabolites (e.g. Shock & Canovas, 2010), and mineral surfaces that could have served both as a catalyst and a template for 'self-sustained reactions capable of undergoing Darwinian evolution' that define life (e.g., review by Cleaves et al. 2012). Unlike the favourable situation for amino acids, data are much more limited for nucleotides and their spontaneous condensation on mineral surfaces has not yet reached the required level for polymerization under ambient pressure condition. As the formation of the peptide and phosphodiester bonds would release water, they should be favoured under low water activity. Such conditions can be achieved in natural environments either subjected to dry/wet cycles, or with high salinity, or at hydrothermal vents or even deeper.

In order to evaluate the latter hypothesis, we have developed hydrothermal reactors optimized and dedicated to adsorption measurements up to 140 MPa and 120°C. We have first tested the stability of nucleotides and minerals under such conditions. Nucleotides are stable for 48 hrs at least below 100°C, and our targeted clay, namely nontronite doesn't show any detectable dissolution. Our first results tend to indicate that the adsorption of deoxyguanosine monophosphate (dGMP) onto nontronite is favoured at moderate temperature and pressure of 35 MPa or higher and will be presented with our newest results.

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Structural evolution of textured phyllosilicate materials probed by in situ high temperature X-ray diffraction

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The use of phyllosilicates is well established in the field of traditional ceramics. Since, most of such raw materials are readily available. Regarding sustainability issues, and physical and mechanical characteristics of phyllosilicates, a renewed interest is growing for their use in order to produce innovative technical ceramics. The phyllosilicates raw materials are polycrystalline materials that contain many mineralogical phases, which makes their structural analysis quite difficult. The present work aims at studying by in situ high temperature X-ray diffraction the evolution of the initial texture and structure of 1:1 phyllosilicates.

The raw phyllosilicate materials used in this work are a kaolin (KRG) and an halloysite (H) containing particles with platelet-like and tubular-like shapes respectively. Samples are prepared from various mixtures of halloysite and kaolin (0, 50, and 100 wt. %) and shaped using tape casting.. The expected texture originates from the particles morphology of these natural raw materials and the tape casting process. SEM observations and in situ XRD analysis performed at the ESRF on the D2AM beamline have been used to evidence the preferential organization of clay particles and the structural evolution upon thermal treatments respectively.

The results show that the kaolin particles are preferentially oriented in such a way that the (00l) crystallographic planes are parallel to the casting support. On the contrary, halloysite particles are less oriented. The dehydroxylation occurs in the range 475-650 °C and 500-675 °C for KRG and H respectively. During the dehydroxylation, the particles size of kaolinite decreases, but the starting texture is kept. However, the particles size of halloysite increases between 20°C and 300°C, and decreases in the interval of 300°C - 675°C, this is probably due to the shape changes of the halloysite tubes. The starting temperature of mullite crystallization is about 1100 °C for the kaolin and 1075 °C for the halloysite. Isothermal treatment at 1225 °C induces simultaneously an increase of the amount of mullite and a variation of the relative intensity of the (120) and (210) diffraction peaks of mullite. This last behavior is more pronounced for KRG than for H, and is relevant to a time-dependent stoichiometry of mullite in the beginning of the crystallization.

Key words: texture, phyllosilicates, tape-casting, in situ high temperature X-ray diffraction, synchrotron.

Acknowledgments

The authors would like to thank N. Boudet and S. Arnaud for assistance during the XRD measurements at high temperature on the D2AM beamline. The European Synchrotron Radiation Facility is gratefully acknowledged for the beamtime.

Clay-based bionanocomposites for controlled delivery of neuroprotective drugs in the treatment of Alzheimer's disease

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Clay-based bionanocomposites are suitable carriers for the controlled delivery of drugs in order to facilitate their oral administration (Alcântara and Darder, 2018). In the current work, bionanocomposites were prepared by adsorption of two 7-azaindole derivatives with different substitution at position 5 (-OCH_3, -H) on the layered clay montmorillonite (MMT) and the tubular one halloysite (HNT), followed by encapsulation of the resulting hybrid materials in an alginate-zein matrix and its processing as microbeads. Both 7-azaindole derivatives show an interesting neuroprotective profile in several in vitro models of neurodegeneration and seem promising for the treatment of Alzheimer's disease (Lajarín-Cuesta et al., 2018).

Their intercalation in MMT was confirmed by X-ray diffraction, giving rise to basal space values around 1.9-2.0 nm in the hybrid materials, and the amount of entrapped drug was determined to be around 31-36 g per 100 g of MMT. In the HNT-based hybrids, the drug uptake was around 15-21 g per 100 g of HNT when the adsorption was carried out at alkaline pH values close to 10, most likely favored by the neutral charge of the drugs under these conditions. The resulting hybrid systems are no cytotoxic, as confirmed from studies carried out in cultures of human neuroblastoma cells, and showed a similar neuroprotective effect against okadaic acid, the inhibitor of the protein phosphatase 2A (PP2A). The drug release in liquid media that simulate the gastrointestinal tract was previously evaluated using the 7-azaindole derivative/clay hybrid systems, but the MMT systems showed a strong retention of the intercalated drugs, while the HNT materials showed a rapid release of the drugs. Thus, the encapsulation of the hybrid materials in a biopolymer matrix composed of alginate and zein was required in order to optimize the release from the HNT systems. The gelation ability of alginate facilitates the processing of the bionanocomposites as microbeads, while zein reduces the hydrophilicity of the system, resulting in a gradual and controlled delivery of the adsorbed neuroprotective drugs.

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Hydration behavior by X-ray diffraction profile fitting of smectite-bearing minerals in a Plio-Pleistocene mudrock from Eugene Island, Gulf of Mexico

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The clay mineral hydration process is reversible at temperatures <100 °C and strongly affect wellbore stability, fines migration, permeability, and pore pressure dispersion. The hydration behavior of smectite-rich material as a function of relative humidity (activity of water, a_w, controlled by salinity) and temperature was studied using *in situ* X-ray diffraction on a material retrieved from coring in the Gulf of Mexico. X-ray diffraction profile fitting was used to explore the competition for water between hydratable phases across a range of relative humidity, 2% to 90%, and temperature, 25 °C to 95 °C, conditions. X-ray diffraction profile fitting of Eugene Island region material employed a modified multi-specimen approach in which proportions of minerals were modelled using Ca-exchanged preparations in air-dried and ethylene glycol solvated states. Across the range of hydration states, the mineral proportions and crystallographic parameters remained constant from the multi-specimen approach and only the number of water layers in hydratable phases varied. Quantitative clay mineralogy of Eugene Island region, Gulf of Mexico, sourced material showed a natural material with a discrete smectite component and a mixed-layered illite-smectite, both capable of hydration/dehydration. A sample from the Jurassic Haynesville Formation was used as a control sample to reflect high thermal and diagenetic maturity. This illite dominated sample had no hydration/dehydration behavior with changes in relative humidity and temperature. Results of this study predict that changes in pore water salinity, represented by variable relative humdity or a_w, could also be a viable mechanism in smectite rich mudrocks for generating overpressures in mud-rich sediments during early burial where the degree of overpressure is controlled by the total sedimentation rate, the ratio of permeability to compressibility, and time.

Study of the interaction between clays and alkali-activated slag's hydrates in stabilized poured earth concrete

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The main benefit of earth construction is its ability to narrow and regulate heat and humidity flow with the outside environment, especially thanks to its capacity to exchange water in both liquid and gaseous states. Nonetheless, clays are a weak and unstable binder, thus it's needful to stabilize them with a stronger one, such as cement, but this kind of reinforcement leads to a decrease of thermal capabilities. Stabilization by alkali-activation could be an alternative to cement, improving mechanical strength, stability to water and maintaining thermal capabilities and ecological benefit of poured earth concrete.

In this study, blast furnace slag and sodium hydroxide solutions are used as raw materials for alkali-binder formation and added to three natural earth samples for stabilization. Cation-exchange capacity and electrical charge density of clays play a role in both hydration and stabilization process. The aim of the study is to characterize and evaluate the interaction between clays particles of natural earth and hydrates produced during slag's hydration. First of all, sodium and calcium adsorption on clays particles surface are evaluated by direct measurement with specific ionic sensors during quenching test in four different sodium hydroxide solution in presence of slag or not. Hydrates produced in presence of clays are then characterized by thermal analysis (DTA-TGA), X-ray diffraction (XRD) and *in situ* infrared spectroscopy (FTIR) analysis to evaluate the impact of clays on slag's hydration process.

The three different earth samples tested show different sodium adsorption amounts and kinetics depending on the type and amount of clay particles present in raw earth. Hydration speed and hydrates formed are thus both impacted by clays activity in different ways depending on the mineralogical composition of natural earth. Scanning electron microscopy (SEM) observation also show that hydrates morphologies are different from those obtain with slag alone.

Finally, clays and hydrates interface is investigated mechanically with a pull-off test. This test allows to investigate if stabilization is reached by hydrates percolation or by adhesion between clays and hydrates particles. Comparison with portland cement hydrates would allow to partially understand stabilization mechanisms and why thermal behavior could be different between these two types of stabilization.

Stabilization with alkali-activated slag, by improving mechanical strength and stability to water improves the potential use of raw earth materials for sustainable construction in any kind of environment.

Tuning redox state and ionic transfers of nano-Mg/Fe-(4/2) Layered Double Hydroxides using electrochemical and gravimetrical techniques

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A layered double hydroxide (LDH) consists of a stacking of positively charged brucitic layers due to the substitution of some divalent cations M(II) with trivalent cations M(III). The charge compensation is managed by the ionic species intercalated into the interlayer spacing *i.e.* water and anions A^{n-}, leading to the general formula: $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n}).mH_2O$. As a consequence, LDHs provide a high capacity for anion exchange.

For wide applications in terms of energy storage device or water treatment, the reversibility of the ion transfer between the electrolyte and the interlayer spacing needs to be further investigated. A reversible ion transfer between the electrolyte and the LDH can be controlled by tuning the redox state of nano-LDH lamellar sheets. The low electronical conductivity performance of the LDHs is promoted by preparing thin films of LDH coated on a working electrode surface.

Only a few studies explored the reversible ion transfer phenomenon related to the cyclic oxidation/reduction of electroactive cations within the layers for the most conductive LDH (Co/Ni-LDH, Ni/Al-LDH…) by probing the mass variation with Electrochemical Quartz Crystal Microbalance (EQCM). To the best of our knowledge, no study has been conducted yet on less conductive LDH like Mg/Fe-LDH, Mg/Al/Fe-LDH, Fe/Fe-LDH.

Studying gold coated nano-Mg/Fe-LDHs particles with the EQCM technique demonstrates the "faradic related capacity of LDHs". The concomitant electrochemical control of (i) the physical and the chemical conditions at the interface, (ii) the oxidation state of the valence of iron constituting the lamellar sheets and (iii) the point of zero charge allows "the selective" anion intercalation/deintercalation into the LDH interlayers and cation sorption/desorption onto the external sheets at the interface.

Retention of arsenic, chromium and boron on an outcropping clay-rich rock formation (the Tégulines Clay, eastern France)

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In many countries, environmental impact of toxic chemicals has to be considered for the implementation of industrial facilities. The assessment of the toxic chemical environmental impact for a given facility requires evaluating the mobility of the various toxic chemicals potentially involved in the industrial activity in its surrounding environment. Numerical evaluations of the migration of the identified toxic elements from the industrial facilities toward the biosphere necessitate a good parametrization of their retention behavior. Outcropping clay-rich formations are considered as a potential host for a radioactive waste repository in many countries. Radioactive waste can contain toxic chemicals such as As, Cr and B leading to evaluate their migration in such clay systems. Sub-surface clay-rich rocks are notably characterized by redox transitions, which can influence the migration of many contaminants[1].

The retention behavior of arsenic (As), chromium (Cr) and boron (B), was investigated for an outcropping clay-rock formation, the Albian Tégulines Clay (France, Aube) currently studied as potential a host-rock for long-live low activity level (LL-LL) radioactive waste At the vicinity of the surface, Tégulines Clay is affected by weathering processes leading to contrasted geochemical conditions with depth. One of the main features of the weathering is the occurrence of a redox transition zone near the surface. Batch sorption experiments of As(V), As(III), Cr(VI) and B were performed on samples collected at two depths representative either of oxidized or reduced mineral assemblages. Batch sorption experiments highlighted a distinct behavior of As, Cr and B oxyanions. The *in-situ* redox state of the Tégulines Clay samples has a significant effect on Cr retention (Cr(VI) heterogeneous reduction reactions followed by Cr(III) precipitation). On the contrary, As(V) reduction into As(III) is moderate and its retention slightly affected by the *in-situ* redox state of the Tégulines Clay. As(V) retention is higher than As(III) retention. Boron retention is strongly influenced by its natural abundance in the Tégulines clay samples and the distribution coefficient of B (Kd) is expected to be very low for *in-situ* conditions due to the significant amount of natural B in the pore water[2]. The comparison of the retention properties of two Tégulines Clay samples towards three oxyanions with contrasted chemical properties highlighted the roles of clay mineralogy, natural abundance, and reducing capacity of the investigated materials.

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Climatic and sea-level control of Pliensbachian clay mineral sedimentation in the Cardigan Bay Basin, Llanbedr (Mochras Farm) borehole Wales

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Early Jurassic climate is characterised by alternating cold and warm periods highlighted by studies based notably on oxygen isotopes measured on belemnite guards and other marine invertebrate shells. These climatic changes include changes in the hydrological cycle and, consequently weathering and runoff conditions. In order to clarify the erosion and weathering conditions during the Pliensbachian, we determined the mineralogical composition of the clay fraction of 132 samples taken from the entire stage drilled in the Llanbedr (Mochras Farm) borehole (Cardigan Bay Basin). The clay mineral assemblages are composed of various proportions of chlorite, illite, illite/smectite mixed-layers (R1 I-S), smectite, and kaolinite, with possibly occasional traces of berthierine. The occurrence of abundant smectite indicates that the maximum burial temperature never exceeded 70°C. Consequently, clay minerals are considered mainly detrital, and their fluctuations likely reflect environmental changes.

The variations in the proportions of smectite and kaolinite are opposite to each other. Kaolinite is particularly abundant at the base of the *jamesoni* Zone, in part coinciding with the d^{13}C negative excursion corresponding to the Sinemurian/Pliensbachian Boundary Event, and through the *davoei* Zone, whilst smectite is abundant in the upper part of *jamesoni* and base of *ibex* Zones and through the *subnodosus*/*gibbosus* subzones of the *margaritatus* Zone. The kaolinite-rich intervals reflect an intensification of hydrolysis and an acceleration of the hydrological cycle, while the smectite-rich intervals indicate a more arid climate. The *spinatum* Zone is characterised by a distinct clay assemblage with abundant primary minerals, R1 I-S, kaolinite reworked from previously deposited sediments or from Palaeozoic rocks, and probably berthierine originating from contemporaneous ironstone-generating environments of shallower waters. This mineralogical change by the end of the Pliensbachian likely reflects a transition from a dominant chemical weathering to a deeper physical erosion of the continent, probably related to a significant sea-level fall consistent with a glacio-eustatic origin.

The role of natural microbial extracellular polymeric substances on fibrous Mg-clays formation

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Many authors have investigated the adsorption of bio-organic molecules to clay mineral surfaces to analyse the involvement of these minerals in the origin of life. Complementary, in this work we studied the chemical composition of natural extracellular polymeric substances (EPS) to determine the role that these organic molecules play in the formation of fibrous Mg-clays, mostly Palygorskite (Pal) $[Si_8O_{20}(Mg_2Fe_2)_{0.1}(Mg_2Al_2)_{0.9}(OH)_2(OH_2)_2]_1.\ nH_2O$. The analysed EPS were obtained from microbial mats of "El Longar", a hypersaline playa lake (Central Spain), characterized by Mg^{2+}-(Na^+)-(Ca^{2+})-$SO_4{}^{2-}$-(Cl^-) brines. Del Buey et al. (2018) and Cabestrero et al. (2018) have reported that Pal and a variety of Mg-Sulfates precipitate within the microbial mats that seasonally develop in this lake. Based on both TEM imagery and the greater abundance of Mg-clays at the surface of the air-exposed mats, Del Buey et al. (2018) concluded that Pal nucleates and grows within the EPS as they dehydrate.

Results of the chemical characterization of the EPS from "El Longar" microbial mats provided new insight into the potential of these substances in the crystallization of Pal. As chemical analyses of purified EPS carried out by ICP-AES show an elemental composition that includes Si, Al, Mg, Fe, Ca, Na and K, among others. These elements are strongly bound to EPS and their presence fit well with the Mg-clays composition and would justify its nucleation. Along the same line, the use of ITC confirmed a high binding affinity (k) of this EPS for Mg and Ca. On the other hand, acid-base titration and ATR- FTIR results shed light into the various organic functional groups that attached metallic elements. It is relevant the presence of amide and amino functional groups, which could be involved in the fixation of the Si to the EPS (Ehrlich et al., 2010). Moreover, the mineralogical analyses of natural EPS (XRD) show the presence of the complete assemblage of newly formed minerals, including Pal.

These results will help to constrain the mechanisms of Mg-clays mineral formation such as Pal in natural systems, which can open a window into the geologic past of Earth and Mars, where the Mg-clays date back to > 3.5 Ga (Bristow and Milliken., 2011).

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The peculiar thermal effect of transverse anisotropy on the thermal response of the Callovo-Oxfordian claystone

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Various researches on the thermo-hydro-mechanical behaviour have been conducted on the Callovo-Oxfordian claystone, a possible host rock for the deep geological disposal of high level exothermic radioactive waste in France. Among these, particular attention has been devoted to the thermal volume changes occurring when the claystone is heated under constant in-situ stress conditions. To do so, an accurate monitoring of the changes in axial and radial thermal strains of a specimen of the Callovo-Oxfordian claystone, heated under constant isotropic confining stress conditions close to that prevailing in the Bure Underground Research Laboratory, was carried out, by using strain gages stuck perpendicular and parallel to bedding.

A peculiar and novel behaviour feature was observed. The effect of the transverse isotropy of the claystone on thermal strains were confirmed, but it was also shown that the thermo-elasto-plastic overall volumetric response was mainly due to the axial response, in which some influence of the adsorbed water is suspected. Conversely, the reversible radial response observed along a temperature cycle could be modelled through a simple homogenisation method that confirmed that it was governed by the thermo-elastic expansion/contraction response of the various constitutive minerals, with no effect of adsorbed water. Hence, the simultaneous occurrence of an elastic thermal response parallel to bedding, and of an elasto-plastic one perpendicular to bedding, was evidenced.

Ion sieving effects on Cs incorporation and exchange in cancrinite and sodalite formed in highly alkaline solutions

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Cancrinite and sodalite are two most common feldspathoids form when highly alkaline nuclear waste solutions from uranium processing plants leak and interact with silicate minerals in sediments or soils. The feldspathoids formed in these solutions often have particle sizes of a few tens of nanometers to a few micrometers. The importance of these minerals in incorporating radioactive nuclides such as Cs into their structures and therefore, regulate the environmental fates of the nuclides, have been noticed. Yet, the stability of the incorporated nuclides and other metals in the feldspathoids and the general ion exchange reactions of these feldspathoids in the environment have not be systematically characterized. The objective of this study was to determine the ion selectivity and ion exchange capacity of the feldspathoids for Cs, Na, K, and Ca.

It was observed that that cation-anion pairs in the alkaline solutions played critical role in directing the formation of the cancrinite and sodalite, and in determining their particle sizes and morphology. Both cancrinite and sodalite were able to preferentially incorporate Cs in their structures over Na during the formation of the feldspathoids, and cancrinite had a higher preference than sodalite. When exchanged extensively with Na, K, and Ca at 80 °C, nearly 90% of the Na in cancrinite and sodalite can be replaced by K, but Ca is less efficient in exchanging Na or Cs. Less than 15% of the incorporated Cs in sodalite and even less than 2% of the incorporated Cs in one cancrinite formed in the presence of nitrate were replaced by Na K, or Ca exchange, suggesting the stability of incorporated Cs in the structures of the feldspathoids. It appeared that the Cs occupied different sites in cancrinite when the accompanying anions are different. When nitrate was absent in the synthesis solution, 57% of the incorporated Cs was replaced by K, suggesting at least a portion of the Cs residue in the 12-member ring tunnels of cancrinite. The X-ray diffraction analysis and elemental mapping indicated that K and Ca did access the interior of the individual cancrinite and sodalite particles, and the crystallographic unit cell dimension *a* of sodalite was enlarged by K exchange. These observation suggested the radii, hydration energy, and valence of the cations were the determinative factors in the ion selectivity and exchange reactions in cancrinite and sodalite. The mobility of the ions in the feldspathoids have the ordered of Na>K>Ca>>Cs. The ion sieving effect was largely due to the aperture size of the cages or channels in the feldspathoids. The aperture sizes of the beta-cage in sodalite and epsilon-cage in cancrinites are about 2.2 Angstroms, with some structure flexibility of the frameworks, they are large enough for the dehydrated ions with radii less than 1.3 Angstroms to pass through but limit the pass of larger ions such as Cs. This ion sieving effect implied that the fate of the incorporated Cs will be determined by the chemical stability of the feldspathoids in the environment.

Enhancing the understanding of clay mineralogy concepts by active interacting with students with real and virtual models as well as field, lab, and class room demonstrations

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Students and visiting scientists in the Soil Mineralogy class, which covers the Clay Mineralogy, at Texas A&M University have very diverse backgrounds. They are trained in geology, soil science, petroleum engineering, civil engineering, chemical engineering, agricultural engineering, material sciences, and toxicology. The diverse backgrounds of the students make the teaching challenging and yet exciting. They reflect the interdisciplinary nature of Clay Mineralogy. With some commitments from both the students and the instructor, the students can have good and quick understanding of the concepts despite their uneven entry levels when they come to the class. Over the years, I have realized that the most effective way in enhancing the understanding clay mineralogy concepts is to create opportunities for the students to connect the mineralogy concepts to something the students know or can see or manipulate in their daily life. Five approaches that I have used in the class are: 1) Expose students to real mineral specimens in the field as early as possible. When observing the minerals in the real setups in the field, our class discusses the geochemical processes, genesis, structures, properties, benefits and problems of the minerals. 2) Ask students to build real physical model and virtual computer models, and ask them to get structural information such as relative shifts and rotations in layer stacking from these models. 3) Interact with students when they interpret the mineralogy data such as XRD and FTIR from their own samples, it is often the uncertainties and surprises under the SEM and TEM excite the students. 4) Demonstrate mineral formations and transformations in the class with the participation of students. Some minerals such as Fe, Al, Mn oxides, allophane, LDH can be easily demonstrated in a few or a few tens of minutes, and students can participate in the syntheses. 5) Have lectures recorded for distance students to listen and for students to review.

Is dehydroxylation a sole trigger of radiogenic argon diffusion in micas?

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Retention of radiogenic argon (^{40}Ar*) in a crystal lattice of micas and other micaceous minerals is the basis of K-Ar and ^{40}Ar/^{39}Ar geochronology methods. A model of thermally-induced release of ^{40}Ar is conventionally translated to the mica's ability to retain thermal history of geologic processes [1]. Here we question the validity of this approach based on ^{40}Ar/^{39}Ar step-wise heating spectra and provide another evidence that Ar release from micas is primarily controlled by their dehydroxylation [2], i.e. by the formation of H_2O from structural OH groups and its further migration out of the crystal structure.

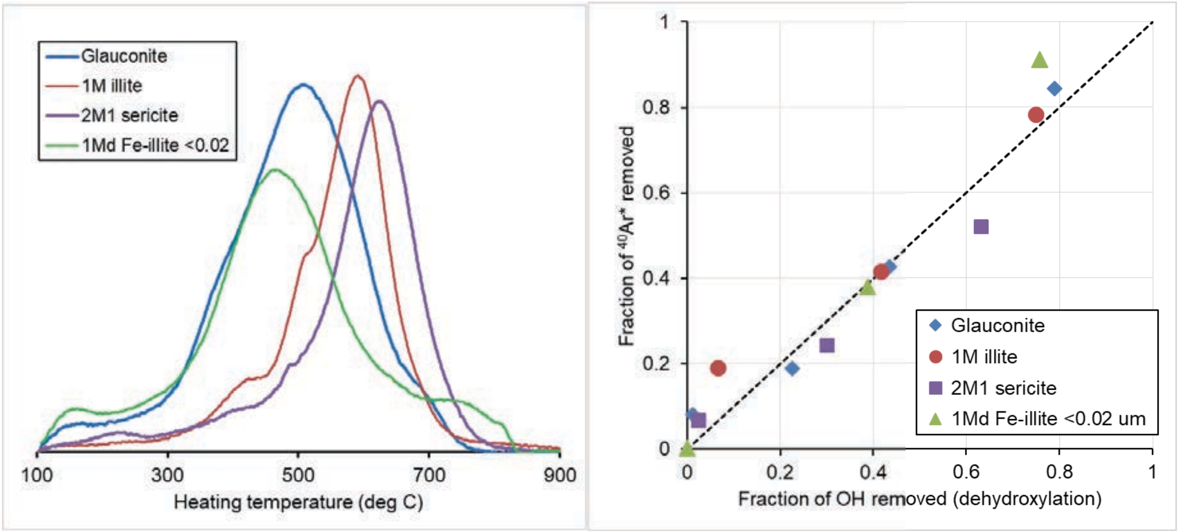

Figure 1. First derivative of thermogravimetric (mass loss) curves for four studied pure micaceous mineral standards (left) and the relationship between ^{40}Ar* content and OH groups content normalized to those of the untreated sample (right).

Micaceous materials of different structure and composition were preheated ex-situ. The % of removed ^{40}Ar* correlated linearly with their degree of dehydroxylation (% of OH thermally removed), regardless of the actual preheating temperature (Figure 1). Based on the correlation and similar effective dimension of Ar atom and H_2O molecule, and the same crystallographic position of these species in the interlayer [3], we suggest that the same mechanism is responsible for the simultaneous release of both species. Argon removal from the micaceous interlayer proceeds thus layer-by-layer or crystal-by-crystal [3].

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The riddle of Cu-layered double hydroxides solved by general principles of hydrotalcite synthesis

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Layered double hydroxides (LDHs) are 2-D anionic clays formed by isomorphous replacement of M^{2+} by the M^{3+} cations, offering a homogeneously dispersed mixed cation system. Their tunability and ease of synthesis under very mild conditions of coprecipitation make them attractive precursors of mixed oxide catalysts. In this project, a basic and classical member of this family, hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$), has been modified by the transition metals (Cu, Fe, Ni) with an aim to produce a tailored redox catalyst. However, this structural alteration was confronted by various unclear hypothesis which have been studied and discussed in detail in this work. A wide range of cation size (M^{2+}/M^{3+}) can be easily incorporated into the stacked sheets of the LDH, with the exception of some structural changes.[2] However, this fact does not seem operative in a Cu-Fe LDH system synthesized in the absence of another divalent cation.[1] It has been early reported that the ratio between Cu^{2+} and the second divalent cation should be equal or lower than one. The higher copper content distorts the structural symmetry in LDH. A tentative explanation of this phenomena is attributed to the Jahn Teller effect in copper, which was later considered as an established fact.

On the other hand, despite this effect of distortion, copper behaves conventionally with other cations; for instance, a Cu-Al LDH system exist in nature (woodwardite) and synthetic ones have been claimed to be obtained with no special difficulties. Though mixed oxides from Cu-Fe LDH have been reported but no evidence of successful synthesis of parent Cu-Fe LDH has been claimed in the literature nor identified as natural mineral, despite Fe^{3+} being a frequent component of hydrotalcite super-group minerals. Given the situation, the phenomena could therefore, not merely be correlated with the distorted symmetry of Cu. Furthermore, based on the density functional theory, an optimized structure of Cu_3Fe LDH has also been proposed.[3] This uncertainty in structural stability raised several questions that required a detailed study of step-wise formation mechanism of the LDH. This was done by the titration of the same concentration of each single cation (Cu, Fe, Ni, Al) with NaOH under conditions identical to the mixed cation titration experiment.

Results indicated that under same physical parameters, in a nickel rich to zero LDH system, a complete shift in crystalline phase from Ni-Cu-Fe LDH to CuO, highlighting the crucial part of divalent cation within a Cu-Fe based system. The role of pH (4.5-12) was also studied in order to investigate any possibility of a well crystalline Cu-Fe LDH system, however no evidence on formation of the desired phase could be achieved over this range and the formation of amorphous iron oxidized material was seen. On contrary, Cu-Al and Ni-Cu-Al LDHs were obtained as very well crystalline materials. A study of the precipitation curves of each cation provided an explanation of the difference between Cu-Fe and Cu-Al system based on a sequential mechanism of LDH formation. As a result, we concluded that Cu-Fe LDH system is primarily dependent on solubility domains of hydroxides.

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Characterization of Tagaran natural clay and its efficiency for removal of cadmium(II) from Sulaimani industrial zone sewage

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The fine fraction of the Tagaran natural clay (TC) from the Kurdistan region of Iraq-Sulaimani was characterized using XRF, XRD, SEM, TG/DTA, FTIR, and N_2 adsorption. The clay was evaluated with respect to its efficiency as an adsorbent for the removal of Cadmium (Cd^{2+}) from Sulaimani industrial zone sewage. The dominant clay mineral of the Tagaran clay mineral was saponite, with minor amounts of chlorite. Cd-adsorption studies were conducted as batch experiments. The effect of initial pH, equilibrium time, temperature, clay dosage, and Cd^{2+} concentration was studied. Results were evaluated using Langmuir, Freundlich, and Temkin isotherms. All isotherms were linear with Langmuir to better fit the experimental isotherm data. Kinetics could be fitted by applying a pseudo-second-order reaction kinetics model. In addition, the activation energy and the amount of calculated and experimentally determined heavy metal loads were consistent. The thermodynamic studies showed spontaneous endothermic adsorption. Amongst the local clays, the Tagaran clay is a candidate material for the production of an adsorber material for removing Cd^{2+} from aqueous solutions.

Keywords: Tagaran Natural Clay; Cadmium; Isotherm; Sewage; Saponite

Effect of salinity on clay-mineral nano- to micron-structural assembly: characterization by afm, cryo-tem and cryo-sem

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Clay-mineral assembly and the consequent elastic modulus of the clay-mineral tactoids, strongly affect the mechanical properties of soils. Young's moduli of kaolinite, illite and montmorillonite, air-dry tactoids, were measured by AFM, with averages of 14.8, 21.5 and 32.4 GPa, respectively. These values are in agreement with theoretical calculations reported. Clay-minerals within shales were found to have a stiffness in the range 18-40 GPa, which was stiffer than organic matter but softer than calcite grains. The samples were re-measured post hydration (except montmorillonite due to extensive swelling) with deionized water and the elasticity of kaolinite and illite escalated to 29.5 and 46.1 GPa, respectively. Both observations can be explained by the degree of clay-mineral surface hydration since water at the clay-mineral surface, behaves like a spring, enhancing elasticity. Upon saturating the clay-minerals samples with ionized water (5 and 50 mM NaCl) the elasticity of kaolinite and illite decreased to 9.9-9.3 and 12.4-10.4 GPa, respectively. Increasing ionic strength decrease repulsive forces between the clay-minerals particles which compresses the electric double layer, which we suggest, increases the alignment of the clay tactoids reflected by a reduction in elasticity.

Clay, montmorillonite and kaolinite, nano-structure as a function of ionic strength was further characterized by transmitting (TEM) and scanning (SEM) cryogenic microscopy to calculate 010 plane distance and the degree of alignment, respectively. Cryo-TEM scans of the 010 planes of the clay-minerals were imaged and the nano distances calculated. The distances between the kaolinite or montmorillonite platelets are in agreement with standard XRD diffractions. On the micron-scale, cryo-SEM micrographs were collected for kaolinite, illite and montmorillonite from distilled and ionized water, and the 2D-FFT of the micrographs were applied and summed radially to estimate the degree clay-minerals alignment. The alignment direction distribution was fitted into a Gaussian distribution and the full width half maximum (FWHM) was calculated with a higher FWHM indicating higher alignment. For all clay-minerals the degree of alignment was significantly higher with the increase in ionic strength ($p<0.0001$). FWHM raised from 4.4×10^5, 2.9×10^5 and 1.4×10^5 to 7.3×10^5, 5.7×10^5 and 4.4×10^5 for montmorillonite, illite and kaolinite, respectively. These results supports the AFM observations. Finally, applying AFM, Cryo-TEM and cryo-SEM measurements to characterize clay-mineral assembly as a function of solution ionic strength, sheds light on the alignment and mechanical properties of clay-minerals.

Utilization of computer vision for characterizing the sensitivity to disaggregation of soils immersed in water

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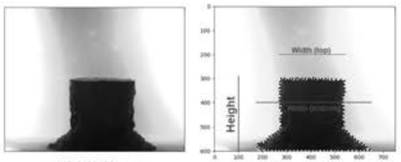
Dissagregation is a phenomenon occurring when soils are immersed in water. It is a kind of erosion consisting in the removal of particles, caused by water infiltration in the soil. Sensitivity to dissagregation is a key characteristic for assessing the reliability of clayey constructions located in an aquatic environment, such as earth dikes and dams.

A known test for determining the sensitivity to dissagregation is the Crumb Test, which consists in placing a cubic sample of soil (15 mm wide) in water and observing particles dispersion at given time intervals. It is quick and simple, but its results are qualitative. In this study, we present an enhanced crumb test, based on computer vision. Computer vision is an effective way to get precise measurements of the sample, with a short time step between measurements. In this new test, photographs of the soil sample (having a cylindrical shape, with a 5 cm radius and height) are taken every seconds during its dissagregation in water. Each Photograph is processed thanks to an OpenCV code to get a contour of the soil sample. Measurements (height, width at the top, width at the bottom) of the sample are then extracted from this contour. Figure 1 shows an original image and the resulting processed image (contour is shown in a black and white line).

Those 3 measurements are automatically plotted in a graph showing their evolution over the course of the test. Tests performed on various soil samples showed the importance of the mineralogy and the water content on dissagragation speed. Figure 2 shows graphs for a clayey soil, at low (a) and high (b) water content. We can see that, at low water content, the sample collapses after 250 seconds, whereas it stays stable during the whole hour of the test at high water content.

This new test gives useful information for geotechnical diagnostic of old levee: it helps to estimate their sensitivity to internal and external erosion mechanisms.



a) Original image b) Processed image

Figure 1:processing of a photograph

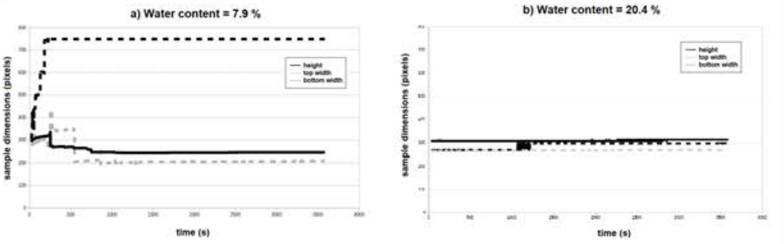


Figure 2: effect of water content for a clay sample

Structural factors affecting the crystal-chemical variability in Al-rich K-dioctahedral $2M_1$ micas

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To reveal factors that determine the different ranges of compositional variations in high- and low-temperature Al-rich K-dioctahedral micas, relationships between structural parameters and cation composition were analyzed for two sets of data: (1) structure models of synthetic $2M_1$ nicas in the series muscovite-phengite-aluminoceladonite and (2) Al-rich, K-dioctahedral $2M_1$ micas with refined structures. The dependences of the unit-cell parameters on cation composition and the variations in tetrahedral and octahedral lateral dimensions and sheet thicknesses, interlayer distances, and tetrahedral rotation angles were analyzed and compared with those found previously for the series $1M$ illite - $1M$ aluminoceladonite.

The similarities in the variations of unit-cell parameters with cation composition observed in $2M_1$ and $1M$ natural and synthetic K-dioctahedral micas imply that these variations should be controlled by similar, albeit not identical, structural factors. These factors, which are related to the ability of tetrahedral and octahedral sheets having different lateral dimensions to form a layer with uniform two-dimensional periodicity, are realized in a different manner in micas formed under different P and T conditions.

Extremely high temperatures and pressures in a closed system under laboratory conditions allow structural readjustment of the differently sized tetrahedral and octahedral sheets for a wide range of cation compositions (from muscovite to aluminoceladonite through phengite). In nature, under the conditions of metamorphism, the temperatures and pressures are not high enough to enable this readjustment for the formation of micas having aluminoceladonite-like compositions, which, in particular, would require reduction of the *a* and *b* parameters to ensure higher tetrahedral rotation.

Unlike muscovites and phengites, micas in the illite-aluminoceladonites series are formed under low-temperature and low-pressure non-equilibrium conditions in systems with highly heterogeneous compositions. This suggests that along with the structure, other factors would have a significant effect on the occurrence of $1M$ aluminoceladonite. At the same time, the readjustment of the lateral dimensions of tetrahedral and octahedral sheets in $1M$ K-dioctahedral micas may be facilitated by the more heterogeneous composition of the environment leading to a wide range of cation compositions. Additional factors that could favor the occurrence of the $1M$ aluminoceladonite structure as compared to the $2M_1$ polytype could be the relatively longer O-O distances across the interlayer and the relatively higher interlayer distance values.

Structural features of clay minerals in metasomatites at the Antei-Streltsovskoe uranium deposit (Russia)

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Antei-Streltsovskoe deposit (ASD) is located in Zabaykal'sky Krai of Russia in the eastern part of the biggest Russian uranium ore field, called Streltsovskoe (SOF). SOF is confined to a caldera formed in the Late Mesozoic. Later the area of the ASD was subjected to a complex low-temperature metasomatic alteration which resulted in three stages of mineral formation: pre-ore stage (140-135 Ma), uranium ore stage (135±2 Ma) and the post-ore stage (135-117 Ma) (Ishukova, 2007). In view of the multistage nature and duration of the hydrothermal processes at the SOF, there are still many unresolved questions about the conditions and time of mineral formation, detailed phase identification and structural and crystallochemical features of highly dispersed clay minerals. The aim of this research is to study clay minerals from the wallrock metasomatites, to clarify some disputable aspects of the genesis of this unique deposit.

56 clay fractions of core samples from wells 4 and 7 were selected for the study. These wells pass at depths of 800-2200 m through the late Paleozoic granites of the Streltsovskaya caldera basement (Ishukova, 2007). Its comprehensive study included mineralogy (XRD, SEM), geochemical (microprobe analysis, EDS), crystallochemical (XRD, FTIR spectroscopy, TG/DTG) and isotope-geochronological (Rb-Sr).

The main process of granite argillization at the ASD results in the widespread pre-ore formation of dioctahedral K-micas (mixed-layer illite-smectite with 11-16% smectite interlayers content, trans-vacant (Mg, Fe)-poor 1Md illite and 2M1 muscovite). Moreover, mixed-layer illite-smectites are widespread at depths up to 1000 m and in a narrow section of 1500±20 m, confined to the fractured zone. Illite and muscovite are spread throughout the studied section and form a mixture with an almost constant ratio of 1:3 (muscovite:illite). Immediately after the ore stage berthierine was formed, then on the post-ore stage it was followed by the formation of chlorite, kaolinite, and smectite. Smectite was found at depths up to 1000 m and in the area of 1500±20 m in association with kaolinite, micas and berthierine. 1:1 minerals of the kaolinite-serpentine group make 5-10% of the clay fraction of the studied samples, however, in the depths of 1500-2000 m their content increases to 20%. According to thermal analysis and FTIR spectroscopy, kaolinite has a poorly ordered structure. At depths above 2000 m, berthierine is replaced by a mixed-layer chlorite-serpentine which according to the modeling of XRD patterns contains up to 10% of serpentine layers and has a composition close to clinochlore.

This study was partially financed by the laboratory budget project # 0136-2014-0009.

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Fluorohectorite, a promising material for drug delivery

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Biocompatible encapsulated drug delivery materials are highly desired as they provide for controlled release of bioactive agents, thereby improving the effectiveness of medical treatments. Some of the key properties of better materials for drug delivery include high adsorptive capacity, which can be realized with smectites, a family of clay minerals.

Here we will discuss on the influence of pH on encapsulation of the bioactive molecule ciprofloxacin (CIPRO), a widely used antibiotic, by the synthetic smectite fluorohectorite (FHt). The ensemble of results gathered during this study provided for a deeper understanding about the complexation of an amphoteric drug molecule in smectites as well as molecular interactions within the composite structure. By means of X-ray powder diffraction (XRD), thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TGA/FTIR) and inelastic neutron scattering (INS), we showed that uptake of CIPRO is more efficient at acidic pH [1]. Based on geometric considerations, and despite having similar interlayer volume available, we concluded that at acidic pH, the CIPRO-FHt complex contained one CIPRO molecule per unit cell, while at neutral pH the CIPRO content was about half. Additionally, it was evidenced that adsorption of CIPRO by FHt facilitated removal of residual water from the interlayer, providing additional evidence that intercalation is the main adsorptive mechanism. Finally, via bacterial and toxicological tests, we expect to show that the effectiveness and toxicity of pure CIPRO is unaffected in the clay–drug complex [2].

At the end of this talk, we will give an overview in how the findings exposed in this contribution can be easily extended to other bioactive agents as well as other clay mineral types, assisting new studies in the encapsulation of bioactive molecules by clay minerals.

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Effect of vermiculite clays on the performance of urease inhibitors in soil ammonia volatilization

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Ammonia volatilization is a major pathway in N loss in direct-seeded, delay-flooded rice production in southern USA. Urease inhibitors are commonly used to improve N use efficiency but the effectiveness may vary with their interactions with soil clay minerals. A couple of laboratory incubation experiments were conducted to determine the effects of the interactions of urease inhibitors [Agrotain Ultra, Factor, N-Fixx PF, NitroGain, N-Veil, and Nitrain] and soil vermiculite clays in reducing NH_3 loss through volatilization, under aerobic and waterlogged conditions, both at 15, 20, 25, and 30 °C. Urease inhibitor and clay type and amount significantly affected ammonia volatilization under aerobic condition. Agortain Ultra, NitroGain, and Nitrain could effectively reduce ammonia volatilization of surfaced applied urea. Compared to the clay soil, the sandy loam soil had greater ammonia volatilization loss. However, under anaerobic condition, urease inhibitors were not so effective in reducing ammonia volatilization as being observed under aerobic condition. Also, soils did not have significant effect on ammonia volatilization during flood. Given anaerobic condition, hydrolyzed N existed mainly as ammonium instead of nitrate. Ammonia volatilization incresed with increasing temperature and affected the effectiveness of urease inhibitors. Our study indicated that mitigation of ammonia volatilization loss in rice production varied with urease inhibitors and environmental conditions.

Behavior of clay-rich soil /cement mixtures prepared by deep soil mixing method

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In the hydraulic binder domain, the presence of clay aggregates has been known for a long time to be harmful to hardened mortar or concrete material. However the deep soil mixing technique to reinforce dikes or soils for foundation mixes the existing soil with cement (CEMII or CEMIII). A better understanding of the interaction between anhydrous cement powder, clay and water is therefore required in order to predict the hydraulic or mechanical performances of the soil mixing material and if they match with the targeted values. The present study scanned the properties of cement mixtures with variable natures of clay (4 kaolinites, 2 illites and 1 montmorillonite as well as siliceous sand as reference). The formulation of mixtures aims to obtain the optimum properties with a quantity of cement fixed at 140 kg/m^3 which represents around 8% in mass of the soil to be treated. As the quantity of water added to mixture controls the final properties via the appearance of increasing porosity with higher water content, a method based on liquid limit LL is chosen to fix the lower water content to add to achieve a self compacting paste (formulation is positioned at the beginning of the working range). Then, macroscopic material properties are studied in parallel with microstructural characteristics.

Globally, the more water sensitive the clay is, the lower the compressive strength UCS of the hardened paste appears. It is important to note that the curing is very slow, ranging from several days to several weeks (during this period mechanical test is not possible). The highest dispersion in UCS is observed with the four tested kaolinitic clays whose behaviors range from that of sand to the one of illite/montmorillonite. It indicated that the clay mineralogy is not the only determining parameter. In each clay family, the cation exchange capacity CEC (or methylene blue value VBS as well as plastic index PI) may vary and such parameters are good indicators to classify clay materials in a first approach. Indeed, CEC reveals not only the clays water sensitivity and then their ability to compete for water during cement hydration, but also their ability to adsorb Ca^{2+} cations used for CSH precipitation. On the contrary, clays may favor in various proportions the long term pozzolanic effect that allows to reinforce the soil mixing material by additional CSH formation. Furthermore, clays coat the particles of anhydrous cement and by physical screening, they prevent the proper development of a 3D network of CSH that bind neighboring aggregates. In this case, the mechanical properties are impacted by the size of clay aggregates (or balls) linked to the soil preparation method (remoulding,..), and by the clay capacity to disperse in cement mixture. As an example, the low dispersion of illite in cement (favoring aggregates of several tens of microns) increases the performances of mixtures while an intimate mixing at micron scale of kaolinite particles with cement reduces the resistance. Such results may at first seem surprising considering the higher water sensitivity of illite in comparison with kaolinite.

Control of the binder setting time, pH value and viscosity of the Callovo-Oxfordian argillite in alkali-activated grout – role of additives

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The french national radioactive waste management agency Andra, is actually developing the Cigéo project for the geological disposal of high level and intermediate level long lived radioactive waste. If the construction of the disposal is accepted, the digging of the facilities will lead to the excavation of a large amount of Callovo-Oxfordian (COx) argillite. The valorization of this raw material by alkaline activation is actually studied in the purpose to develop a grout. This binder must present an important setting time (above 24 hours), a low viscosity (between 0.5 and 5.0 Pa.s) and a moderate pH value (between 10 and 11). To control these properties, it is necessary to adapt the binder formulation by adjusting the alkaline silicate solution and the mineral source. However, to reach the proper characteristics, the mixture optimization is not sufficient and the use of additive is required.

The binders are prepared from the mixing of the alkaline-silicate solution and the mineral source based on calcined argillite mixed with metakaolin. If necessary, additive are added directly in the reactive mixture (during the mixing). The setting time values are evaluated by viscosity measurements follow-up over time and the pH values are obtained by immersion of the consolidated samples in a small amount of water ($\text{mass}_{\text{water}} = 2\ \text{mass}_{\text{sample}}$) and measurement by pH meter after seven days of immersion. The structural evolutions are investigated from X-ray diffraction and nuclear magnetic resonance spectroscopy.

A potassium based silicate solution with a moderate reactivity is selected in order to limit the alkalinity and to delay the geopolymerization. The use of additive is studied with phosphate-based and boron-based additives. Phosphate based additives induce a strong increase of the setting time by limiting the polycondensation (phosphate bonds to the aluminum), but result in a low consolidation. Boron-based additives allow to improve both the pH value and the setting time, close to the focused properties. For example, the addition of 2.5 $\%_{\text{weight}}$ of boric acid lead to a setting above 20 hours and a pH of 11.2. These evolutions have been related to the insertion of the boron in the geopolymer network in three or four coordinated atoms.

In the depth understanding of reversible ionic transfers of Layered Double Hydroxides by *in operando* electrochemical and gravimetric measurements coupled with Grazing Incidence Wide Angle X-ray Scattering

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A layered double hydroxide (LDH) material consists of a stacking of positively charged brucitic layers due to the substitution of some divalent cations M(II) with trivalent cations M(III). The charge compensation is managed by the ionic species intercalated into the interlayer spacing i.e. water and anions A^{n-}. This leads to the general formula: $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{x/n}).mH_2O$. As a consequence, LDHs provide a high capacity for anion exchange.

For wide applications in terms of energy storage device or water treatment, the reversibility of the ion transfer between the electrolyte and the interlayer spacing of the LDH needs to be further investigated. Tuning the oxidation state of the electroactive metallic sites with electrochemistry reversibly modifies the positive charge excess within the layers. The low electronical conductivity performance of the LDH is promoted by preparing thin films coated on a working electrode surface. The related ion transfer is probed by coupling electrochemistry with a quartz crystal microbalance sensitive to the ng (EQCM).

Here, we investigate for the first time the nature, kinetics, exchanged concentration and mass of each ion species transferred from the electrolyte to the material related to the oxidation and reduction of the electroactive components of the LDHs. This is made possible with the *ac*-electrogravimetry technique, developed at LISE, that couples electrochemical impedance and mass/potential transfer functions measurements.

The *in situ* grazing-incident-wide-angle-X-ray-scattering (GIWAXS, 20 keV) coupled with EQCM at synchrotron enables to measure the change in the interlayer spacing of the LDH as well as the mass variation of the material in solution during cyclic oxidation/reduction of the metal sites. It confirms and demonstrates further the mechanisms of the ionic transfers between the electrolyte and the interlayer distance.

Bioflm exopolymeric substances induce the aggregation of clay and sand in sedimentary environments

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In sedimentary environments, clay and sand are segregated by hydrodynamic processes. Yet, clay coatings, i.e. thin clay envelopes lining sand grains, are abundant in modern and ancient coastal sedimentary deposits. Here, we present laboratory experiments where we produced clay coated quartz sands similar to those observed in modern estuarine sands. These coatings were produced at ambient temperature by mixing exopolymeric substances (EPS) derived from intertidal diatom biofilms with clay and sand mineral standards. The clay standards were mixed based on the clay mineralogy observations on the Gironde estuary (France). The imaging of sediment-EPS mixes with cryo-scanning electron microscopy and atomic force microscopy demonstrates that EPS form organic bridges between clay and quartz. The physico-chemical properties of EPS were characterized independently through assays and fourier transform infrared spectroscopy. The results show that several EPS components (e.g., proteins, polysaccharides) have a potential to complex to quartz and clay. We propose a multiscale conceptual model for clay coats formation according to these observations. Our findings provide novel insights in the importance of biofilms, in the formation of clay coats.

Fougerite, the key mineral to understand bioenergetics mechanisms at the origin of life?

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Research on biological energy conversion has shown that the catalytic centres of the implicated enzymes are clusters of transition metals which strongly resemble certain minerals prompting the hypothesis that the emergence of life on our planet may have been initiated by mineral-borne metals. Our project proposes a first experimental test of this hypothesis via comparison of the catalytic properties of di-iron hydrolases and in particular soluble methane monooxygenase to those of the structurally affine mineral fougerite. Our approach represents a radical departure from the traditional research on prebiotic synthesis of organic molecules towards the investigation of a thermodynamically more sensible emergence of life from metabolic reaction networks harboured and performed by minerals.

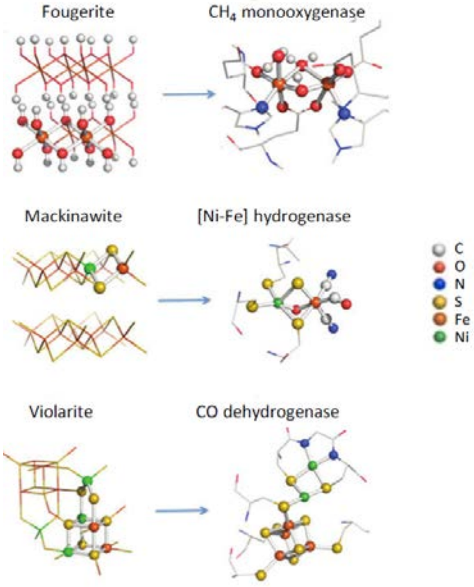

Figure 1: structural comparison between minerals and the active site of metallo-enzyme

A) fougerite with methane mono-oxygenase,

B) nickelian mackinawite and [Ni-Fe] hydrogenase

C) violarite and CO dehydrogenase. (Nitschke et al., 2013).

Synthesis of iron rich clays in the Fe/Si system using statistical experimental design

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Iron rich phyllosilicates of the 1:1 type like serpentines have been observed at various interfaces of materials [1]. Unfortunately, the naturally occurring forms are not readily available and they are very often associated with other minerals, which makes the study of their various properties challenging. Therefore, the objective of this study is to explore the possibility to synthesize iron-rich tri-octahedral clay minerals with tailored chemical composition and structure. The most common method for the synthesis of serpentine reported in literature is the hydrothermal one using microwaves, solid or gel precursors [2]. It has been previously stated that the pH plays a major role in the nature of the obtained products [3].

A first set of experiments allowed to prove the feasibility of the chosen synthesis method and to determine a relevant range for the parameters of the system. Then, a design of experiments (DOE) methodology was used to find the optimum synthesis conditions for iron-rich serpentine with molar $(Fe/Si)_{ini}$=1.50. Three parameters were studied: the initial molar ratio (OH/Fe) was varied from 2 to 4, the temperature from 80°C to 180°C and the duration of the hydrothermal treatment from 1 to 7 days. The statistical approach adopted here allows to minimize the number of experiments for a maximum of relevant information. Starting from the DOE, the behavior of the system can be mathematically approximated and a parametric study can be carried out to estimate operating optimums. For the same X-Ray diffractogramme of oriented preparation, the ratios of 001 reflection peaks intensity and area between 1:1 and 2:1 type structures were chosen as criteria.

The results showed that the nature of the obtained clay (1:1 vs 2:1 type) is strongly dependent on the $(OH/Fe)_{ini}$ molar ratio, regardless of the duration of the hydrothermal treatment. Indeed, the highest $(OH/Fe)_{ini}$ molar ratios, favored the formation of 2:1 clay minerals whereas lowering the ratio to ~ 2.2 favored the formation of 1:1 type. For $(OH/Fe)_{ini}$ molar ratio < 2.2, only iron oxides were formed. Moreover, these results demonstrate the feasibility of the central composite design of experiments. In addition, a validation step showed that the nature of the obtained phases was in line with the mathematically predicted responses.

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Memoir of an Illitist

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A study of illite crystal thickness distributions (CTDs) has led to an understanding of crystal growth in general. Illite CTDs have three fundamental shapes: asymptotic, lognormal and an intermediate shape formed as the first type of CTD grows into the second type. The asymptotic CTD forms during simultaneous nucleation and crystal growth, whereas the lognormal CTD results from growth without simultaneous nucleation. In these studies, illite crystal thicknesses are measured by Fourier analysis of XRD peak shapes according to the Bertaut-Warren-Averbach method (MudMaster program) after the effects of swelling on XRD peak broadening have been removed by treatment with PVP-10 polymer.

The relative growth rate of illite crystal thicknesses (T, in nm) can be described mathematically by the Law of Proportionate Effect (LPE):$T_{j+1} = T_j + e_jT_j$, where T_j is the initial crystal thickness, T_{j+1} is the thickness after one subsequent growth cycle, and e_j is a random number that is independent of T and that varies between 0 and 1. The LPE algorithm is iterated for a given number of times for 1001 crystals by the GALOPER program, and, upon collection of the resulting thicknesses into size classes, naturally occurring illite CTD shapes are duplicated. These shapes are related to two parameters, alpha, which is the mean of the natural logs of the thicknesses, and beta^2, which is their variance. Reaction paths for illite formation are revealed in plots of these parameters on an alpha-beta^2 diagram.

From a study of crystal size distributions (CSDs) in the literature, and from the results of our own experiments with K-alum and calcite crystallization, as well as from our measurements of the sizes of naturally occurring crystals for a variety of minerals, we discovered that, like illite, most minerals display asymptotic or lognormal size distributions. Therefore, mineral growth in nature can be described by the LPE. The rate of illite thickness growth is limited by the rate at which new material can be incorporated into the illite surface (surface limited proportionate growth). However, as minerals grow larger than clay size, the growth rate becomes limited by the rate at which nutrients can be transported to the mineral surface. During such supply limited proportionate growth, e_j in the above equation essentially becomes a constant (it appears as a scaling factor), and the early formed shapes of the CSDs are preserved as crystals grow larger (i.e., beta^2 remains constant as alpha increases). Such growth is described as “proportionate growth” because crystals tend to grow at a rate that is proportional to their size. In other words, in the same system, larger crystals increase in linear dimension faster than smaller crystals.

One other fundamental CSD shape, rarely found nature, was crystallized in our experiments: the reverse skew of the universal steady state shape predicted by LSW theory for Ostwald ripening. We have not found this shape for clays, but have produced it for calcites nucleated at high levels of supersaturation (omega>100). This unique shape has also been observed for some naturally occurring garnets. Extremely small crystals, unstable due to their large surface areas, nucleate in heterogeneous solutions at high supersaturation, and then dissolve to contribute growth material to larger crystals that are thermodynamically more stable. The Ostwald CSD shape, initially formed at very small crystal sizes, then is preserved by supply controlled proportionate growth as the crystals grow larger.

In summary, the shapes of CSDs for illite and other minerals reveal growth mechanisms and reaction pathways for crystallization.

A rheological approach on the study and determination of fundamental structural parameters of hydrated bentonite systems

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Two different water-bentonite slurry systems have been characterized in both the conventional rheological methods (API – American Petroleum Institute) and more modern rheometry techniques, such as dynamic testing and steady shear. The aim of this work is, through combination of these methods, to draw conclusions about the fundamental structural parameters that differentiate the two bentonite types. Structural parameters are direct reflections of interparticle orientation, their configuration at colloidal scale and weak forces acting on them. Specifically, those two raw smectitic clays are intentionally selected to exhibit different rheological behavior in order to provide ground for speculation and building a theory for the observed differences, based upon various structural parameters (such as particle size of hydrated clay platelets, degree of delamination/ particle release, layer charge density, predominant exchangeable cation, etc.). These methods are further investigated/ validated by other traditional characterization methods (particle size analysis of dried slurries, SEM, Thermal Analysis etc.). Eventually our work seeks to develop a methodological protocol where widely rheological methods' results, such as response of slurry to oscillations and rotation, thixotropy phenomenon at high and low shear rates, plastic viscosity, etc., are correlated to these fundamental parameters and can be used as a measurable direct indication of them. This sort of approach of using rheology as a tool to determine bentonite's intrinsic/structural parameters at wet state, is believed to provide a handy and quick tool to draw very useful information about performance of different bentonite types and to predict their gelling and thixotropy behavior in aqueous systems. Rheology at high and low shear rates as a means to describe sufficiently the microstructure and the interparticle configuration in water-bentonite slurries, is expected to become essentially a selection tool of different bentonite grades for specific industrial applications.

Oxidation of Benzyl alcohol over Nanoporous Ruthenium supported on DD3 kaolin

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The activity of Ruthenium nanoparticles in the oxidation of benzyl alcohol with molecular oxygen was investigated. The aim was to synthesis nanoparticles materials by chemical formation of reduction of $RuCl_3 \cdot 3H_2O$ ionic exchange on DD3 kaolin , mesoporous and microporous material with $NaBH_4$ (reducing agent). The nanoporous materials are characterized by XRF, XRD, MET, EDX, and BET measurements, were used to determine the character of catalyst. The excellent yield was obtained for Ru-DD3(5%) catalyst about 97%. The conversion is equal to 100% and the benzaldehyde selectivity is about to 97%. In all cases, the formation of benzoic acid was not observed. The oxidation results were better for Ru-DD3 (5%) then other catalysts and comparable to Ru-HZSM-5 (5%) but the yield of benzaldehyde does not exceed 67%. Ru-DD3 (5%) present a higher stability during five repeated runs. The observed results indicate that Ru-DD3 (5%) can be used as versatile and stable catalysts for aerobic oxydation of alcohols reaction.

Key-words: Aerobic; oxidation; Benzyl alcohol; Ru nanoparticles; DD3; ZSM-5; SBA-15.

Activated Algerian kaolins as low-coast potential adsorbents for the removal of Derma Blue R67 acid dye

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There are significant amounts of unused dyes remaining in wastewater from dyeing industry. The release of these effluents causes abnormal coloration of surface waters and there is a risk of toxicity. This research involved the efficient adsorption of anionic dyes (Bleu Derma R67) by local natural and treated clay; Djebel Debagh (DD3) and Tamazert (KT2) a low-cost materials abundant in highly weathered soils from Algerian East. Adsorption experiments were accomplished using acid dye adsorbed on activated kaolins (DD3 and KT2) by acid treatment. These two clays were first treated by acid in order to enhance their retention capacities, and then characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area measurements (BET method), surface charge (PZNPC), and electrophoretic mobility (Zetaphoremeter).

Key words: Activated kaolins, Acid dye, Characterisation, Adsorption

Mesoporous silica synthesised by a local kaolin as efficient adsorbent for the real effluent textile treatment

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In 1992, Mobil company synthesized and characterized the first mesopoous material **[1]**. Since then, these materials have attracted the interest of many researchers. This interest is justified by their particular properties such as a regular arrangement of the channels, a modulable pore size of 2 to 30 nm greater than zeolites, and a high specific surface area greater than 1000 $m^2.g^{-1}$. Physicochemicals propreties allow to use them in various and varied fields such as catalysis, separation, chromatography, biochemistry and adsorption.

In our work the mesoporous silica synthesised by local raw clay is a new nanostructured material for environmental textile effluent treatment applications. The DD3 (Djebel Debagh) Kaolin comes from the municipality of Guelma in Algeria and it has been chemically and thermally treated. In addition, the pluronic L35 (EO11PO16EO11) has been used as a structuring agent.

X-ray diffraction, X-ray fluorescence, transmission electron microscopy, and nitrogen adsorption-desorption were used to evaluate the textural and structural properties and composition of the synthesized material. The synthesized material gives a surface area of 161 m^2 / g which is superior to (92 m^2 / g) the surface area of nanostructured materials in the literature **[2]**. Its adsorption properties have been tested on textile industry effluents and indicate a good efficiency of treatment by a reduction of most parameters (BOD, COD, etc ...). This suggests that this new mesoporous material synthesised by clay available and inexpensive could have applications in the environmental field.

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Characterization and evolution over time of chemical composition of Moroccan architectural ceramics glazes: example of Saadian tombs

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Historical Islamic buildings of Marrakech impress by their filigree architecture and colorful facades and many of them therefore belong to the UNESCO world cultural heritage. Particularly the carefully arranged and gorgeous decorative ceramics, called zellige, give the buildings their typical and imposing appearance. However, in some monuments, the zellige have reached an advanced deterioration phase and its ceramic and glazes have been increasingly weakened due to human and environmental impacts over time. Restoration attempts have been done in several periods, but there is no historical archive of these restorations. This study deals in particular with glazes of the Saadian tombs, one of the jewels of Islamic historical sites and the most visited since its discovery in 1917. The site contains 3 categories of zelliges: the original zellige from the 16th century, the first restoration material in the first half of 20th century, and the recent restoration material. All recent zelliges are originated from Fez, the first site of manufacturing zelliges in Morocco. The aim of this study is to characterize the chemical composition of the different glazes ceramics and to emphasize their evolution over time.

Historical ceramic materials study requires an effective element detection and non-destructive tool. Portable X-Rays Fluorescence (pXRF) was used to determine the chemical composition of past and recent glazes. All samples are lead-silica type glazes with 25-59 wt.% of PbO and 51 wt.% of SiO_2. The colouring agents used for the original glazes are copper (Cu^{2+}), iron (Fe^{3+}) and manganese (Mn^{2+}) for the green, yellow and black glazes respectively. For the blue glaze, its opalescence is probably related to the incorporation of phosphorus (P_2O_5). The recent glazes present a different chemical composition, reflecting new formulation used in the Moroccan ceramic industry. For instance, calcium and potassium oxides were substituted by other elements like lead oxide as flux in the glaze mixture. Iron and copper are increasingly used for black, yellow and green colors, while the use of phosphor for blue color has been replaced by other elements such as cobalt and copper.

This study underlines that the enamels of past and recent zelliges are characterized by distinct chemical compositions. In the absence of restoration records, the chemical composition of the glazes could be an important method to distinguish between the different restoration periods in the historic building of Marrakech. However, further studies are needed to establish a link between the chemical composition of glazes and the degree of preservation of historical zelliges.

Potentiality of raw bentonite for removal of heavy metals from acidic phosphogypsum waste

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The production of phosphoric acid from phosphate rocks gives rise to phosphogypsum (PG) waste. About 5 tons of PG are produced for 1 ton of phosphoric acid. The PG content produced each year in the world exceeds 280 Mt/year (Pérez-López et al., 2007). Morocco produces, by year, 15 million tons of PG residues coming mainly from phosphate ore processing industry. PG is considered an acidic by-product (pH = 3), due to residual phosphoric, sulfuric and hydrofluoric acids contained in the pores. It also contains heavy metals and radioactive elements as rhodium.

Our study deals with the ability of raw bentonite to neutralize the residual acidity of PG and its cation exchange properties to trap some heavy metals, lead (Pb) and cadmium (Cd) in particular. In this study, Moroccan raw bentonite (B) was used for the removal of heavy metals in order to keep the process cost as low as possible. B-PG-water mixtures were prepared with variable content of PG and bentonite ($0 \leq B / (PG + B) \leq 1$ and solid / water ratio = 1%). pH values and heavy metals amounts were monitored during 60 days. Mineralogical (XRD) and microstructural (SEM) were performed on raw bentonite, PG and the mixtures.

Bentonite and PG have constant pH values of 8.5 and 3.5, respectively. The pH values increase with increasing of the bentonite amount (pH = 5.5 with 10% of B, pH = 7.5 with 90% of B). The concentration of Pb decreases with decreasing bentonite amount after 7 days, from 1.2 µg/L to 0.4 µg/L for 0 to 90% of bentonite, respectively. A further decrease of Pb concentration up to 0.1 µg/L is obtained after 60 days. Likewise the Cd content decreases from 0.2 µg/L to concentration below the limit of detection by atomic absorption spectrometry.

Blue-green algae (i.e., Cyanobacteria) were developed in the mixtures (B-PG), the enrichment of the water with phosphorus leading to eutrophic conditions. These microorganisms consume metals as basic micronutrients for their fundamental biochemical processes as respiration and photosynthesis. Consequently cyanobacteria contribute, jointly with raw bentonite, to heavy metals absorption.

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Effects of raw yellow clay addition on geopolymer synthesized from metakaolin

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The global warming is caused by the emission of greenhouse gases and is one of the great problems of the society. The manufacture of Portland cement involves the use of a large amount of energy resources and the use of fuels which implies an environmental impact. The search for new alternative or green cements is necessary to limit such emissions. The most promising green cement is alkaline or geopolymeric cement due to its properties and low environmental impact, being considered the cement of the future. They are obtained by the chemical interaction between alkaline solutions and silicoaluminates, as metakaolin [1, 2].

In this study, raw yellow clay was valorized as a substitute of commercial metakaolin in the synthesis of new geopolymer materials. Yellow clay was sieved and calcined at temperature of 750 °C. Several samples (0-100 wt. % of yellow clay) were synthesized by mixing NaOH solution and sodium silicate solution with calcined clay and metakaolin. The samples were cured under controlled conditions (60 ºC and 99 % relative humidity) for 24 h. The specimens were then demold and kept at ambient conditions for 7, 28 and 60 days of curing. The geopolymers were characterized by FTIR, XRD, SEM and physical, mechanical and thermal properties were determined. It was demonstrated that samples based on clay and metakaolin present an amorphous consolidated appearance that characterize the polycondensation reactions. The results indicated that raw yellow clays provided good geopolymers in the presence of metakaolin and alkaline solution.

Ackwologements

This work has been funded by the project *Development and characterization of new geopolitical composites based on waste from the olive industry. Towards a sustainable construction (MAT2017-88097-R)*, FEDER / Ministry of Science, Innovation and Universities, State Research Agency.

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Design of eco-cement clinker by valorizing wastes from the ceramic, the marble and the aluminum industries

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In this research work a new type of eco-cement was investigated valorising industrial wastes from different production processes, replacing the typical raw materials (clay and limestone) for cement production. The clay has been replaced by the chamotte residue, which is a ceramic powder coming from ceramic fragments of defective pieces (bricks, tiles, etc.), manufactured at 950ºC. The limestone has been replaced by sludge from cutting blocks and polished marble tables process, which are currently disposed in landfills and contain mainly $CaCO_3$ in their chemical composition. In addition to these two main wastes, a third industrial waste has been added to improve the characteristics of the cement, which is a residue of aluminum oxide (PAVAL) from the production of secondary aluminum and which is mainly composed of Al_2O_3.

The development of this new type of cement is based on the inversion of the Alite-Belite ratio, with a proportion of Alite (C3S) at 9wt% and Belite (C2S) at 65wt%, as main components. The main characteristic of this cement is their lower clinkering temperature (1350-1400ºC), mainly due to the fact that the Belite phase is formed at lower temperatures compared to the Alite phase (the main component in the Ordinary Portland Cements, 1450-1500ºC), which means that less fuels are needed for the process and shorter firing time, resulting in lower greenhouse gas emissions to the environment.

The techniques used for the study of industrial wastes and the design of the belite-type cement were X-ray Powder Diffraction (XRD), X-ray Fluorescence (XRF), Thermal Analysis (DSC/TG), Modified Bogue Equation and Quality Indices (LSF, AM, SM), Free lime content, Optical Microscopy and Scanning Electron Microscopy (SEM-EDX).

All these characteristics allow the belite-type cement to be framed within the circular economy concept, since we effectively use natural resources by manufacturing a new sustainable product through wastes from other industries that are currently disposed of in landfills.

Acknologements

S. Martínez-Martínez thanks the Ministry of Education, Culture and Sports for a fellowship of University Professor Training.

Port dredge sediments as raw materials in the manufacture of fired clay bricks

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Dredging is a vital activity for the exploitation of ports. On average, 1.5 million m^3 of sediment are dredged for 6 months in the port of Bejaia, Algeria. This volume includes annual maintenance (the amount of sediment that will be removed each year to ensure the passage of the ship). In the present work the effect of the incorporation of port dredged sediments, as secondary raw material in the manufacture of ceramic clay bricks were evaluated. Different percentages of sediment wastes (0, 5, 10, 15, 20, 50, 100 wt %) were added to clay (usually use as raw material in the Algerian clay brick factory). The raw materials and the mixtures were characterized by DRX, FRX, SEM and DTA analysis. The physical characteristics (linear shrinkage, bulk density, apparent porosity and water absorption), mechanical (compressive strength) and thermal properties (thermal conductivity) of the bricks fired at 850 ºC and 950 ºC were investigated. These results indicate that the amount of port dredged sediment and the firing temperature were two key factors determining the quality of the bricks. The bulk density decreased according to the amounts of sediment and the firing temperature. The addition of up to 20 wt% sediment waste for the bricks fired at 850 ° C and up to 15 wt % for bricks fired at 950 ° C produced an increase in the compressive strength due to the decrease in water absorption and apparent porosity and a decrease in thermal conductivity. Additions of 50 wt% and 100 wt% of waste decrease the mechanical properties. This study reveals that the recovery of port dredge sediments as raw material in the field of construction materials can be a real solution and alternative in the manufacture of bricks.

Keywords: Port dredged sediment, clay, bricks, firing temperatures, mechanical and thermal conductivity

Heavy rare-earth element enrichments in kaolin gangue materials

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The coarse fractions (i.e. discarded gangue called informally grit) of two kaolin producing units (Cretaceous Buffalo Creek Member of the Galliard Formation and the Jeffersonville Member of the Eocene Huber Formation) were studied for their rare-earth elemental contents. The heavy mineral subfractions of these coarse fraction materials removed from these kaolin producing units contained high amounts of the rare-earth elements (Total REE; 1,646-5,012 ppm). Yttrium was the most abundant rare-earth éléments (555 - 2175 ppm, or 34-44 % of the REE) in these heavy mineral subfractions. The rare-earth element inventory was enriched in the heavy rare-earth elements (Gd-Lu, Y) by 10-140 times relative to heavy rare earth concentrations in Upper Continental Crust. The heavy mineral subfractions contained rutile, anatase, zircon, ilmenite, staurolite and trace amounts apatite, kaolinite. Small amounts of xenotime (Y-phosphate) have been found so far in the Buffalo Creek Member heavy subfraction. Less than 1% of total Eu and 2.5% of total Sc were leached by ammonium sulfate. The remaining REE were not detected from these leach analyses. The occurrences of the REE and the enrichment in the HREE can be attributed to the presence of zircon and xenotime in Buffalo Creek heavy subfractions. The enrichment in HREE in the heavy mineral subfraction is different from the light rare-earth element enrichment patterns seen in the clay and fine silt fractions of these kaolin producing formations2. The occurrences of the REE seen in the coarse fractions of these kaolin producing units comprise a novel domestic REE resource.

Eocene Esna Shale as a new source for modern and archaeological pottery in Egypt

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As a new source (Esna Shale) of the raw materials for the pottery industry in Egypt which literatures of the ancient and recent history do not referenced it, this study has been undertaken to identify their components accurately and detail as well as to identify the possibility of using them in other new industries. Samples were collected from the raw materials of El-Mahrousa kiln (one of the most famous places in Qena Governorate, Egypt, for pottery industry and from quarries extracted this formation (Esna Shale) near El-Mahrousa Village to supply the same the raw materials.

This Esna Shale in the west bank of the Nile Valley, Qena Governorate, Egypt, is unconformably underlain by Tarawan Formation and is conformably overlain by Thebes Formation with a gradational contact in-between. Lithologically, the Esna Shale Formation has similar lithological characteristics. It is mainly consists of vari-colored shales intercalated with argillaceous limestone in parts. Their detailed petrographic, mineralogic, geochemical and geotechnical characteristics were determined using several techniques including, thin-section examination, X-Ray diffractometry, IR analyses, scanning electron microscopy and X-Ray Fluorescence.

The Esna Shale Formation is texturally classified as clayey silt and silt. Particle-size distribution is somewhat similar in almost all samples examined.The XRD patterns of whole-rock samples show that the Esna Shale are mainly of phyllosilicates, calcite, feldspars (plagioclase and K-feldspar) and quartz.Their clay fractions consist entirely of poorly crystalline dioctahedral smectite with a fully turbostratic stacking mode (63.1%),I/S mixed layer(17.7%), kaolinite with lower crystal degree (13.4%) and well crystallized illite (5.8%).

In agreement with XRD analysis, the IR spectra of the raw clay and its <2 µm fraction confirmed the presence of smectite with its dioctahedrality, kaolinite, calcite, quartz.

The major and trace elemental concentration on whole rocks of the studied shales are compared with published average shales. In general, the bulk compositions of the shale in the present study compared with the published average shale compositions is significantly different. Silica (SiO_2) is the dominant constituent (49%) and considered to be dominantly terrigenous in origin. The SiO_2/Al_2O_3 ratios of the studied samples is exactely similar to that of montmorillonite and confirmed by the XRD results. The Al_2O_3 concentration (15.03%) is thought to be a good measure for detrital influx. The average content of CaO (8.64%)is considered to be dominantly of biochemical origin and may be used as marine indicator.

The mineralogy of whole rock samples plotted in the ternary diagrams proposed by Fiori et al. (1989) for classification in the Italian tile industry reaveals that nearly all the studied samples fall in the field of cottotoscano (porous products).Based on clay mineralogy, most samples lie outside the theoretical composition field for bricks because of their high smectite contents. Based on the charts proposed by Fiori et al. (1989), the chemical data for the samples studied lie in the field of white stonewares. The particle-size distribution as plotted on a Winkler chartreveals that nearly all the samples are unsuitable for making ceramic products.

Characterization and description of alkaline activation of raw kaolin

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Alkaline activation of calcined kaolin is well known to produce an alternative binder requiring less energy consumption than hydraulic binders. In addition to its use in alkali-activated binder (AAB), calcined kaolin are used as supplementary cementitious materiel. However, calcination processes are also costing and polluting which may justify the use of raw kaolin when low mechanical properties are expected. Due to its crystalline structure, kaolinite is less reactive than calcined kaolinite which has a highly disordered structure. Thus, in this study we investigate the alkaline activation of raw kaolin without prior thermal treatment. Chemical pretreatments, inspired by Mackenzie, are proposed to describe the effect of high alkalinity on raw kaolin in a binder system.

In this work, kaolin Speswhite® model was chosen and several alkaline activation were done in different ways at 40°C in closed reactor. First, raw kaolin added to a silicate sodium solution (Geosil®) is used as the reference of alkaline activation (AA) of raw kaolin. Chemical pretreatments with NaOH at 5 and 10M during 1, 3 and 7 days were carried out in order to reduce kaolinite crystallinity and then, to increase its reactivity. Finally, AA of pretreated kaolins were performed by adding silicate sodium solution. The complex evolution of these systems are followed using X-ray diffraction (XRD) analysis, ^{29}Si and ^{27}Al NMR, Infrared spectroscopy and scanning electron microscopy (SEM) in order to describe the formation mechanism of new phases.

As expected, AA of raw kaolin showed low reactivity after 7 or 90 days of curing. Nevertheless, gel phases are observed and depend on the curing time. After NaOH pretreatments at 5 and 10M, pretreated kaolins have similar behavior at 3 and 7 days. Hydroxysodalite-type zeolite (HS) are formed whatever the pretreatment concentration. After AA (curing time of 90 days), initially pretreated kaolins revealed a large variety of formed phases. Indeed, AA of pretreated kaolins at 10M led to the formation of HS and the same silicate gels observed after direct AA of raw kaolin. At 5 M pretreatment and 1 day, AA of pretreated kaolin after 90 days shows the formation of X-type zeolite and depolymerized silicate gel. In contrast, at 7 days of pretreatment and same curing time, Phillipsite-type zeolite is formed with another more depolymerized silicate gel than the one formed at 5M. Finally, AA of pretreated kaolins in open reactor showed than zeolite formation are totally inhibited even at 10M. This condition of curing results in the formation of a new disordered phase more rich in aluminum whose 27Al and 29Si NMR signatures tend to resemble the geopolymer signatures. In this work, way to modify the alkaline activation of raw kaolin is demonstrated.

Formation of metakaolinite and metadickite during dehydroxylation

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Metakaolin is produced by calcination of kaolin. Metakaolins are used in huge quantities for construction as supplementary cementitious material and as geopolymer precursor. During calcination thermal reactions of kaolin components, *e.g.* dehydroxylation of kaolinite, occur. Understanding the structural changes during dehydroxylation of kaolinite is crucial for optimization of the industrial scale production and reactivity of metakaolin.

Serious problems arise in selecting suitable reference materials of kaolinite as variation of structural order-disorder of polytypes is very common. Kaolinites are known to contain domains of dickite layers resulting in a disordered structure. In kaolinite layers with vacant B octahedral cation sites are stacked regularly. The dickite structure is characterized by a translation of a/3 of the layers and alternating stacking of layers with vacant B octahedral cation sites and layers with vacant C octahedral cation sites.

The dehydroxylation temperature (T_{DHX}) of kaolinite polytypes increases in the following order Halloysite < Kaolinite ≤ Dickit ≈ Nakrit. Thereby, the volume of kaolinite decreases and the volume of dickite increases (Schomburg and Störr, 1984). On the other hand, disorder decreases T_{DHX} up to 100 K for each polytype. Therefore, disordered kaolinites dehydroxylate at lower temperatures than well ordered kaolinites but there are controversial results about the reactivity in alkaline solutions. Some studies found that dehydroxylated disordered kaolinites show a better reactivity in alkaline solutions (Snellings et al. 2012) while other authors report contrary findings (Tironi et al. 2014).

In the present study, Density Functional Theory (DFT) modeling method as defined in the Vienna ab initio simulation package (VASP) for the calculation of the electronic structure was employed to get a better understanding of the formation process of metakaolinite and metadickite during dehydroxylation and of their resulting properties. Results are compared with experimental data from simultaneous thermal analysis and ^{27}Al MAS NMR spectroscopy.

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Mineralogical, chemical and physical study of ceramics from Nditam (Centre, Cameroon/ west central Africa): preliminary results

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The present abstract is a part of the project about the petrophysical study of thirteen ceramics of early Iron Age from Nditam (2000-3000 BP) in the central part of Cameroon. The aim of the project is to determine technological features and the material used for the production of these ceramics. The analytical methods for the mineralogical and chemical study are X-ray diffraction, optical microscopy, X-ray-fluorescence, thermal analyses and scanning electron microscopy, while physical characterization will be focused on hydric tests and mercury intrusion porosimetry. The work is in progress; therefore, only preliminary results are given in this abstract. The first results obtained by X-ray diffraction revealed three groups of ceramics according to the range of firing temperature deduced by their mineralogy.

Group 1: muscovite, kaolinite, k-feldspar and/or plagioclase and quartz. Only two sherds present this composition. The estimated firing temperature is below 500°C due to the presence of kaolinite.

Group 2: muscovite, k-feldspar and/ or plagioclase and quartz (nine sherds are concerned). The estimated firing temperature is below 900°C because of the presence of mica and probably above 500°C due to the absence of kaolinite.

Group 3: quartz and k-feldspar and/or plagioclase without phyllosilicates (only two sherds). The estimated firing temperature is above 1000°C due to the absence of mica and below 1100°C because of the absence of mullite.

These differences of temperature ranges can be explained by the irregularities of the time of firing in bonfires.

Key word: Nditam (Cameroon), ceramics, mineralogy, firing temperature

Technology vs. typology transfer in seaborne interactions: the Bronze Age pottery in Central Adriatic

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During the central centuries of the II millennium BCE (ca. 1650-1300), the two opposite shores of the Adriatic Sea were very well connected. Spatial analysis of pottery types identified Northern Apulia and Central Dalmatia as key hubs of the trans-Adriatic interaction network. In some sites in Northern Apulia, beside local models, a large number of typical Dalmatian shapes have been found.

92 pottery samples were analysed from three sites: the Manaccora Cave, on the coast of Mount Gargano, i.e. the Italian site with the largest quantity of foreign Dalmatian shapes; Rat (Island of Brač) and Vranjic (Split), both in central Dalmatia, where a few typical Italian shapes were also found among local models.

Petrographic (OM), mineralogical (XRPD), chemical (XRF) and microstructural analyses (IA) were designed to characterize imports and local productions and to test the hypothesis of a trans-Adriatic technological transfer. Petrographic analysis highlighted two different tendencies: ceramics from Dalmatia present extremely repetitive inclusion patterns (mainly calcite, sometimes with quartz), whereas vessels from Manaccora are far more variable in terms of petrofacies (alongside calcite and quartz, we also find volcanic, sedimentary and grog inclusions in various combinations) and technology (quantity and orientation of pores and firing temperature ranges). The patterns of primary and secondary porosity were useful to distinguish further between the technological features of the two Croatian sites. Bulk chemical data essentially confirmed the petrographic groupings and reveal two opposite trends: in Northern Apulia foreign Dalmatian shapes were usually produced locally, whereas all Italian shapes recovered in Central Dalmatia have been imported from Northern Apulia.

These data offer new insights into the trans-Adriatic interaction dynamics, and support the archaeological hypothesis of intense mobility across the Adriatic Sea.

The cargo of amphorae and the ceramics of the shipwrecks *La Madonnina A* and *B* (Campomarino, Maruggio - Taranto, Italy)

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Between 2013 and 2018, as part of the educational activities promoted by the Laboratory of Underwater Archeology - held at the Taranto department of the University of Bari Aldo Moro and in collaboration with the Superintendence of Archeology, Fine Arts and Landscape for the provinces of Brindisi, Lecce and Taranto - have been classified in a systematic way the findings of underwater provenance as a result of reconnaissance carried out between 1964 and 1968 along the coast of Taranto and Ionian Salento, coordinated by Peter Throckmorton, researcher-pioneer underwater archeology, assisted by collaborators belonging to different foreign institutions (University of Pennsylvania Museum, British School at Rome) and Italian (National Museum of Taranto, Italian Navy). The artifacts were, about fifty years later, systematically studied to allow a new interpretation of the routes, the frequentation of the coasts, the circulation of goods, and the presence of port areas and minor landings.

Particular attention was given to the remains of the excavation of the shipwreck La Madonnina A and B, dated the first one, at the end of the 4th century BCE, and the second one at the 1-2ed century CE, investigated in the summer of 1965 at the coast of Campomarino (Maruggio, Taranto). The study of the equipment and the on-board ceramics and of the amphorae that constituted the load of the wreck La Madonnina A allowed to reinterpret the two types of containers, more precisely circumscribing the dating of the wreck and redesigning the hypothesis of origin of this wreck boat. For the later shipwreck, La Madonnina B, the classification has allowed to identify mainly amphoras belonging to the same form but with different modules.

The petrographic analysis on thin section of 34 potsherd from the two shipwrecks allowed to verify the hypothesis of provenance useful to retrace the route of these two boats. None of the samples was ascribed to the petrofacies available in the area of Taranto. Twenty-nine out of 34 samples are fragments of amphorae of different provenance, with five samples of on board ceramics partly show the same fabrics observed in the sherds of amphorae. As a whole, about 80% of the pottery fabrics identified are from Aegean area (e.g. Corinth, Samos) and 20% from Magna Grecia (e.g. Naples area, Basilicata). These petrographic data helped to identify unclassified samples, amphorae imitations and to confirm the archaeological hypothesis of the circulation between the Aegean and Ionian Sea of these ships.

Mineralogy, geochemistry and genesis of clays interlayered coal seams succession in the Neogene lacustrine Orhaneli and Keles coal deposits, Bursa, western Turkey

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The Late Miocene-Pliocene units comprises claystone, marl, coal seam, siltstone, organic-rich shale, sandstone, conglomerate were deposited in lacustrine environment and associated with volcanic materials such as tuff and tuffite, and continued upward wtih Pliocene age andesite and basalt. Miocene and Pliocene units are affected by NW-SE and N-S trending faults. The geological, petrographical, mineralogical (XRD, SEM), and geochemical analyses were performed on the A6, C and H16 panels at the Bursa-Orhaneli and Keles basin. Rhyolitic tuff and andezitic tuffite, sandstone, organic-rich sandstone and organic-rich shale host rocks of the coal deposit are characterized by partially or completely argillized and sericitizatied sanidine, plagioclase and muscovite with rock fragments and organic matter in carbonate and clay matrix. Smectite, kaolinite, and illite are associated with quartz, feldspar, pyrite, aragonite, calcite, dolomite and gypsum. Association of illite with kaolinite, and smectite flakes edging and coating relict feldspar and volcanic glass grains and muscovite and/or muscovite with organic materials in the bituminous shale is consistent with diagenetic process. The presence of pyrite with kaolinite and illite platelets, microorganisms on degraded feldspar, and the occurrence of smectite as a coating on organic matter indicate biological involvement in the diagenesis. The slight enrichment of heavy rare earth elements (HREE) compared to light rare earth elements (LREE) with a positive Eu and Ce anomalies reflects fractional crystallization of feldspar and amphibole. Alteration of feldspar, biotite, and volcanic glass resulted in the concentration of Al, Fe, Mg, and K in a stagnant envrionment and precipitation of smectite and illite in an alkaline environment. Kaolinite precipitated in an acidic open hydrological system. An increase in Ni/Co and V/(V+Ni) ratios in altered units also suggest anoxic and anoxic to dysoxic conditions Association of argillization and silicification with coal, microorganisms, pyrite, and gypsum indicates a swampy environment and partial hydrothermal processes. The wide range δS isotope values (-1.5–15‰) indicate a mixed diagenetic and hydrothermal origin for the sulphide minerals.

Keywords: Smectite, Illite, Kaolinite, Coal, Bursa-Orhaneli-Keles coal deposits, Turkey.

Imaging clay nanoparticles *in vitro* and *in vivo* using dark field hyperspectral microscopy

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Clay nanoparticles are becoming increasingly popular in biomedical research. The use of such clays as halloysite, kaolin and montmorillonite in fabrication of drug delivery vehicles, tissue engineering scaffolds, antimicrobial coatings and cell or hair engineering[1] has stimulated the application of less convenient imaging methods to visualise and quantitatively detect clay nanomaterials within complex biological samples. Dark field microscopy supplemented with hyperspectral data acquisition has become an important tool in characterisation of nanoscale particles[2] because this technology allows for imaging nanoparticles in wet unfixed samples. This makes possible to detect nanomaterials within live cells and even live microscopic multicellular organisms. Importantly, dark field imaging does not require any specific labelling of nanomaterials, which can be detected using a simple light scattering-based visualisation. Moreover, dark field microscopy can be applied simultaneously with fluorescence microscopy, allowing for investigation of compartmental distribution of nanomaterials in cells, tissue and organisms. Therefore, unsurprisingly dark field microscopy has been utilised to image and map distribution of nanoclays in biological samples. Nanoclays, as relatively large nanoparticles, are perfect candidates Dark field microscopy has been recently used to image halloysite nanotubes uptake and intracellular distribution, to monitor the delivery of anticancer drugs,[3] and to investigate the biocompatibility of halloysite-doped cell supportive biopolymer scaffolds.[4] Imaging of nanoclays taken up by protists[5] and nematodes[6] using dark field microscopy was applied to investigate the distribution of nanoclays and to monitor in situ the interactions with organelles and tissues. Hyperspectral nanoclay detection and quantitative mapping has also been performed to identify nanoclays and confirm complexation with (bio)macromolecules. The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University and funded by Russian presidential grant MD-6655.2018.4.

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Glucose oxidase@CoMn Layered Double Hydroxides modified electrodes for electrochemical detection of glucose

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Layered double hydroxides (LDH~~s~~) are getting considerable attention as electrode modifiers in electrochemical applications, especially for enzymatic biosensor development[1]. In such application, LDH have been often used as host matrices to immobilize suitable enzymes for electrochemical detection, such as GOD@Zn_3Al-Cl LDH for glucose biosensors (GOD: glucose oxidase)[2]. However, formulation of these Enzyme/LDH biohybrid materials with redox mediators or conducting heterostructures is needed to insure electron transfer and/or electrochemical relay through the membrane. In this present work, we continue to explore the attractive multifunctionality of LDH by combining their unique properties as host structures for enzyme confinement and their electrocatalytic properties of intra-layer metal cations for redox transformations. We focused first on the synthesis of electroactive CoMn-LDH, potential candidates not much investigated for the amperometric detection of H_2O_2 (Eq.1)[3], a key step in the functioning of a glucose biosensor (Eq 2).

$$H_2O_2 \xrightarrow{\text{CoMn-LDH}} O_2 + 2H^+ + 2e^- \qquad \text{(Eq. 1)}$$

$$\text{Glucose} + O_2 \xrightarrow{\text{GOD}} \text{Gluconolactone} + H_2O_2 \qquad \text{(Eq. 2)}$$

Results will be presented for a series of Co_RMn LDH (R = 1, 2, 3, 4, 5), prepared by co-precipitation under optimized conditions to avoid the formation of thermodynamically favorable oxide and hydroxide phases (MnO_2, Mn_3O_4, β-$Co(OH)_2$). Formation of LDH phases was confirmed by XRD analysis and FTIR spectroscopy. The XPS analysis gives evidence of the joint presence of Co(II), Co(III), Mn(II), Mn(III) in the LDH structure a key point for the electrochemical performance of the material. XPS and EDX were used to quantify the Co/Mn atomic ratios in the prepared CoMn-LDH. LDH with a Co/Mn ratio 3:1 displays the purest crystal phase and the best electrochemical properties. The electrocatalytic performances of the Co_3Mn-LDH in the oxidation of H_2O_2 were investigated. The LDH was deposited as thin films on the surface of pyrographitic carbon electrode. The deposits are characterized by cyclic voltammetry in basic medium to study the redox signal of the 3d-Metal cations in the LDH layers, then in a neutral medium (Tris-HCl buffer pH 7) in the presence of increasing concentrations of H_2O_2. The calibration curves were then established by chronoamperometry. Finally, a GOD@CoMn-LDH bioelectrode was prepared and then tested for the electrochemical detection of glucose.

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Applying chlorite as a thermometer in the FEBEX *in situ* test

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Bentonites are an essential component of a multi-barrier system securing the long-term safety of the final disposal of nuclear wastes. An important issue for performance assessment is to demonstrate the long-term preservation of the bentonite properties over the long term. The dismantling of the second part of the FEBEX *in situ* test (Grimsel, Switzerland) provided the opportunity to quantify the modifications of the bentonite after heating (100 °C) and hydration at real conditions of a high level nuclear waste repository system during 18 years of experiment.

Recent studies (Fernández et al., 2018) have identified Fe-rich chlorites containing aluminium in samples obtained after dismantling of the bentonite barrier by different techniques: XRD, FTIR, SEM and TEM. In other samples, saponite was also detected. The chlorites were found at the frontal part of the Heater#2 and in protrusion samples taken from holes of the liner supporting and surrounding the Heater#2. In addition, wet chemical analysis revealed the proportion of Fe(II) and Fe(III) in a chlorite rich sample (~93 wt.% and 7 wt.%, respectively).

Fe-bearing chlorite or trioctahedral smectite saponite are described as neoformed phases at temperatures higher than 150 °C and lower than 100 ºC, respectively. However, the highest temperatures expected in the FEBEX *in situ* tests were lower than 100 °C. Therefore, the estimation of the temperature and conditions of chlorite formation in this experiment is of interest. The neoformation of chlorite with a determined composition corresponds to changes in ambient physicochemical conditions within the bentonite barrier, including temperature (T), pressure (P) and redox conditions, as well as the pore water composition.

In this work geothermometers, based on combination of thermodynamic calculations with a semiempirical approach based in a big database of compositions of chlorites, have been applied to estimate the temperature during chlorite formation under the hydrothermal conditions occurred in the FEBEX *in situ* test. Preliminary results point out formation temperatures around 200 ºC, although the influence of variables such as pressure, Fe^{3+} content, silica equilibrium and salinity are also analysed. The oxygen gas fugacity (fO_2) was obtained from the $Fe^{3+}/\Sigma Fe$ ratio and used to estimate the redox conditions during chlorite formation. These redox conditions allowed to understand the mineral assemblages controlling the redox state in the FEBEX *in situ* buffer depending on the $fO_2(g)$: magnetite-Fe(II)-rich saponite, chlorite-sulfides-oxides(Fe), magnetite–sulphides-hematite.

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Use of clays in peloids' manufacture for cosmetic use

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The clay minerals have been used for medicinal purposes since ancient times. The pelotherapy is the use of muds (peloids) in an external way for cosmetic or therapeutic purposes, in the form of plaster, mud bath or facial masks. These muds usually consist of a mixture of clay minerals and mineral-medicinal waters (MMW).

In this paper we study some properties of three peloids made with MMW from the following resorts located in the province of Granada (Spain): Alicún de las Torres (sulphated calcic, magnesic, strong mineralization), Zújar (chloride, sulphated calcic, magnesic, sodic, strong mineralization) and Graena (sulphated calcic, magnesic, strong mineralization). The solid phase is a mixture of kaolin and bentonite (9:1, w:w). The maturation time was three months.

During the process of preparation and maturation of the peloids, the following changes have been produced: 1) There is a transfer of solutes in the peloids from the mineral phase to liquid phase. 2) Kaolinite crystallinity (Hinckley Index, HI) decreases during maturation process (three months) from 0.71 (raw kaolin) to 0.55. Smectite crystallinity (measured as Integral Breadth index, IB) increased slightly: from 1.24 (raw bentonite) to 1.17 (IB decreases when smectites crystallinity increases). 3) Cation exchange capacity (CEC) values are higher than that of the mineral phases, probably due to the development of a more complex particle's architecture. 4) The concentration of exchangeable magnesium and calcium increases (almost triples, in A3 Alicún's sample); however, exchangeable sodium and potassium decrease (almost a half). 5) With respect to the thermal behavior of the peloids, the cooling time was: G3 (12.32 min.) > A3 (11.75 min.) > Z3 (11.37 min.) of Graena, Alicún and Zújar samples (three months), respectively; the time spam between maximum and minimum values was nearly one minute. 6) The particle size of the peloids (mainly clayley and silty) was inherited from the raw material. 7) In respect of microfabric features, an increase of clustering and porosity during the maturation process was observed, especially in Alicún and Zújar samples.

Based on all the results, we laso discussed the effect of the type of MMW on fitness of the peloids for cosmetic use.

Curvature-induced hydrophobicity at imogolite-water interfaces: 'The nanotube effect'

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Imogolite aluminosilicate nanotubes are commonly found in volcanic soils, where they exert a control on carbon dynamics, but also in industrial settings where they are synthesized with varied compositions and sizes. Synthetic imogolites have been used for the removal of contaminants from industrial effluents, and they are considered for a range of other applications including gas adsorption, and as inorganic supports for organics with different functionalities. In spite of their environmental and industrial relevance, the wetting properties of imogolite remain poorly understood. Here, an experimental and computational study is presented in which a comparison between the hydrophilic/hydrophobic properties of gibbsite–a planar aluminum hydroxide–and the external surface of synthetic imogolite–the curved counterpart of gibbsite, is made. Atomic force spectroscopy experiments showed that, in spite of their identical surface structure, the curved imogolite surface has a lower hydrophilicity than gibbsite. Molecular dynamics simulations confirmed this observation providing a molecular-scale explanation: the curvature of imogolite prevented the formation of in-plane H-bonds along the directions of the nanotube circumference, lowering the enthalpy of adsorption of water molecules and increasing their translational entropy, which are on the contrary strongly H-bonded to the planar surface of gibbsite. The different arrangement of surface H-bonds and the subsequent differences in the hydration properties affect as well the acidity constants of surface functional groups.

This 'nanotube effect' could be relevant to other nanotubular systems with high curvatures, impacting their wetting properties, their colloidal stability and potentially enabling the formation of strong organo-nanotube complexes via hydrophobic interactions.

A combined experimental and numerical analysis of anisotropic diffusion of water in clay porous media

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Due to the strongly anisometric shape of clay particles, their mutual arrangement in compacted porous media is most often associated with the development of anisotropy in both particle orientation and interparticle pore network. Such anisotropy in particle orientation is also enhanced during burial diagenesis and has significant impact on the directional dependence of preferential fluid diffusion.

In order to get additional insights into the role played by particle orientation on orientational dependence of water diffusion, two clay porous media were prepared using reference kaolinite KGa-2. Two distinct protocols were applied to obtain these samples, which display similar porosity but contrasted anisotropy degree. Particle orientation was measured by 2D-X ray diffraction after resin impregnation of the samples whereas experimental measurement of the water self-diffusion tensor was obtained by exploiting 1H Nuclear Magnetic Resonance Pulsed Gradient Spin Echo attenuation.

A sequential deposition algorithm was used to mimic the three-dimensional organization of clay porous media for particles having elliptic flat disk morphology. Different porous media were generated at constant distribution in particle geometry but different anisotropy degrees, ranging from almost isotropic to very anisotropic orientation of particles. Water mobility within these porous media was determined by numerical simulations of Brownian Dynamics, based on the consideration of water probes diffusion in interparticle porosity. The obtained results regarding water diffusion coefficients are found to be in fair agreement with experimental data. This allows getting additional insights onto the role played by particle organization on the overall macroscopic diffusion of water and on the associated self-diffusion tensor.

Determination of a normal palaeo-geothermal gradient comparing the reaction progress of clay minerals calibrated with organic maturity indices

Dedicated to the 90th birthday of Hans Krumm

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Based on the large data set of the authors from different orogenic belts, geodynamic setting with a normal geothermal gradient were selected. In these studies clay mineral versus organic matter correlations show in the vitrinite reflectance (VR)/Kübler Indices (KI) plot from Ferreiro Mählmann et al. (2012) gradients with "moderate (normal) geotherm" conditions. Using maturity modelling and clay mineral reaction progress studies a normal temperature gradient of 25 to 35 °C was estimated.

In the Lower Austroalpine (Eastern Switzerland) a 20 myr lasting metamorphic overprint caused a clay mineral (CM) – organic matter (OM) thermal equilibrium among the indices used (Ferreiro Mählmann, 2001) establishing a significant gradual sensitive correlation. For New Caledonia, an identical correlation has been published (Potel et al., 2006). There, prior to re-equilibration of the CM/OM sediments underwent a high-pressure subduction event as detected by studying the indices to determine maturity, temperature and grade of diagenesis to incipient metamorphism. The CM/OM indices are in equilibrium or close too it, showing nearly identical thermal estimations despite being subject of a pluri-facial metamorphic history. In the eastern Helvetic Alps (Rahn et al., 1995) and Northern Calcareous Alps (Petschick, 1989, Krumm et al., 1988) similar correlations were found. Comparison between different regions became possible using KI standardization and data discrimination as recommended by Ferreiro Mählmann et al. (2012) and Warr and Ferreiro Mählmann (2015). In both parts of the Alps a poly-thermal history of short durations (5 to 10 Ma) caused similar CM/OM trends, but dis-equilibrium is shown by lower significant regression statistics.

Compiling the results, the following correlations can be calculated for a moderate geotherm (55 to 75 mWm^2) at normal temperature gradient condition (25 to 35 $^\circ\mathrm{Ckm}^{-1}$):

VR $R_{max}\% = 1.445\ KI^{-0.885}$, $KI = \Delta°2\Theta$, $r^2 = 0.88$ (limited to values between 0.2 to 0.6 Δ°2Θ).

This result confirms the correlation published for normal gradients from the Lower Austroalpine (Ferreiro Mählmann, 2001) between KI grades of 0.19 to 0.48 Δ°2Θ:

VR $R_{max}\% = 8.6 – 17.7\ (KI) + 11.1\ (KI)^2$, $r^2 = > 0.8$ (between 0.80 to 0.95 for different areas)

With increasing depth (z) a VR gradient of 1.4 ± 0.2 $R_{max}\%\mathrm{km}^{-1}$ is determined and a KI gradient of 0.09 ± 0.002 $\Delta°2\Theta\mathrm{km}^{-1}$ is observed. The methodical limit is given by VR at 9.1 $R_{max}\%$ = KI at 0.125 Δ°2Θ (representing the technical limit of the XRD measurement device).

It is to conclude that a normal geotherm can be described by the VR/KI correlation, while even different heating episodes may cause the same VR/KI regression. For detection of a poly-phase or pluri-facies thermal history many CM/OM indices with very different kinetics have to be used. This is e.g. demonstrated by the strongly differing amount of smectite content at equal VR/KI values versus structural depth.

Massive open online clay course, a 21st century approach to teaching clay science

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“A massive open online course (MOOC /muːk/) is an online course aimed at unlimited participation and open access via the web. In addition to traditional course materials, such as filmed lectures, readings, and problem sets, many MOOCs provide interactive courses with user forums to support community interactions among students, professors, and teaching assistants (TAs), as well as immediate feedback to quick quizzes and assignments. MOOCs are a recent and widely researched development in distance education, first introduced in 2006 and emerged as a popular mode of learning in 2012. ”-*Wikipedia*.

Massive Open Online Clay Courses (MOOCCs) may be videoed single-topic tutorials of laboratory procedures, or all the learning materials for “semester-long” courses in soil science, geology, geochemistry, materials science and industrial applications.

A number of the current web-presented materials on clays may be located by using common search engines. Their content and utility are mixed as they are not commonly peer-reviewed. Built-in procedures for verification of content by professors and students may take a long time. Course management systems (Moodle, Blackboard Learn) are available to guide MOOCC development and use. The number one concern for the future is that these new materials and approaches increase learning. Other non-trivial matters relate to intellectual property ownership and how the cost of the programs will be shared by guests and credit-seeking students.

Thermodynamics and partitioning of halogens (F, Cl, Br, I) in phyllosilicates: analytical petrology coupled to geochemical modelling

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Studying the partitioning of halogens between minerals in metamorphic rocks is crucial to better constrain their geochemical cycle as well as understanding fluid/mineral and mineral/mineral interactions. Phyllosilicates are among the most important carriers of halogens in metamorphic rocks, even though halogens are generally found in minor (<1 wt%) to trace (<0.1 wt%) amount in natural metamorphic silicates. Knowledge about minor and trace element partitioning of halogens is still limited on both theoretical and applied grounds. The present study focusses on incorporation of halogens (F^-, Cl^-, Br^-, I^-) into hydroxyl sites in biotite, phengite and chlorite. Measurement of trace amounts of halogens has recently been improved and allows investigation of minor to ultra-trace halogen concentrations in metamorphic rocks. *Ab-initio* modelling of halogen-hydroxyl substitution in end-members allows estimating the energetic cost of incorporating moderate to low concentrations of halogens in crystal cells as well as studying crystal strain. From this, estimated partition coefficients between minerals are compared to measurements in natural phyllosilicates.

This study combines several analytical methods to measure minor and trace halogens. Electron microprobe (CAMPARIS, Sorbonne Université) is used in biotite, phengite and chlorite to quantify F and Cl with average detection limits of about 200 ppm for F and 35-40 ppm for Cl. In addition, Cl, Br and I are measured by laser-ablation mass spectrometry (ALIPP6, Sorbonne Université). Measurements on bulk rocks are conducted using mass spectrometry in solution mode for homogeneous samples. Calibration is carried out using international and house standards.

Ab-initio modelling of halogen substitution with hydroxyl group in phyllosilicate end-members (phlogopite, clinochlore, muscovite) and simple hydroxides is carried out with the CRYSTAL program (e.g. Dovesi et al., 2014). A major difficulty is reaching dilute concentrations of halogens which are modelled as defects in the mineral structure. Current limitations are on the order of 1 weight percent for halogen concentration. This allows estimating partition coefficients for moderately dilute halogen concentrations. Comparison between measured and estimated partition coefficients is underway.

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Hydrothermal synthesis of layered and tunnel manganese oxides from Mn mining residues from Amazon (Brazil)

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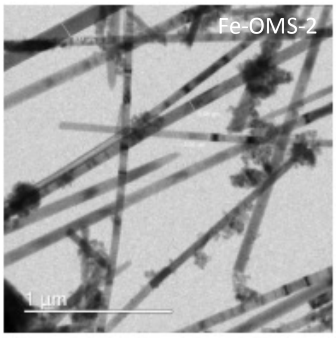
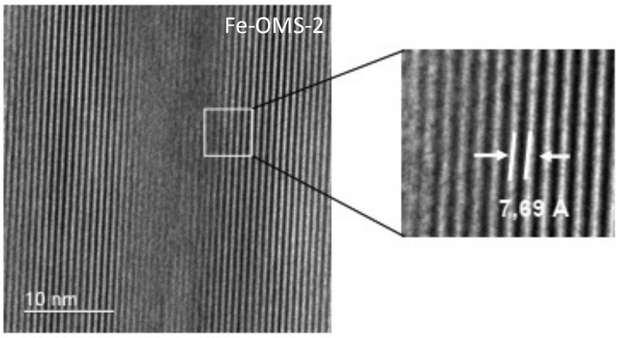
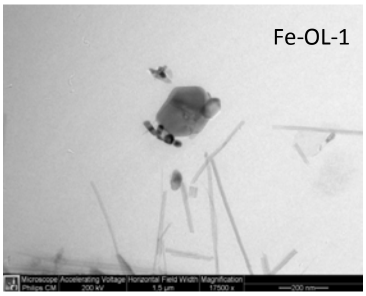
In the present work, the Mn mining residues (45,41 % MnO and 8,21 % Fe_2O_3, weight molecular) from Amazon (Brazil) were evaluated as low cost raw material to obtain layered and tunnel manganese oxides with particular attention to the Fe-birnessite (Fe-OL-1) and Fe-hollandite (Fe-OMS-2) structures, respectively. In the first step, Mn residues has been converted into Fe-OL-1 under hydrothermal reaction with NaOH solution at 170 ºC for 4 days. As a second step, "tunneling" experiments have been performed under hydrothermal treatment to convert layered (Fe-OL-1) into tunnel phase (Fe-OMS-2). The transformation processes were monitored by means of X-ray diffraction, Raman spectroscopy and Scanning electron microscopy. High-Resolution Transmission Electron Microscopy revealed the nanolayers and nanowires nature of the Fe-OL-1 and Fe-OMS-2 particles, respectively.







Iron-based layered double hydroxides as drug carriers: advantages and challenges

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Layered Double Hydroxides (LDHs) have been studied for decades for application in different knowledge fields, whose interest to act in drug storage and as delivery systems may be highlighted. This class of materials has the general formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}\bullet zH_2O$ (M^{2+}: divalent metal, M^{3+}: trivalent metal, A^{n-}: n- valent anion) with a structure based on brucite-like layers. The presence of Fe^{3+}, endogenous, is an alternative to the Al^{3+}, the most common trivalent cation present in the LDHs compositions. Biocompatibility and the possibility to interfere in tissue regeneration are some of the advantages possessed by Iron-based LDHs[1]. However, there are few papers reporting hybrid LDHs composed only by iron. The intercalation of organic species and drugs has been challenging in the presence of iron, and for the ZnFe-LDHs even the isolation of pure phases is difficult. In order to understand how iron effects the LDHs formation, two series of pristine LDHs with expected compositions $Mg_2Fe_{1-x}Al_x$-Cl and $Zn_2Fe_{1-x}Al_x$-Cl, with x equal to 0, 0.25, 0.50, 0.75 and 1, were synthetized by the coprecipitation method. Regarding to the drug storage capacity evaluation, anions derived from the non-steroidal anti-inflammatory naproxen (NAP) was encapsulated by ion exchange reaction. X-ray patterns of the pristine phases present the characteristic peaks related to LDHs, with the exception of the Zn_2Fe-Cl material, due to its low phase occurrence between amorphous phases or poor structural organization. The higher Fe^{3+} ionic ratio compared to the Al^{3+} was reflected in the 110 planes position, corresponding to atomic planes in the layers, which were displaced to low angles according with the increase of iron content, indication the Fe^{3+} incorporation in the layer structure. TEM images of the Zn_2Al-Cl and Mg_2Al-Cl samples showed thin plates with predominance of regular and distorted hexagons, respectively. Although in general M^{2+}/M^{3+} ratios have been closed to the expected, a mixture of phases containing distorted hexagons and iron rich phases (acicular and small non-plates objects) are present. Albeit X-ray patterns indicated the NAP intercalation and IR and Raman spectra are closely resembling, the increase in non-LDHs phases according with the increase in iron amount may explains the decrease in NAP molar percentage of encapsulation, varying from 58 to 38 % for the Mg-LDHs and from 74 to 14 % for the Zn-LDHs. To conclude, to make iron-based HDLs therapeutic vehicles even more interesting, presenting higher store capacity, synthetic conditions and methods may be revisited in order to propitiate only the obtainment of pure.

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Layered double hydroxides @ Fe_3O_4 nanoparticles for drug release of ciprofloxacin

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Nowadays, biomedical efforts try to join therapeutic and diagnostic activities using one unified material. These "theranostic" materials are able to deliver the imaging agents and drugs to the target site effectively. Inorganic compounds such as layered double hydroxides (LDHs) are being extensively studied to develop carriers for drugs and bioactive molecules due to their biocompatibility. Among the inorganic nanoparticles, those that exhibit superparamagnetic properties, such as iron oxide (magnetite or maghemite), can be applied as contrast agents for diagnostic imaging. In order to achieve carriers of controlled size and high degree of dispersion in physiological media, a deep investigation on synthetic parameters (reagents concentration, pH value, temperature etc.) is needed.

This study explores: (i) the synthesis, (ii) physico-chemical properties, (iii) *in vitro* release kinetics studies and (iv) the biocompatibility by *in vivo* assays of drug delivery systems of nanosized and nanoprobes materials based on commercial antibiotic ciprofloxacin intercalated MgAl and ZnAl LDHs structures and decorated by an imaging agent such as magnetite nanoparticles.

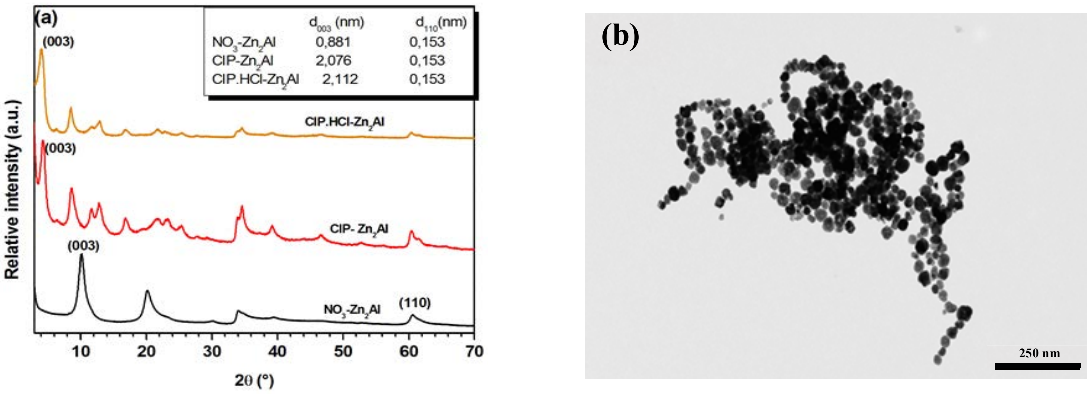

Figure 1: (a) PXRD patterns of ciprofloxacin intercalated Zn-Al LDH, (b) TEM image of Fe_3O_4 obtained by solvothermal method.

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Alkylpyridinium montmorillonite as new adsorbent for diclofenac

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The presence of drugs in water is of major environmental concern due to the ecotoxicological impacts and cumulative effects that are observed even at low concentrations (Ondarza et al., 2019). Diclofenac (2-[(2,6-dichlorophenyl)amino]benzeneacetic acid) is a nonsteroidal anti-inflammatory drug and its presence in aquatic medium is not adequate due its low bio degradability and high ecotoxicity (Oliveira and Guégan, 2016). Among the treatment for drug removal, adsorption is highlighted as an alternative. Organophilic clay minerals are used to removals of the organic pollutants from aqueous solution (Brito et al., 2018). In this work, 1-dodecylpyridinium (C_{12}py) chloride was used to prepare organophilic bentonites. Organobentonites were obtained using the surfactants in the proportions of 100% and 200% of the CEC of the pristine bentonite (74.64 cmol(+) Kg^{-1}) for 5 min at 50 ^{o}C over microwave irradiation. The solids were applied for drug removal where the influences of the pH, adsorbent dosage, contact time and initial drug (pKa 4.1) concentration were systematically investigated. X-ray diffraction, infrared spectroscopy and CHN elemental analysis were used to characterize the solids before and after adsorption. The values of the basal spacings were 1.56 and 1.66 for C_{12}py-100% and C_{12}py-200, respectively. The values were higher than that one observed for pristine sample, 1.12 nm. The drug removal showed distinct adsorption capacity for diclofenac on organophilic samples and was 13.02 mg g^{-1} for C_{12}py-100% at pH 6.0 and 60 min, while the amount was 25.00 for C_{12}py-200% at pH 6.0 and 20 min. The results suggested the better performance of the C_{12}py-200% sample and is an indication that the quantity of surfanct influenced the drug interaction.

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Keywords: Organoclay, intercalation, adsorption, sodium diclorofenac, depollution

Characterization and origin of a Fe-rich bentonite from Westerwald (Germany)

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The Westerwald region is one of the largest and oldest clay mining areas of Germany. A thick (up to 70m) kaolinite-illite clay sequence, dated from the Eocene and Oligocene, is mined for the ceramic industry. Those clays were protected from the erosion by a large basalt layer produced by an intense volcanic activity during the Upper Oligocene and Miocene.

This study aims to characterize a greenish bentonite layer found in three different quarries between the kaolinite-illite clay sequence and the overlying basalts. More than fifty samples were investigated by quantitative XRD, TGA, CEC, granulometry, SEM, FTIR and chemical analysis (major and trace elements).

The XRD performed on different bentonite samples confirm that the main mineral phase is a dioctahedral smectite (67-95%). All 3 deposits contain a variable amount of kaolinite, quartz, authigenic K-feldspars, anatase and illite/micas. Talc and goethite, present as traces in the 2 first quarries, are more abundant in the 3rd one.

The smectites are Fe-rich (>0.3 Fe^{3+} atoms per half cell-unit) montmorillonite with a dehydroxylation temperature around 500°C, which is typical of non-ideal smectites with a *trans*-vacant structures. The structural formulae of this smectites are heterogeneous. However they systematically show a charge location mostly in the octahedral sheet and exchangeable Ca and Mg cations. This was confirmed during the determination of the cation exchange capacity.

The samples from the third quarry were quite different. In addition to the Fe-rich montmorillonite, a trioctahedral smectite is also present. They are detected thanks to a second d_{060} reflection at 1.53Å and a different dehydroxylation temperature, around 800°C.

The trace element analyses show that this bentonite deposit is the result of the weathering of basic pyroclastic rocks, related to the overlaying basalts. Bentonite from the third quarry shows a different geochemical fingerprint and its mixt origin is currently under investigation.

Sequestration of orthophosphate by Ca_2Al-NO_3 Layered Double Hydroxide – Insight into reactivity and mechanism

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The continuous depletion of worldwide phosphate resources, mainly used as fertilizers and food production, threaten the world food supply by the end of the century. Added to these human and economic dangers, a major environmental concern arises from the dissemination of PO_4 in the environment and its accumulation in surface waters through land farming and wastewaters discards causing harmful eutrophication of inland and coastal waters[1]. Consequently the recovery of PO_4 from WWTP and the recycling into slow-release fertilizers offer new perspectives for the development of sustainable PO_4 management processes. Interestingly, Layered double hydroxides (LDHs) with chemical formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}[A^{n-}{}_{x/n}.mH_2O]^{x-}$ (M^{2+}, M^{3+} and A^{n-} being metal cations and anions), as unique anion exchangers, rank amongst the most selective and efficient adsorbents for PO_4 anions[3]. Among the LDH, hydrocalumite-like Ca_2Al LDH react with great quantities of PO_4 (400 mg PO_4 per gram of LDH) due to the chemical conversion into various $CaPO_4$ phases. This behavior makes Ca_2Al- LDH a very promising PO4 sorbents and potential SRF[3]. However more investigations are needed to better understand the mechanism of PO_4 sequestration by CaAl- LDH and characterized the resulting phases.

This study reports the mechanism of reactivity of phosphate anions ($HPO_4{}^{2-}$) with Ca_2Al-NO_3 LDH. Sequestration of PO_4 by Ca_2Al-NO_3 was quantified by fitting the adsorption isotherm with a Langmuir model. Adsorption capacity (65.2 mgP/g of LDH) greater than the theoretical anion exchange capacity indicates further mechanism of sequestration. Partial dissolution of $CaAl-NO_3$ results in precipitation of multiple $Ca-PO_4$ phases. Combined characterizations by XRD, ^{27}Al and ^{31}P NMR, FTIR/Raman and SEM highlight the competitive precipitation of hydroxyapatite and brushite within the LDH structure. Multiple environment of PO4 anions offer promising perspective for $CaAl-NO_3$/PO4 as slow release fertilizer.

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Novel multifunctional core-shell material based on SiO_2@LDH/Gox/metalloporphyrin for hybrid catalysis

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Hybrid materials are attractive solids for the confinement of multifunctional chemoenzymatic catalysts[1] to develop new selective, efficient and sustainable organic synthesis[2]. However, controlling the confinement of multifunctional catalysts in nanostructured hybrid materials to implement one-pot multi-step reactions remains a challenge and only few papers have been reported[3]. We recently demonstrated both the co-immobilization of four enzymes in layered double hydroxide (LDH) for the one-pot synthesis of phosphorylated sugars[4] and the hierarchical synthesis of SiO_2NP@LDH-Mn^{III}P (P=Porphyrin) core-shell catalyst for the selective cyclooctene oxidation[1].

Here, we report the co-immobilization of glucose oxidase (Gox) and Mn^{III}P or Sn^{IV}P metalloporphyrins in SiO_2NP@Zn_2Al-LDH nanospheres to investigate sequential production of H_2O_2 (Gox), cyclooctene oxidation (Mn^{III}P) and epoxide opening (Sn^{IV}P). SiO_2NP@Zn_2Al-LDH NPs were prepared using a multi-step coprecipitation process[1] and fully characterized by solid state techniques. Gox was immobilized in the Zn_2Al-LDH shell and Gox activity was determined by the reaction involving the oxidation of D-glucose and H_2O_2. The supported enzyme retains 50% of the activity of the free enzyme measured in solution (57 U mg^{-1}) and is still active in acetonitrile indicating the viability of the catalytic study in this medium. Mn^{III}P and Sn^{IV}P were immobilized on the core-shell and characterized. The solid support prevent Mn^{III}P aggregation and auto-oxidation, increasing the catalytic activity. This supported hybrid chemioezymatic catalyst is studied for the sequential production of H_2O_2 (enzyme), cyclooctene oxidation (Mn^{III}P) and epoxide opening (Sn^{IV}P).

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Water/Water Pickering emulsions stabilized by Layered Double Hydroxides nanoparticles for enzyme encapsulation

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Stabilization of emulsions by solid nanoparticles, known as the Pickering process, investigated since many years for food, pharmaceutical, cosmetic and petroleum applications, offers new perspectives in the nanostructuration of nanocomposite structures (armored particles, capsules, Janus nanoplatelets) and the functionalization of hybrid materials[1]. While water-in-oil emulsions are more commonly stabilized using amphiphilic molecules, the stabilization of water-in-water emulsions needs the accumulation of nano- or micro-particle at the liquid-liquid interface to rule out the low interfacial tension of W/W emulsions. 2D nanoparticles such as clay or graphene oxide nanosheets may display favorable surface charge control and high aspect ratio to stabilize w/w emulsions[2]. W/W emulsions based on incompatible polymers such as gelatin/dextran[3] or PEO/dextran[4] stabilized with respectively gibbsite or cellulose nanocrystals have recently been reported.

In this work, our objectives was to investigate the ability of MgAl-Layered Double Hydroxide nanoparticles to stabilize W/W emulsions. Colloidal suspensions of $Mg_RAl\text{-}CO_3$ LDH with variable surface charges were first prepared using a controlled-morphology synthesis (size < 100 nm) and LDH nanoplatelets were then self-assembled with gelatin/dextran (G/D) or PEO/Dextran emulsions. Effects of polymer weight percentage, G/D and PEO/D ratio, mechanical shearing, polymer/LDH mass ratio and LDH surface charge on the kinetic stability of the emulsions were investigated and imaged using optical microscopy. Polymers and LDH were labelled with fluorescent structural probes, rhodamine, ITC-Fluorescein and fluorescein respectively for confocal microscopy imaging. Formation of LDH micro-vesicles were clearly demonstrated.

Encapsulation of enzymes is under investigation in order to design new micro-reactors for one-pot biocatalyzed synthesis of hydroxylated aminoacid or sugars. Biocompatibility of theses chemically friendly systems for enzyme encapsulation and activities was first evaluated.

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Real-time Evaluation of Natural Organic Matter Deposition Processes onto Model Environmental Surfaces

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Natural organic matter (NOM) is ubiquitous in aqueous systems and dynamically partitions onto/from environmental surfaces. However, such interfacial processes have not been uniformly quantified *in situ* and in real time. In this work, adsorption and deposition processes of Suwannee River humic acid (SRHA) and Suwannee River fulvic acid (SRFA), as model NOM, were evaluated for a series of environmentally relevant interfaces. Real-time, interfacial phenomenon, including deposition, release, and adlayer viscoelastic properties, were quantified over a variety of water chemistries *via* quartz crystal microbalance with dissipation monitoring (QCM-D). Specifically, adlayer mass and deposition rates of SRHA and SRFA were evaluated as a function of NOM concentration/molecular weight (fraction), pH, electrolyte composition (type and concentration), and collector surface type. For these, the adsorption of SRHA onto aluminum oxide (Al_2O_3) and polystyrene (PS) surfaces follows the Langmuir isotherm model. Rapid, near-monolayer formation of SRHA/SRFA adlayers were observed on Al_2O_3, hydroxyapatite (HAP), and poly(L-lysine) (PLL) surfaces, but not on PS or iron oxide (Fe_3O_4) surfaces. The presence of divalent cations (Ca^{2+}/Mg^{2+}) at relatively low concentrations (0.5 - 5.0 mM) significantly enhances the mass of SRHA/SRFA deposited onto the surfaces of silica (SiO_2), Al_2O_3, and PS. Viscoelastic properties of the adsorbed layer based on the ratio of dissipation to frequency revealed a relatively unique adlayer structure for SRHA in the presence of 5.0 mM Ca^{2+}.

Transport of uranium in Clay rocks: studies on the effect of chemical perturbations.

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Migration of uranium within sedimentary rocks is of interest in various fields such as mining industry, environmental monitoring or radioactive waste management. Many case-studies detail mechanisms of uranium transport in natural media. For example, it was shown that adsorption-diffusion is a key factor during transport through geological barriers. Yet, the behaviour of the system "uranium/sedimentary rock" is still difficult to predict. Indeed, the speciation of uranium in aqueous solution displays an extreme sensitivity to physicochemical conditions, e.g. concentration of dissolved inorganic carbon, pH and redox potential. This issue led to the development of various operational models, sometimes with contradictory adsorption parameters [1]. These apparent contradictions are mostly due to experimental uncertainties or difference in the hypotheses used to develop the geochemical models. For example, the effective adsorption on mineral surfaces of mixed complexes $[UO_2^{2+}/Ca^{2+}{}_x/CO_3^{2-}{}_y]^{(y-1-x)2-}$ is still matter to debate and results from spectroscopic methods could help to ascertain some hypotheses.

The behaviour of uranium in Callovo-Oxfordian (COx) clay rock was studied in the context of a French retrievable disposal for High-Level Long-Lived radioactive waste. Important steps were made recently in the understanding of U(VI) chemistry and adsorption at various temperatures on model clay minerals and on COx clay rock [2]. The poster will present on-going studies on transport of uranium at various experimental scales. Adsorption was quantified on crushed clay rock in batch experiments and by in-situ infrared spectroscopy (ATR-FTIR). Diffusion data were measured on intact samples, up to decimetric scales. Then, studies focused on the effect of chemical perturbations. For example, the influence of different organic molecules potentially released by radioactive waste degradation was quantified. Similarly, the effect of redox disturbances on adsorption will be discussed, e.g. the impact of sediments oxidation in near-field of disposal, or the reduction of U(VI) in the far-field of geological environments.

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Adsorption of *Salmonella* by natural clays and clay-based advanced materials in contaminated waters

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In this work we have studied the capacity of four natural clays (montmorillonite, saponite, sepiolite and palygorskite) and the porous clay heterostructures (PCH) obtained with them to eliminate S*almonella* from waters.

The XRD profiles show that the synthesis of PCH with montmorillonite and saponite produces the expansion of the interlayer space between the type 2:1 sheets, a strong delamination along the *c* axis, and, moreover, a slight reduction of the particle size along the *b* axis. The synthesis of PCH modifies the XDR profile of palygorskite suggesting the loss of the structural ordering. The XRD pattern of sepiolite show the synthesis of the PCH does not generate any structural modification. These structural changes involve large changes in the textural characteristics of the starting materials. The synthesis of PCH in montmorillonite generates an increase in the specific surface area (SSA) from 50 to 683 m^2/g, where the external surface increases from 25 to 548 m^2/g. Similar observations are found with saponite (125 to 684 m^2/g) and palygorskite (92 to 612 m^2/g). Although no structural change was observed in sepiolite, the PCH synthesis increased the specific surface area from 182 to 768 m^2/g. Although increases in the micropore surface are observed, the increasing in SSA is due, in a greater extent, to increases in the external surface.

Studies of the kinetics of adsorption of *Salmonella* in natural clays show that not all materials reach the maximum adsorption at the same time. It should be noted that in palygorskite the maximum adsorption is reached during the first hour of contact, whereas saponite and palygorskite reach the maximum adsorption at 2 h and montmorillonite reaches the maximum adsorption at 4 h of contact. This shows differences in the mechanisms through which the adsorption of *Salmonella* occurs in the clays used that can be explained by differences in the accessibility of active adsorbent centers. These natural clays show very different *Salmonella* adsorption capacities. On the one hand, montmorillonite and sepiolite show lower adsorption capacities of *Salmonella*, eliminating 24 and 33% of the *Salmonella* present in the waters, respectively; and on the other hand, saponite and palygorskite eliminate 94 and 99% of the *Salmonella* present in the waters. In addition, it was found that the synthesis of the PCH with the different clays influences differently the adsorption yields of the different clays used. For example, the synthesis of PCH with sepiolite significantly improves the capacity of adsorption (from 33 to 67%), with saponite and palygorskite it does not seem to have significant influence and on the contrary in montmorillonite the capacity of adsorption suffers a strong decrease (of 24 to 16%).

Prediction of Boom Clay characteristics using grain size data

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The Boom Clay is a clay formation of Oligocene age outcropping in the northeast of Belgium. Over the last decades it has been researched as a potential host formation for the disposal of highly active and long-lived nuclear waste. In this context, physicochemical properties promoting the sorption of radionuclides to clay minerals need to be quantified in detail. These properties include the cation exchange capacity (CEC) and the specific surface area (SSA). Both parameters have been studied in detail, with sample sets ranging from 21 samples (for the SSA) to 54 samples (for the CEC) (Frederickx *et al.*, 2018). Considering that the Boom Formation is over 100 m thick and known for its rhythmic variation of fine-grained and coarse-grained layers, these numbers of measurements can be considered insufficient to be truly representative for the entire formation.

Instead of performing more measurements to improve the representativeness, a different strategy was elected. Throughout the history of Boom Clay research, a large number of grain size measurements have been performed. The distribution of clay minerals, which determine to a large extent the CEC and SSA, is known to be related to the grain size, with most clay minerals occurring in the finer fractions. This implies that it should be possible to relate the grain size distribution to the CEC and the SSA.

In a first step, the complete set of grain size measurements were harmonized. Due to differences in the sample preparation over the years, including the inconsistent use of an ultrasonic probe for dispersion, the distributions differ from one dataset to the next. For the conversion, all grain size data was transformed using a centered log ratio transformation (Aitchison, 1986). Partial least squares regression (PLSR) models (Wold, 1975) were built based on training data consisting of samples from identical depths in the Boom Formation. The harmonized grain size data were then used to predict both the SSA and the CEC, again using two separate PLSR models, resulting in 222 data points for both parameters. The increased sample size and the accompanying increased representativeness implies that future modelling efforts will be more accurate. In the future, efforts can be done to move towards a continuous record of the CEC and SSA over the entire formation, by including down-borehole measurements in a statistical model.

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Synthesis of an imidazoline-nickel phyllosilicate monolith and its optical properties

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Layered inorganic/organic hybrids have attracted much attention as potential novel materials, as the presence of both inorganic and organic moieties gives them interesting properties. They have reported layered inorganic-organic hybrids in which the inorganic and organic moieties bonds covalently with each other.$^{1)}$ We use the term "monolith" for this type of layered compound here. This present study aimed to synthesize a layered inorganic-imidazoline monolith with a transition metal as an octahedral cation of the inorganic moiety. Further we have investigated ultraviolet-visible (UV-VIS) absorption and emission for the synthesized monolith.

An imidazoline derivative was slowly added to aqueous solutions or suspensions of metallic salts or metallic hydroxides under continuous stirring at room temperature. After sufficient stirring, starting mixtures were obtained. The starting mixtures were reacted at 80 ~ 170°C for 10 hr. to 1 week. Reference samples were also prepared with using tetraethoxysilane ($Si(OC_2H_5)_4$) instead of the imidazoline derivative. Samples after the heat treatments were characterized by inductively coupled plasma optical emission spectroscopy (ICP-OES), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR), UV-VIS-NIR (near infrared), and fluorescence spectroscopies.

XRD and FT-IR results show an inorganic moiety is similar to 2:1 phyllosilicates, and FT-IR spectra show several absorption peaks attributed to an imidazolyl group and Si-C. A model for the synthesized samples is proposed, which has a layered structure and comprises inorganic layers with the imidazolyl group located between them. A cation octahedral sheet is sandwiched between two siloxane sheets to form a 2:1 phyllosilicate-like layer, and each siloxane sheet bonds to the imidazolyl group via the S-C covalent bond. The synthesized monolith with a transition metal exhibits absorption relating to the inorganic moiety and imidazolyl group and scant emission. Another monolith without the transition metal exhibits both absorption and emission in relation to the imidazolyl group.

Acknowledgement We are grateful to Mr. S. Takenouchi, NIMS, for the elemental analyses as well as Mr. K. Kosuda, NIMS, for the SEM observation.

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Cristal-chemical characterization of clay at the nano and subnanoscale: new opportunities from Cs-corrected TEM in scanning and precession modes.

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Several types of characterization techniques, such as XRD, IR spectroscopy and thermal analyses, are commonly used for the determination of the phase composition and crystallographic structure of clay minerals in natural samples, including the quantification of the compositional and structural defects.

However, those techniques provide a statistical view of the occurrence of different clay particles, their polytypic variants and their defects in the sample. Therefore, the transmission electron microscope (TEM) may be a very interesting tool to complement these studies with the investigation of the crystal structure and heterogeneities at the scale of individual particles.

New Cs-corrected TEM equipped with various detectors allow simultaneous acquisition of different information (crystal morphology, elemental composition and valence, and atomic arrangement in the direct and reciprocal space) on the same particle with improved spatial resolution, using lower voltage less destructive for sensitive materials such as clay.

Stacking faults and interstratification of different crystallographic layer types of similar or different chemical composition in mix-layer phases can now be imaged in high-angle dark field scanning mode (HRSTEM-HAADF), which displays chemical contrast richer in information that conventional HRTEM phase contrast. Coupled with X-ray spectroscopy (HRSTEM-EDS), it offers the possibility to image the heterogeneous distribution of interlayer cations that may exist at the nanometric or atomic scale.

At a larger scale, precession electron diffraction, used together with tomography, allows probing the 3D reciprocal space of individual clay particles and investigates their crystallographic structure. Finally, electron diffraction acquired in the scanning mode allows mapping of the crystal phase distribution among the clay particles, or their crystal orientation distribution to investigate the texture of the clay platelets assemblages.

Compositional constraints in inferring the provenance of 2nd c.AD pottery from Roman *Napoca*

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The provenance of the 2nd century A.D. household pottery found in the city of *Napoca* (present day Cluj-Napoca, Romania) in the Roman Dacia province were studied by means of optical microscopy, X-Ray powder diffraction and cold field emission scanning electron microscopy coupled with energy dispersive X-ray spectroscopy in order to find if they were locally produced or were imported. Geological marls and marly clays of Miocene age cropping out in the surroundings of the city were sampled and compositionally compared with the sherds.

The sherds show a homogeneous composition, with a microcrystalline to amorphous illitic/muscovitic matrix embedding small-sized aplastic inclusions. The latter are mostly quartz and feldspar, rare lithoclasts such as quartzites and micaschists. Fine-grained carbonates as well as Miocene foaminifera are frequent.

The Middle Miocene marly clay from the surroundings of the site shows similar mineralogical and micropalaeontological content (Miocene foraminifera) to the ceramic sherds and proves to be the best candidate for the raw material used to produce this household pottery.

The combination of different analytical methods, including micropaleontology, is a powerful tool in inferring the knowledge of the local population in searching nearby raw materials suitable for good quality ware. The potters found excellent carbonate-rich clays (marly clays) which most likely were well processed and the foraminifera tests were preserved even at higher temperature of firing. The mineralogy and the paleontological content prove that Miocene marls and marly clays were used to produce, locally, the pottery.

Acknowledgements. The authors thank Dr. L. Silye for help in identifying the fossil remnants. The study was financed by the Excellence Research Program (Romanian Ministry of Education and Ministry of Research) through the UEFISCDI/CNCS projects PN-II-ID-PCE-2011-3-0881 and PN-III-P4-ID-PCE-2016-0229. C.I. acknowledges subsidy by the Russian Government to support the Program of competitive growth of Kazan Federal University.

Functionalization of montmorillonite clay via intercalation of amino acids for anti-acne clay mask formulation

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The Philippines is rich in clays and clay minerals but with limited applications for utilization. Clays have a wide range of applications because it can be modified further through functionalization. Functionalized clays can be utilized in the cosmetics industry which is one of the growing industries in the country because of the various skin conditions experienced by Filipinos and because of the growing interest in utilizing functionalized clay for cosmetics application, specifically for clay masks. However, some functionalizing agents used for clay were found to be toxic at significant concentrations according to some studies.

This study aimed to functionalize montmorillonite clay using amino acids such as arginine, leucine, histidine and lysine for clay masks for acne treatment. Expansion of the interlayers of purified montmorillonite samples due to the intercalation of the amino acids were confirmed via XRD. The final clay mask product exhibited an acidic pH due to the binding of the basic chain of the amino acids to the clay structure. The amino acid-functionalized clay was found to release nitric oxide and collagen for acne treatment and damaged skin repair.

Multiple light scattering, sedimentation behaviour of suspensions and crystallite size features of reference clay minerals.

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Mechanisms of sedimentation of a set of clay minerals with different compositions and a wide range of crystallite size (in the diffraction direction 001 *) were studied. The studied clays were: a dioctahedral smectite (SWy-1, Wyoming Bentonite SWy-1), dioctahedral calcium smectite (SAz-1, Cheto Bentonite), trioctahedral saponite (EST sample from Yunclillos), a trioctahedral hectorite (BHT, trade name Bentone HC) and a reference kaolinite (KGa1, Georgia kaolin).

A correspondence between crystallite thicknesses measured from scanning electron microscopy (SEM) images and apparent crystallite sizes calculated from X Ray powder diffraction data (XRPD) in the 001 * diffraction were found. In the case of kaolinite the data obtained by XRPD were similar to the mean size obtained by SEM. However, in all smectites, the data obtained by XRPD were close to the maximum frequency or to the minimum of each statistic of SEM size measurements.

Crystallite sizes were measured for the considered clay minerals were also obtained in different fractions of the clays obtained by sedimentation (from < 20 µm to <0.5 µm) of each sample, and no significant differences were found in each sample except for smectites EDS-SWy-1 and EDC- SAz-1

The main mechanisms of sedimentation for the selected clay minerals were studied by means of multiple light scattering (MLS) and correspondence between greater backscattering velocity and greater crystallite sizes was found.

The predominant sedimentation mechanisms recognized by MLS were: sedimentation by agglomeration (in KGa1 and SAz-1), sedimentation by compression (SWy-1) and heterogeneous sedimentation in BHT and EST. The order of backscatter variation velocity observed was: KGa1 > SAz-1> SWy-1> BHT> EST, and the higher values corresponded to minerals of greater 001* crystallite sizes.

On the influence of the presence of oriented fibers within random powders of palygorskite in X-Ray diffractograms

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Palygorskite is modulated phyllosilicate with an extremely complicated structure which is still discussed nowadays (García-Rivas *et al*., 2017). The first structural model was proposed by Bradley (1940), who considered a monoclinic structure, belonging to the *C2/m* space group, for a sample of palygorskite from Attapulgus (Georgia, U.S.A.). Years later, several authors such as Zvyagin *et al*. (1963) and Drits and Sokolova (1971) described palygorskites having also a monoclinic structure, belonging to the *P2/C* and *C2/m* space groups respectively. On the other hand, Preisinger (1963) described an orthorhombic structure belonging to the *Pbmn* space group for a palygorskite from Palygorskaja. A comparative study by Christ *et al*. (1969) showed that palygorskite could either have a monoclinic or an orthorhombic structure. This was ratified by the research of Chisholm (1990), who proposed that palygorskite could be a mixture of phases, therefore explaining the complexity of the resolution of its structure. Several Rietveld refinements were performed by different authors considering the two phase model (Artioli *et al*., 1994; Chiari *et al*., 2004; Post and Heney, 2008), although the results are not completely satisfactory.

An interesting question which has barely been considered until the moment to explain the difficulty of the resolution of its structure is if the fibrous morphology of palygorskite could enhance a certain degree of orientation while conducting random powder diffraction experiments. The routine side packing of samples for conventional X-Ray diffraction as well as the placing of random powders within rotating capillaries for the performance of high resolution X-Ray diffraction experiments at Synchrotron facilities can enhance certain degree of orientation of the fibers, making them perpendicular to the X-Ray beam.

To observe this influence of orientation, simulations considering a slight variation of the structural models proposed by Chisholm (1992) were carried on using XOP/XPOWDER, for powder diffraction simulations, and ANAELU, for oriented fiber diffraction simulations. These simulations were latter summed in different proportions to observe the role that certain proportions of oriented fibers play within the resulting diffractograms, focusing our attention on the region of interest defined by Christ *et al*. (1969) and Chisholm (1992) comprised between 4.5 and 4.0 Å.

Unfrozen water in clays and the freezing characteristic curve of geosynthetic clay liners

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Geosynthetic clay liners (GCLs) are bentonite-based engineered hydraulic barriers with worldwide applications, including recently in the Arctic and Antarctic [1] circumpolar regions. Adequate hydration of the bentonite component of the GCL is necessary for durable and safe hydraulic performance, but under freezing conditions encountered in these regions, hydration is strongly controlled by the ice formation and melting processes, which are best understood through the freezing characteristic curves (FCC) of the bentonite. During either of these processes, the pore-structure can change in smectites, making complete characterization difficult. Until now, limited experimental data exists for GCL behavior in extremely cold conditions.

As fine-grained materials, the pore structure of a particle of clay mineral (containing perhaps many thousands of individual layers) controls water uptake and transfer [2]. The present research demonstrates that application of inelastic neutron scattering (INS) to Na-montmorillonite at different initial water conditions, enables for the first time an assessment of the FCC for a commercial GCL. Analysis of the elastic fixed window (EFW) curves of variously hydrated montmorillonite, as a function of temperature, enables determination of the fraction of unfrozen water at any sub-zero temperature [3].

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Migration and stabilization of uranium in clayey weathered waste rocks

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Granitic waste rocks piles which measure in the hundreds of metric tons in France is the heritage of 50 years of uranium mining. These rocks are predominantly overburden (<20 ppm) removed to access to the ore body with a few percent of economic waste rocks below the lower end of the cut off level (100 ppm). Weathering of the piles induces localized uranium migration and subsequent reconcentration systematically observed in the clay fraction of the arena and the technosoils. The understanding of the long term reactivity of these rocks and their geological repository is essential for developing strategies which address related environmental issues.

These waste rocks piles are described as technoregoliths with a high specific surface area and large porosity. The fate of U depends on the mechanical and chemical alteration efficiency and of its mineralogical host. U(IV) form, which composes the uranium ore (uraninite ($U^{IV}O_2$) or coffinite ($U^{IV}(SiO_4)_{1-x}(OH)_{4x}$), and known to be insoluble in reducing conditions, is rarely observed and essentially in micrometric minerals trapped in quartz grains. But uranium in monazite or remaining uraninite trapped in weathered feldspar or biotite is potentially mobile. Prevalent oxidizing conditions cause the formation of clay size $U^{(VI)}$ phases such as secondary uranyl phosphates concentrated in the fine fraction (2µm) of the arena or the technosoils associated to phyllosiclicates or eventually ferrihydrite. The high cation exchange capacity of these minerals enhances the stabilization of U by sorption process. The variability of species among the phyllosilicates, smectites, kaolinites, vermiculites, chlorite, underline a heterogeneity among the alteration processes. In paleotechnosoils a competition in the U sorption between phyllosilicates and ferrihydrite may be also observed.

Finally if XRD, SEM, TEM and electron microprobe techniques provide valuable spatially-resolved data, they do not allow the determination of U speciation at the molecular scale. X-ray Absorption Spectroscopy experiments, as EXAFS and XANES, complete these observations providing unique information on U-speciation in such oxidizing conditions favorable to the mobility of U but where U sorption on Fe oxy-hydroxides and/or smectites contribute to its retention.

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Tayal, A *et al.* RSC Advances (**2019**), submitted

Reactivity of different flash-calcined clays for geopolymer synthesis

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Over the last decades, geopolymers have gained tremendous interest as promising new binders, environmentally friendly and with good working properties. These ecomaterials result from the activation of an aluminosilicate source by an alkaline solution at room temperature. Metakaolin is one of the most used aluminosilicate precursor due to its high purity and reactivity. Nevertheless, research of low-cost and more available materials has encouraged many investigators to turn to the use of common clays and industrial co-products. In this topic, the objective of this work is to evaluate the reactivity of various flash-calcined aluminosilicate sources at different temperatures. At first, the reactivity of the different aluminosilicate sources was estimated using chemical and structural investigations by XR diffraction and ^{27}Al NMR spectroscopy. Then, the feasibility of geopolymer materials was evaluated. Finally, the measurement of mechanical strength was evaluated by compression tests.

Whatever the aluminosilicate source, the reactivity increases essentially with the increase of purity degree, amorphous phase and wettability value. Further structural informations were given by ^{27}Al NMR concerning the effect of heat treatment temperature on the conversion rate of $Al^{(VI)}$ and $Al^{(V)}$ species to $Al^{(IV)}$. Whatever the studied clay, the flash calcination induces a partial conversion of aluminum compared to furnace calcination. For example, a flash-heat treatment of kaolin from 550 to 700 °C increases the conversion rate from 0.17 to 1.58. The formation of mullite is also noticed. In the case of clays mixture, the octahedral aluminum is present and only decreases in percentage area with the decrease of temperature from 600 to 750 °C. These results confirm that flash heat treatment leads to a partial dehydroxylation of the clay minerals. Moreover, the feasibility study evidences the suitability of the different sources after heat treatment to produce geopolymer materials with different mechanical properties.

Direct TiO_2 immobilization onto palygorskite nanofibers by one-pot mechanical synthesis: characterizations and photocatalytic activity

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The immobilization of various compounds, especially metal oxides like TiO_2, onto clay mineral particles is generally reported to be achieved by wet routes (sol-gel, precipitation, solvothermal…) implying ion-exchange or grafting to edges silanol sites mechanisms[1,2]. This functionalization way of clay minerals, is laborious, time and solvents consuming and yielding to small laboratory amounts. Thus, up scaling of these wet processes for industrial applications is not viable. Thereby, there is a need to find out alternative synthesis method to overcome this issue.

This study is devoted to the successful immobilization of TiO_2 onto Palygorskite fibers surfaces via a one-pot dry mecanochemical route. Indeed, the elaboration procedure smartly involved an in-situ reaction between accessories carbonates present in the raw Moroccan palygorskite clay used in this study and titanyl sulfate ($TiOSO_4$) precursor under variable grinding conditions, essentially the balls /loading mass ratio and the rotation velocity. Upon heat treatment at 600°C in air of as-grinded samples, anatase TiO_2 nanoparticles (≈ 8 nm of average size) were evidenced by XRD and TEM to be supported onto the surface of palygorskite fibers. The developed supported photocatalysts TiO_2/palygorskite exhibited interesting activity towards the removal of Orange G (OG) dye from aqueous media under UV[1)].

The main advantages of this synthesis process are that TiO_2 growth on palygorskite can be achieved by using directly raw clay without needing to be previously purified. Furthermore, it is eco-friendly since no solvent is used and it can yield important amounts. All these advantages make this dry route very attractive for large-scale production[1)].

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Identification and Characterization of Phyllosilicates by Laser-Induced Breakdown Spectroscopy

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Phyllosilicates and other secondary silicate minerals produced by aqueous alteration provide insight into the weathering environment in which they formed, including constraints on ancient water availability and composition as well as the oxidation state. Consequently, these minerals are crucial for the reconstruction of past environments and serve as key indicators of potentially habitable terrains throughout our Solar System. Remote sensing techniques and direct contact science have measured widespread occurrences of phyllosilicates in the Noachian-aged crust of Mars, predominantly nontronite and Mg saponite[1]. Both dioctahedral and trioctahedral smectite clays have been identified in Gale Crater by NASA's Mars Science Laboratory (MSL)[2].

However, although the laser-induced breakdown spectroscopy (LIBS) instrument, ChemCam, is the most used instrument on MSL and is relied upon to direct the rover towards high-fidelity science targets, the LIBS spectra of most phyllosilicates have never been reported, nor has a general review about their major spectral features been written. There is a reasonable basis to hypothesize that ChemCam could effectively identify phyllosilicates as previous studies have demonstrated that broadband LIBS spectra, which contain a material's complete chemical signature, can be used as a powerful tool for geomaterial identification and discrimination[3].

The first part of this study is focused on the capability of multivariate analysis techniques applied to LIBS for the discrimination of a variety silicate minerals. Silicate samples from all the major structural groups were used: 3 cyclosilicates, 6 inosilicates (single chain and double chain structures), 2 sorosilicates, 3 tectosilicates, 6 nesosilicates, and 2 phyllosilicates. Using soft independent modeling of class analogy (SIMCA) with the commercial software *The Unscrambler X*, all silicates were correctly classified with no unclassified spectrum. The second part of this study concerns the characterization of phyllosilicates. Preliminary results are equally encouraging; principal component analysis successfully distinguishes dioctahedral and trioctahedral clays.

The results suggest that phyllosilicates can be reliably detected and adequately characterized using LIBS. With MSL approaching the clay-bearing unit and LIBS instrumentation integrated into upcoming exploration missions, we expect that planetary remote sensing could be meaningfully enhanced by a thorough understanding of the LIBS spectral properties of phyllosilicates. Future work will investigate the fusion of LIBS and Raman spectroscopy data collected under simulated Martian conditions to further understand the power of laser spectroscopy for the identification, classification, and characterization of phyllosilicates on Mars.

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Diagenesis of a Malmian source rock, Vienna Basin: Focus on matrix and pores

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In this study we take a closer look at diagenetic processes and pore development in the matrix of the main source rock for oil and gas in the Vienna Basin, the autochthonous Malmian marls of the Mikulov Formation. These mudstones reach a thickness of up to 1000 m. 46 core samples from 10 different wells which penetrated the Mikulov Formation over a depth range of 1400 m to 8551 m were available. This gives a unique opportunity to study the mineralogical diagenesis within one formation from shallow to deep burial.

Bulk and clay mineralogy of the core samples were analyzed with X-ray diffraction and quantified. The microfabrics of the mudstones were studied on argon ion milled samples with a FEI Quanta 400 FEG scanning electron microscope (SEM).

The bulk samples contain minor amounts of quartz, plagioclase, pyrite and a high amount of calcite; the clay mineral content of the bulk samples ranges between 14 to 47%. The clay fraction contains a prominent illite-smectite (I-S) mixed-layer mineral, illite, chlorite and kaolinite. The amounts of I-S and kaolinite decrease with depth, illite and chlorite increase with depth. A diagenetic overprint can be demonstrated and involves a gradual transformation of smectite to illite through mixed-layer I-S intermediates. The illite content in I-S ranges from 25% for the shallowest sample to 90% for the deepest sample. The ordering of the mixed layer I-S changes with increasing depth from R0 to R1 and R3. The R1 ordering of the mixed-layer minerals corresponds with vitrinite reflectance values of 0.4 % to 0.6 % and a depth of approximately 3000 m.

The elements resulting from the illitization of smectite in the matrix are considered to be sources for a variety of late diagenetic mineral cements. For example, illitization is assumed to provide Fe and Mg for chlorite formation and ferroan dolomite precipitation. Illitization is also a potential source for Si, which is needed for quartz cementation.

During diagenesis not only cements formed, but also nanometer to micrometer size pores developed because of particular framework features or dissolution processes. Organic matter pores (bubble and foamy) developed in deeper, thermally mature samples. Phyllosilicate framework pores between harder grains are commonly observed. Diagenetic cements, like quartz overgrowths or carbonate cements occasionally keep pores open. Additionally, we find fluid inclusion pores in calcite and pores caused by partial dissolution along carbonate grains. From SEM photomicrographs it cannot be observed if these pores are connected, but most likely they do contribute to the effective porosity and gas storage capacity of these rocks.

A new genetic classification of bentonite deposits

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Bentonites are smectite-rich rocks and an economically significant commodity with an astonishing wide variety of applications. This diversity of usage is mostly related to the variable chemical and structural composition of the smectite as well as the type and amount of other non-smectite minerals in the clay. Both factors are strongly governed by distinct processes of clay formation in a specific geological environment and in some cases also by the post-formational overprints. The existing genetic classification schemes of bentonite deposits are often problematic as some proposed classes are in part not exclusive, clear classification criteria are sometimes missing and/or import processes are missing.

A new classification scheme will be presented here. Bentonite deposits are divided into primary and secondary types. **Primary** deposits are the dominant group and formed either by metasomatic processes that lead to the in-situ alteration of an Al-Si-bearing rock into a smectite-rich clay (Transformation subtype) or by direct precipitation from a aqueous solution (Neoformation subtype), while **secondary** deposits are sedimentary accumulations of detrital expandable clay minerals. The latter type is rare and very difficult to identify. **Transformation** bentonites form mostly from alteration of often glass-rich **volcanic or volcaniclastic rocks** in a wide range of geological environments including marine and terrestrial lacustrine settings and are dominated by Al-rich dioctahedral smectites. The glassy protoliths can accumulate in close vicinity (**proximal**) of the volcanic vent, mostly pyroclastic flows and ash-fall deposit, or in a **distal** setting where rather thin fine-grained ashbeds are generated. In rare cases even **non-volcanic rocks** can be transformed to bentonites. The chemical composition of the precursor volcanic rocks from basaltic to rhyolitic, the temperature of smectitization, the involved fluids and the architecture of the hydrologic system are important factors influencing bentonite quality. The role and identification of weathering, hydrothermal and diagenetic processes and later overprints will be discussed.

Neoformation bentonites are the product of chemical precipitation from aqueous bodies, mostly restricted saline and/or alkaline lakes. The dominant trioctahedral clay minerals are saponite and hectorite and very rarely kerolite-smectite or possibly stevensite. The role of trace element geochemistry, ancillary mineral analysis and micromorphological studies in the identification of the genesis of these clays are highlighted.

Ion transport in clays: Comparing ion-exchange, surface-diffusion, and diffuse-layer modeling approaches

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Clays are ideal barrier materials for waste disposal sites. Their low hydraulic conductivity limits mass transfer to diffusion, and their large surface charges retain contaminants. Moreover, they swell upon contact with fresh water, which is important for sealing. All these favorable features of clays are related to their nano-porous structure and to their chemical-mineralogical properties. At the same time, these features complicate the modeling of solute transport in clays. Various couplings between ion transport and the local surface properties exist, and it is a challenging task to include them into macroscopic, continuum-scale transport models.

Models for reactive transport rely on many sub-models that describe for instance interactions between ions and the clay surfaces (sorption models). In this presentation, we outline differences in ion transport that arise from the use of various sorption sub-model concepts. We compare results obtained when considering sorption by ion exchange, sorption in a diffuse layer (with a mean electrostatic or Donnan potential), or a combination of both, within a single porosity or a dual porosity concept. We first focus on anion accessibilities (ratio of anion content in the clay to that in the equilibrium solution) and total cation contents. Interestingly, the total cation content is not just a linear combination of the limiting ion exchange and Donnan cases; it can reach a local minimum for an intermediate case. This makes the estimation of the degree of ion exchange versus Donnan sorption from experimental data (for instance from the Mont Terri DR-A experiment) difficult.

The type of sorption model has also a strong effect on modeled diffusive transport. Simulations of the DR-A experiment show that only an intermediate case can approximately describe the data. However, the transport of Cs is underestimated, unless its diffusion coefficient is increased. An increase of the Cs effective diffusion coefficient can for instance be obtained by a surface diffusion model, which assigns site-specific mobilities to sorbed Cs species. An integration of the surface diffusion model into the mixed ion-exchange/Donnan model needs still to be done.

We conclude that models of different degree of complexity are available that can be used to reproduce many observed experimental features. However, often it is not possible to derive all parameters independently, which limits the quantitative predictive capacity of the complex models. Further experiments that introduce strong perturbations are required in order to better discriminate between different model concepts. This is especially relevant with respect to simulations of interfaces between geochemically contrasting systems (e.g., cement-clay) in engineered barriers, where mineral reactions and porosity changes influence transport. Predictions of the long-term behavior of these interfaces require sophisticated reactive transport models that can reliably handle all expected couplings and feedbacks.

The effect of hydration on the vibrational spectrum of hectorite

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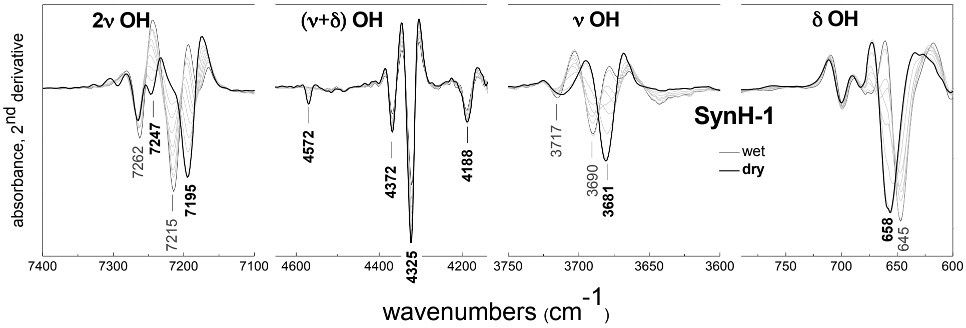
A recent investigation of synthetic hectorites [1] has indicated that their ambient infrared spectra can be described by a convolution of two forms that can be obtained pure at ~80% RH ("wet") and ~5% RH, purging by dry N_2 or heating at >120 ºC ("dry"). For example, the main Mg_3OH stretching mode of Laponite RD was reported to exhibit a ~10 cm^{-1} red shift upon drying that was reversible upon rehydration.

Such hydration effects complicate further the infrared spectroscopic identification of trioctahedral magnesian clay minerals in multimineralic samples, which is already perplexed by interlayer cation effects [2].

In addition, the hydration dependence of the spectra of hectorite appears similar to that reported earlier for sepiolite and trioctahedral-rich palygorskite [3] suggesting that the latter may not be signaling the modulated structure of these minerals as suggested previously.

For these reasons, we report here a very detailed vibrational comparison of synthetic (SynL-1, SynH-1) and natural hectorite (SHCa-1), all from the Clay Minerals Repository of the CMS, as a function of hydration. By analogy to the work of Bukas et al. on sepiolite[4], synchronous ATR and diffuse reflectance NIR data (8000-600 cm^{-1}) are acquired non-invasively as a function of variable H_2O or D_2O hydration and analyzed with 2nd derivatives, as in the figure below.



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Clay availability, ceramic production and import: the case of Apulian pottery and building materials.

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The correlation between the availability of certain raw materials, the production of a specific ceramic type and the import of same/other ceramic types is the topic of this presentation. The case study is provided by the research conducted over the last fifteen years in the territory of northern Puglia.

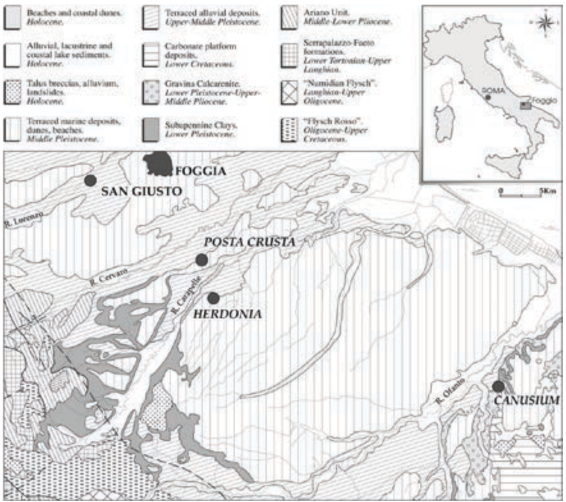

Figure 1. The locations of the archaeological sites and a geological map of the territory under examination.

To date, a sampleset of 291 ceramic finds and 78 samples of ceramic raw materials have been collected and analyzed. The first repertory includes ceramics with different functions (i.e. fine table ware, coarse cooking ware and building materials), coatings (mainly ocher) and structural elements taken from the kilns, covering a wide chronological span (from the 1st century BC to the 8th century AD). The second, instead, includes samples taken from the Sub-Apennine clays, the alluvial deposits and the terraced alluvial deposits, widely outcropping in the territory under investigation.

Raw materials selection, transportation and transformation represented the central concern of our researches, in fact, the characterization of the clay deposits, the assessment of their production potential and a wide range of critical topics, ranging from the preparation of the pastes, to their firing, eventual decoration and commercialization have been taken into account.

The applied methodology implied the comparison and integration of the entire range of geochemical, mineralogical and petrographic analyses performed on both raw materials and ceramics. In this way, which and how local resources were exploited was reconstructed and a "local" information on the best routes to transport raw materials and finished products, together with the traveling times between one site and another, was obtained through Geospatial network analysis.

Stamped bricks and tiles from southern Tuscany (Italy): the exploitation of local raw materials and the imports

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Following the encouraging results obtained from the study of the stamped bricks found at *Cosa* (Gliozzo 2013), a new research has been set on the study of stamped bricks found north of *Cosa*, at *Rusellae*, *Saturnia*, Aianova (Scansano), *Vetulonia* and *Populonia*.

Integrating geological information on locally available raw materials, with geochemical, mineralogical and petrographic results on thirty samples of bricks and tiles, and with archaeological, epigraphic and proposographic data, the overall research focused on 1) the geochemical and mineralogical-petrographic characterisation of the stamped bricks; 2) the distinction between municipal (i.e. local) and urban (i.e. Rome and Tiber Valley) productions; 3) the exploitation modalities of local clayey sources for brick production.

These stamped bricks have never been the subject of an archaeometric investigation and, even extending the area of interest to the stamped productions of southern Tuscany, the only study available to date is the one on *Cosa*'s bricks (Gliozzo 2013). Even pottery found on the same sites has been sporadically studied, not to mention the rarity of archaeometric investigations overall performed on the *instrumentum domesticum* and on local raw materials.

Consequently, this study provides original and indispensable information for a correct reconstruction of both production dynamics and socio-economic relationships in the territory under investigation. In fact, a small part of the investigated repertoire turned out to be of local production, insisting on the local marine clays. The majority of stamped bricks found in the territory under investigation was of "urban production", i.e. imported from the Tiber Valley and the territory surrounding the ancient boundaries of Rome.

Molecular dynamics simulation of an isolated aluminosilicate nanotube (imogolite) in water: Diameter effect on the water properties

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Perfectly monodispersed samples of nanoparticles with a predetermined shape at a specific size is the daily challenge of many researchers around the world. Imogolite is a nanotube that is synthesized monodisperse in diameter. Imogolite was discovered in the late 1960s in volcanic soils and, in 1977 a protocol for their synthesis was published. The chemical formula of imogolite is $(Al_2SiO_7H_4)_{2N}$, with N = 10 for the natural case and N = 11-15 for the synthetic one. As mentioned before, this clay nanotube (NT) has the characteristic of having effective control of its diameter during the synthesis and based on experimental evidence; imogolite nanotubes are highly monodisperse in diameter regardless of the diverse synthesis conditions. The diameter of the NT is around 2.5 nm and its length of hundreds of nanometers.

In this presentation, simulations for isolated imogolite immersed in water are presented changing the values of N from 8 to 15. We also simulated the case of a theoretical plane case (equivalent to N tending to infinity). These systems are studied using Classical Molecular Dynamics Simulations (MD) with LAMMPS and Grand Canonical Monte Carlo (GCMC) simulations. Both employ CLAYFF force field and SPC water model. GCMC is used to estimate the water density in the inner pore of the imogolite at 300 K. Using this water density in the inner pore the MD simulations are initialized. Periodic boundary conditions along the axis of the NT are considered in the NVT ensemble at 300 K. The simulation analysis includes (i) one-dimensional (1D in radial direction) water density profiles form the center of the NT and (ii) water diffusion coefficients in cylindrical regions defined from the center of the NT.

Considering that this session is interdisciplinary, technical details of the computer simulations will not be shown in depth during the presentation, but the emphasis will be given to the importance of the results to motivate the experimental and theoretical collaborations.

Structural transformations of calcined [Ti,Zr]-pillared montmorillonites in relation to thermal evolution of hydrolysates obtained from [Ti,Zr]-pillaring solutions

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Montmorillonites containing mixed [Ti,Zr] pillars are known for their unique physico-chemical (Bahranowski et al., 2015) and catalytic (Michalik-Zym et al., 2015) properties. The aim of the present study was to investigate the effect of heat treatment on the structural characteristics of [Ti,Zr]-pillared Kopernica (Slovakia) montmorillonite in reference to the thermal evolution of hydrolysates formed from the pillaring solutions (Bahranowski et al., 2019). The pH value of montmorillonite suspension during pillaring was 1.2, therefore two types of hydrolysates were analyzed: one obtained by lyophilization of the as received pillaring solution, with pH=0.6, and the other formed by lyophilization of pillaring agent alkalized to pH=1.2. Pillared clay (PILC) and hydrolysate precipitates were calcined for 3 h at 500, 800 and 1000°C, and characterized with PXRD, Raman spectroscopy and FE SEM/EDS. At 500°C a stable PILC structure was formed, but the nature of pillars remained obscure. At 800°C the PILC structure was destroyed, and, simultaneously, the evolution of $ZrTiO_4$ was observed, of crystallinity improving after treatment at 1000°C. Hydrolysate obtained from [Ti,Zr]-pillaring solution of pH=0.6, calcined at 500°C, contained a multiphase mixture of $ZrTiO_4$, Zr-containing anatase, and Ti-containing monoclinic zirconia. The material calcined at 800°C had a similar phase composition. Partial transformation of anatase component to rutile was observed only after treatment at 1000°C, due to the stabilizing effect of Zr admixture. $ZrTiO_4$ and ZrO_2 were the other crystalline phases present in sample calcined at 1000°C. The hydrolysate obtained from [Ti,Zr]-pillaring solution of pH=1.2, calcined at 500°C, yielded a single phase, identified as poorly crystalline zirconium titanate. $ZrTiO_4$, of increasing crystalllinity, remained the only phase found in precipitates calcined at 800 and 1000°C. The results indicate that pH=1.2, generated during pillaring after mixing of montmorillonite suspension with [Ti,Zr]-pillaring solution, favors formation of [Ti,Zr] heteropolycations, which transform into mixed [Ti-Zr] pillars of unique properties.

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Acknowledgments: This work was supported by the NCN grant Opus 2017/25/B/ST10/00768.

Cemented micro-scale fractures in impure chalk sequence: towards understanding clay origin in black chalk exemplified by the Grybów Marls (Oligocene, Outer Carpathians, Poland).

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Fractures form in response to pressure in rocks that have brittle mechanical properties. The fractures provide leakage pathways for fluids, especially in tight, low permeable lithologies. The sequence of the Grybów Marls, which is about 400 m thick, consists of Oligocene impure-chalk type rocks rich in organic matter, deposited during the closing stage of the Outer Carpathian Basin, during its shallowing and separation from the Tethys Ocean. The Grybów Marls are expected to be source rocks for the Outer Carpathian hydrocarbon deposits. The sequence was strongly folded, overthrusted, thrust faulted and exposed at the surface in tectonic windows. The rocks are comprised of 19-89% carbonates (4-48% calcite coccolith fragments, and up to 85% dolomite), 5-53% clay, 4-18% quartz, 1-8% feldspars, and 1-10% pyrite. TOC reaches values from 0.24% to 4.14% and He-porosity ranges from 3.33% to 20.83%. The clay is represented mostly by highly illitic, ordered illite-smectite (originating from the alteration volcanic glass), minor kaolinite, and rare chlorite (Górniak 2017). The outcrops exposed by the Strzylawka Stream located in the Grybów Tectonic Window were measured and sampled (32 samples). Imaging was performed using both an optical and a field emission scanning electron microscope.

The study revealed: (1) a variation in original sediment compositions resulted in alternating fractured and non-fractured beds in the sequence - carbonate-dominated beds (especially dolomite-bearing) revealed microfractures, whilst clay-rich beds revealed ductile deformations; (2) subhorizontal microfractures are postulated to have developed from horizontal stress applied through tectonic compression, whereas the subvertical microfractures formed due to gravity-loading vertical compression related to overthrusting; (3) both subhorizontal and subvertical microfractures were occluded first at their walls by carbonates, but in the former Fe-dolomite and in the later calcite were found to occur; (4) during the final stage of microfracture cementation kaolinite was formed; (5) the presence of secondary organic matter in association with kaolinite suggests hydrocarbon flowed through the microfractures; (6) the source of Mg and Fe for Fe-dolomite that occluded subhorizontal microfractures was related to smectite to illite conversion; (7) the source of Ca for calcite that occluded the latest subvertical microfractures was related to a pressure solution of bioclasts; (8) the source of Si and Al was related to decomposition of remnants of volcanic glass, and the presence of organic acids in the late diagenetic pore solutions was favorable for kaolinite crystallization; (9) these studies proved the authigenic origin of kaolinite formed in black impure chalk, and the process of kaolinite crystallization was associated with the flow of hydrocarbon through the microfractures.

Electron radiation damages to lamellar hydroxides: the case of portlandite and brucite

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Portlandite $Ca(OH)_2$ and brucite $Mg(OH)_2$ are isomorphous. They belong to the family of CdI_2 type compounds with a layered structure [1], giving them interesting physico-chemical and electronic properties for a number of industrial applications. Commercial powders were electron-irradiated at 2.5 MeV, room temperature and high dose rate (~10^8 Gy/h) using the accelerator NEC Pelletron of the SIRIUS platform (Ecole Polytechnique, Palaiseau). They are found stable up to doses in the range of a few GGy [2].

In this paper, we compare the thermal and electron radiation effects, knowing that, according to the available literature, the thermal and electron beam induced decomposition are considered to proceed in a similar way and in an extremely ordered manner, certainly for brucite and by extension for portlandite.

In these layered compounds, one would expect that irradiation, or heating as well, would result in a dilatation along the c – axis. This is just what the Powder X-Ray Diffraction study tells us. But surprisingly a non negligible contraction is remarked in the basal plane of brucite along the a –axis, while a slight dilatation is still observed in portlandite (see below). The results of the XRD study are detailed and hypotheses regarding the underlying damage mechanisms are formulated.

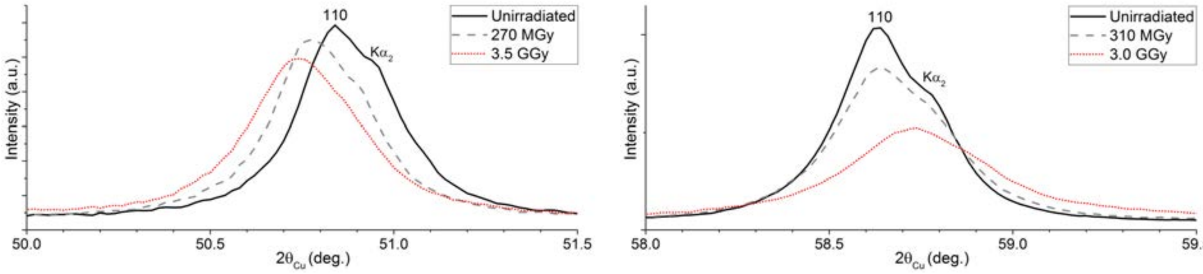

Figure 110 diffraction lines of portlandite (left) and brucite (right) prior to and after electron irradiation.

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Clay sedimentation control in dam reservoir of a semi-arid region: example of Takerkoust (Western High Atlas, Morocco).

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This study concerns the Takerkoust dam, located at the outlet side of N'fis watershed (Western High Atlas, Morocco). It is one of the main strategic reservoirs in Morocco. Built in 1935, it experiences a serious problem of siltation due to soil erosion. In order to reduce the risk of erosion, a new dam was implanted upstream, at Ouirgane in 2008. A paleo-hydrological approach was adopted to understand the sedimentary and environmental processes responsible for clay deposition in the Takerkoust reservoir. The chronology of flood event deposits was recorded by a serie of 8 bathymetric surveys conducted in the Takerkoust reservoir between 1988 and 2016. The sedimentological approach is based on 2 coring campaigns in the dam. A total of 45 samples were analyzed for their grain-size distribution by laser diffraction, clay mineralogy by X-ray diffraction and organic matter content by loss- of-ignition at 550°C (LOI). The uppermost soil horizons from the N'fis watershed, which represent the potential source of sediment in the reservoirs, were also collected and analyzed.

The sedimentary sequences show a laminated deposit organized in couplets with different textures and thickness. A clear correlation is observed between instantaneous maximum flow and the thickness of the couplets. Clay minerals are dominated by illite (30 to 80%) associated with smectite (0 to 55 %), chlorite (2 to 10 %), kaolinite (0 to 15 %), and mixed-layers (0 to 15 %). Smectite exhibits the most important vertical variation of the clay assemblage. Three types of variations can be highlighted:

(1) The intrasequential variation is related to differential settling mechanisms. Illite and kaolinite are deposited first and associated to coarser terms of the sequences. Smectites are associated to the clay fraction of the sequences,

***(2)* The intersequential variation is explained by the spatial irregularity of precipitations. The nature of the clay composition deposited in the Takerkoust reservoir during a given flood reflects the nature of the soils affected by the corresponding rainfall,**

***(3)* The third variation is materialized by an abrupt increase of smectites at the expense of illite at a core depth of ~ 70 cm. This change is consistent with the period of construction of the Ouirgane dam. This dam retains the clays from the Southern part of the basin. Currently, the Takerkoust reservoir receives only smectite-rich clays from the Northern part of the basin.**

This study emphasizes on both the nature and provenance of the clays that settled downinput in the reservoir basin and on the complexity of the mechanisms that controls deposition in semi-arid regions.

Mineralogical and physicochemical characterization for the valorization of the Miocene formations of the Taourirt basin (Eastern Morocco)

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The aim of this study is to characterize and determine a possible valorization of the Miocene sediments of the Taourirt basin. Mineralogical and physico-chemical characterization were carried by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Laser diffraction analysis and Atterberg limits.

The bulk mineralogy of all samples consists of clay (27%), dolomite (27%), calcite (25%) and quartz (19%) with traces of plagioclase (2%). The Tortonian formations consist of 31% of clay <2µm particles with predominance of palygorskite (25%) and smectite (25%) associated to illite (22%), kaolinite (18%), chlorite (4%) and mixed layer illite/smectite (3%). The Messenian deposits are composed by slightly less clay fraction (24%). Their clay assemblages are made by palygorskite (29%), illite (25%) and kaolinite (23%). The presence of palygorskites as fibrous structures is confirmed by SEM micrographs. All samples are rich in silt (2–63 µm) particles (75%) with on average 20% of clay (<2 µm) and 4% of sand (> 63 µm). The plasticity index varies between 13 and 47% for the Tortonian sediments and from 5 to 33% for the Messenian sediments. In addition, the plasticity limit ranges between 31 and 89%, while the elasticity limit is comprised between 27 to 43%.

The Miocene deposits in the Taourirt basin are marl-clay sediments with high carbonates content. They are characterized by a high diversity in their mineralogical composition and present a medium to highly plastic character. According to their projection on the Winkler diagram any application in the ceramic industry, especially as building materials as hollow product, roofing tiles, common bricks and masonry bricks, would require preliminary treatments: a degreaser must be added and the carbonates must be removed with use a particle size separation (250, 300, 600, and 1000µm) by sieving and passing each fraction to the diffractometer, for quantify the abundance of calcite by fraction. Because the elimination of carbonates by chloridric acid is not profitable considering the high of carbonates content (52%). The economic and industrial interest of marl-clay deposits from the Taourirt basin by consequent minimized.

Keywords: Clay minerals, X-ray diffraction, Atterberg limits, Valorization, Taourirt basin, Morocco.

Molecular Modelling of Bioorganoclays

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Interactions of microorganisms and their metabolic products with clay minerals is a common interfacial phenomenon in the environment. Composites assembled by the exchange of naturally occurring cations for charged biomolecular moieties, here referred to as bioorganoclays, are expected find their application as potential future sorbent materials with adjustable properties. However, the fundamental mechanisms governing the formation of biomolecule-clay interface are still poorly understood.

The objective here is to elucidate the complex mechanisms responsible for the formation of bioorganoclays via molecular dynamics simulations. This task includes the determination of probable molecular configurations and the identification of the corresponding binding sites and energies under various physical conditions. Our calculations explain how the phosphatidylcholine molecules arrange at the surface of the clay montmorillonite and indicate that the resulting composite conformational structure and stability strongly depends on the phosphatidylcholine loading.

Aspects of the surface and internal structure of halloysite nanotubes as revealed by various microscopy methods

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Halloysite nanotubes (HNTs) are increasingly being used in technologies such as drug delivery systems, polymer nanocomposites and as flame-retardant materials, amongst many others, where an understanding of the surface properties of the HNTs are a key consideration in the concept, design and technological success. The surface of individual HNTs is, however, most often considered as a simple model system that exposes a continuous outer surface siloxane sheet, an inner alumina sheet around the cavity of the central lumen and aluminol and silanol edge sites only at the termini of the tube and the leading edge of the scroll (Fig. 1). In the current work a variety of microscopy methods including transmission electron microscopy (TEM), atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been used to study the surface and internal structure of both cylindrical and prismatic forms of HNTs. The results show the presence of numerous steps and edges on the surface of HNTs in various patterns that reflect a generally more complex surface form (Fig 2). Imaging by TEM following the adsorption of gold nanoparticles attached to phosphate terminated carbon chains confirms the extent of pH dependent edge sites on the surface of the tubes and the reactivity of the internal lumen surface. The transition of the curved surface of cylindrical forms to the flat sectors of prismatic forms is also revealed by analysis of cross sections by TEM. Overall the microscopy reveals that a much more complex view of the oute riate though the simple aluminol model for the lumen appears co

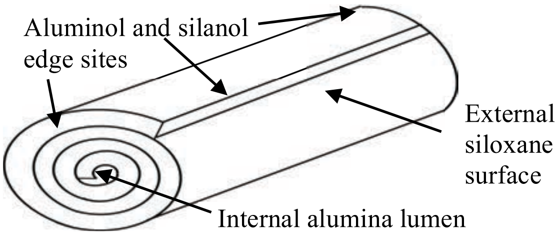

Fig. 1: Simple structure of halloysite nanotubes

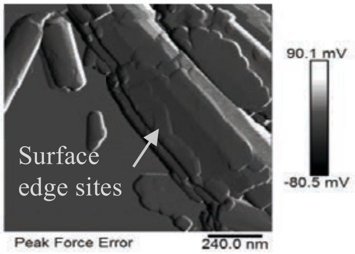

Fig. 2: AFM image of a prismatic halloysite

Mechanism of montmorillonite interlayer hydration from potential of mean force molecular dynamics simulations

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Molecular simulation has been used for over 20 years to investigate structural, thermodynamic, and dynamic processes of clay minerals and their fluid interfaces, including interlayer structure and dynamics, spectroscopy, and swelling. Based on approximate energy expressions dominated by pairwise electrostatic and van der Waals interactions (force fields, FF), clay mineral properties at nanometer length and nanosecond length scales are routinely obtained from such simulations. One property that has been difficult or impossible to explore with molecular simulation is the mechanism of intracrystalline swelling. While some studies have investigated the stepwise hydration of clay interlayers, the mechanism by which water molecules from pore fluids enter the interlayer region has been difficult to obtain from molecular simulation due to limitations in force fields, simulation timescales, or enhanced sampling methodologies. With recent improvements in FF methods (e.g., ClayFF) clay edges and edge-fluid interfaces can now be accurately modeled. In this work we incorporate advances in ClayFF and umbrella sampling molecular dynamics (MD) to investigate molecular details involved in the hydration of a model smectite from the dry state with no interlayer waters (0W) to a one-layer hydrate (1W), two-layer hydrate (2W), and beyond.

In our model system, two Na-montmorillonite particles, each consisting of a single layer with one-dimensional periodicity, are immersed in a water bath, thus allowing water to interact with the external surfaces (basal and edges), and to enter the interlayer region. Interlayer expansion was simulated at 300 K using MD simulation by imposing a harmonic term for interparticle interactions through umbrella sampling. Using the resulting interparticle potential of mean force profile, we calculated relative free energies of the 1W and 2W states, as well as energy barriers between hydration states. The simulations used the ClayFF parameter set, including recently developed M-O-H angle bending parameters (M = Al, Mg, Si) to properly describe hydroxyl groups at edge surfaces. Indeed, disruption of interparticle hydrogen bonding involving these edge hydroxyl groups appears to control the initial expansion from the dry state to the 1W state.

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Model-Based Analysis of organo-clay thin films experimentally probed by polarized ATR-FTIR spectroscopy

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Molecular and particle orientations play a critical role in many aspects of material and environmental sciences. Fluids diffusion, liquid crystal display, polymeric fibers are just a few examples where the molecular/particle orientation determines the macroscopic properties of the materials. Vibrational spectroscopies are some of the few molecular level probes that are inherently orientation sensitive and provide molecular insight into organo-mineral interactions. Infrared spectra of organo-minerals are the result of complex interplay between their intrinsic vibrational properties and the micro-structure and experimental geometry. As a consequence, interpreting infrared spectra of organo-clay is rendered difficult in a quantitative way, and erroneous conclusions are often drawn when frequency or band intensity changes are related to organo-mineral interactions.

This is illustrated in our study where the interactions of phospholipids and swelling clays were investigated. In order to achieve a quantitative description of the organo-mineral interaction and associated structure, a model-based approach was developed which relies on optics theory. Firstly, the optical indices of phospholipid and clays were extracted from the measurement of their polarized ATR reflectance spectra. These optical indices were then combined to design a structural model where the orientation of the clays and the orientation of the phospholipids were treated as adjustable parameters, as well as the relative quantities of phospholipid and clays. The model was further constrained by the input of the layer-to-layer distance in the particles as obtained from XRD measurements.

The calculated reflectance spectra based on the models were then compared to the experimental ones enabling further adjustment of the model until the band intensity and the dichroic ratio were in good agreement. This methodology is believed to give a new insight into the quantitative determination of structure and composition of organo-clay using infrared spectroscopy.

Acknowledgements : The authors thank the European communities (FEDER) and the "Region Nouvelle Aquitaine" for the financial support.

Gold release from AuNP/ZnAlLDH mediated by Horseradish Peroxidase and AuNP influence on enzyme activity

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Gold nanoparticles (AuNPs) are extremely important for the biomedical field. However, the classical synthesis methods involve the utilization of organic compound which increase the toxicity of the final product. Designing a suitable and *green* environment for AuNP stabilization and the achievement of an easy NPs release in presence of a target are challenging approaches. Herein, AuNPs self-assembled on ZnAl-layered double hydroxide (LDH) via eco-friendly and free of organic agents have been fabricated and further released in presence of Horseradish Peroxidase enzyme. X-Ray diffraction, UV-Vis spectrometry, Transmission electronic microscopy, Energy-dispersive X-ray spectroscopy and FTIR spectroscopy techniques have been performed to characterize the structure, the chemical composition, the optical and the morphological properties of the samples.

Results have shown that after synthesis, dispersed AuNPs with diameters in a range of 5-30 nm were obtained on clay surface. The release study revealed that the AuNPs from LDH surface interact with the HRP enzyme via electrostatic interaction and a AuNPs-HRP bioconjugate is released in the solution. The NPs evolution in supernatant was evaluated by monitoring the surface plasmon resonance of the gold nanoparticles via UV-Vis measurements (figure 1a). The activity tests performed for the enzymatic solution have shown that the HRP suffers a significant loss of activity (figure 1b). Furthermore, the increase of pH has a beneficial impact on NPs release. A control study made only in presence of phosphate buffer confirmed that the AuNPs release is possible only if the HRP is present in the system. This study gives new information regarding the behavior of AuNPs in enzyme-based heterconjugates and might be inspiring for future applications of nanogold in biomedicine.

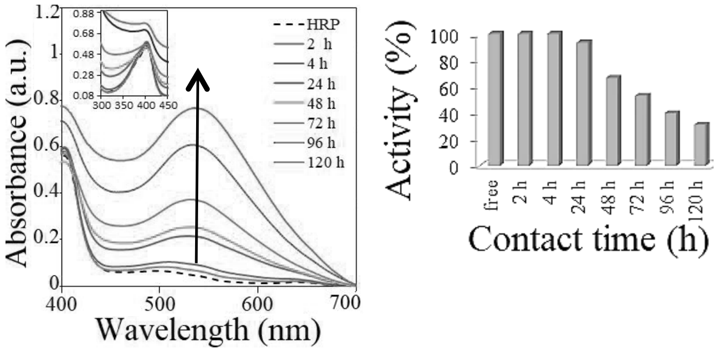

Figure 1 : a) UV-Vis spectra corresponding to AuNPs release in presence of HRP and b) HRP activity evolution.

Self-assembled gold nanoparticles on layered double hydroxide matrix as a photocatalyst for Horseradish Peroxidase activation and cofactor regeneration

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Layered double hydroxides are semiconductor materials able to generate oxidative species when are excited by an appropriate energy sources. In this study, AuNPs/ZnAlLDH self-assembly was designed by exploiting the unique structural memory effect property of the LDHs in the aqueous solutions of $Au(C_2H_3O_2)_3$.

Oxidoreductases are important as biocatalysts for the synthesis of valuable chemicals and pharmaceutical products. Generally, the utilisation of these enzymes is conditioned by the presence of an oxidizing agent (e.g. H_2O_2) or a co-factor (e.g. reduced nicotinamide adenine dinucleotide, denoted as NADH). Previous data point out that the longtime exposure of the enzyme to H2O2 might lead to its irreversible denaturation, while the hight cofactors price makes their regeneration to be mandatory. To overcome this behavior we propose here the photo-activation of a model enzyme called Horseradish Peroxidase (HRP) and the NADH photo-regeneration from NAD^+ in presence of gold nanoparticles supported on layered double hydroxide matrix. The HRP photo-activation was performed in presence reduced ABTS substrate, while the cofactor photo-regeneration was mediated by flavin mononucleotide. The obtained results have shown that the photo-enzymatic ABTS oxidation was possible and NADH photo-regeneration in presence of solar irradiated Au/ZnAlLDH was confirmed. Furthermore, at a pH value of 8, the cofactor photo-conversion yield was 100% (figure 1). This work should be inspiring for future applications of Au/ZnAlLDHs photocatalysts in biochemistry and enzymatic catalysis.

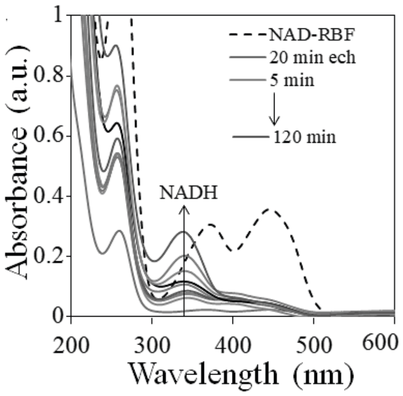

Figure 1: UV-Vis spectra profiles for the NADH solar photo-regeneration in presence of Au/ZnAlLDH; pH = 8.

Combining photo- and enzymatic-catalysis for phenol removal using Horseradish Peroxidase, ZnMeLDH (Me=Al, Cr) and their derived mixed oxides

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In this work we present a comparative study between the removal of phenol from water using two different ways: the photodegradation and the enzymatic degradation. For this, solar sesitive ZnMeLDH and their calcined derivate mixed oxides (MMO) were synthesized. In the enzymatic reaction, horseradish peroxidase enzyme (HRP) was used. The structural, optical and thermal propreties of photocatalysts were investigated by XRD, FT-IR, TG/DTA, TEM and UV-VIS measurements. The materials characterization shows that specific hydrotalcite structures resulted after synthesis, and the calcined catalysts are a mixture between metal oxides and spinels.

Both degradation methods are able to remove phenol from solution via different patways: the step by step phenol photodegradation, in presence of ligth and a solid catalyst, and phenol enzymatic polymerization, when an insoluble product is obtained at the end of reaction. 95 % of phenol was degraded via photodegradation, while 41 % was removed via enzymatic polymerization (figure 1). Because the polyphenols can be valorized further, a comparative analyse of this processes gives new perspectives for combining the photogedradation with the enzymatic degradation, for the remediation of complex pollutants systems.

Since the enzyme attachement on a solide, with enzyme activity preservation, increases its value, we succesfuly immobilised the peroxidase on ZnAl550LDH via adsorption and we tested the new biohybrid in the enzymatic degradation of phenol. Further, the LDH–HRP material was used in the photo-enzymatic degradation of the pollutant. The results have shown that the phenol is simultaneously removed via photodegradation and enzymatic polymerization.

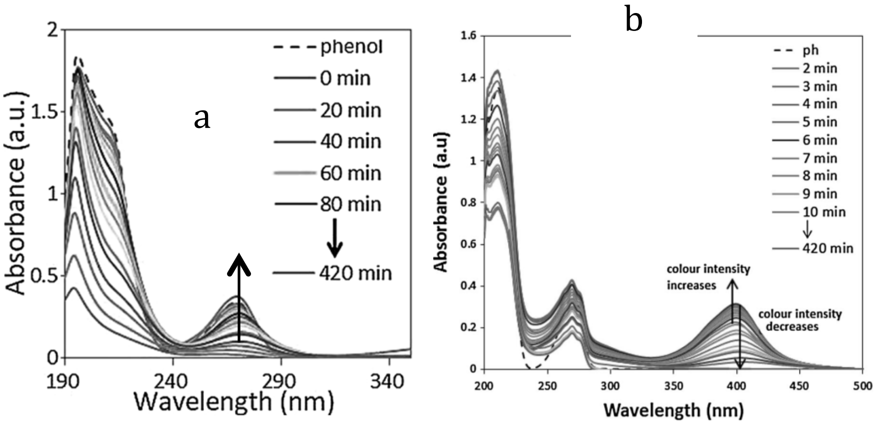

Figure 1: UV-Vis spectra for a) phenol photodegradation and b) phenol enzymatic polymerisation

Clay-polymer interaction in enhanced oil recovery: impacts of clay type, ionic strength and hardness

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Chemical Enhanced Oil Recovery (CEOR) using polymer injection is now considered as an attractive option for reservoirs with permeability less than 100 mD ("low" permeability), in particular where lack of gas supply does not allow gas injection. However, due to the mineralogical composition of these reservoirs naturally rich in clay, high polymer retention is observed. The aim of this work is to study the impact of different clay minerals as a function of polymer solutions characteristics, such as ionic strength and hardness, on the polymer transport properties in "low" permeability porous media.

For this purpose, and in order to evaluate polymer retention, solutions of partially hydrolyzed polyacrylamide (HPAM) in waters of variable ionic strengths and hardnesses were injected in granular packs with well controlled mineralogical compositions in quartz and clays (kaolinite, illite or smectite, investigated separately). The structure of these porous media was analyzed after injection using SEM. In parallel, clay-polymer suspensions were studied in terms of particle size, turbidity and electrophoretic mobility for various clay and polymer concentrations and different ionic strengths.

Injection tests showed that the presence of clays entails sharp increases of irreversible polymer retention even at low salinity, with, among the clays tested, kaolinite leading to the highest retention. There was no direct relation between the specific surface area of the clays and polymer retention. Increasing the ionic strength and hardness also increased the retention in clay containing porous media. Observation of the porous media after injection revealed the formation of clay aggregates only for illite and smectite at high ionic strength.

The study on clay-polymer interaction in aqueous suspensions showed that HPAM shifts the critical coagulation concentration to higher values. Clay-polymer interaction was only slightly influenced by the ionic strength, and no major differences were observed with regard to the clay type. Furthermore, the electrokinetic mobility of the polymer was not affected in the presence of clay, which suggests the incorporation of clay particles into polymer aggregates.

As the amount of polymer involved in the suspensions is high with respect to the available surface area of clays, suspensions tests cannot be directly correlated to experiments in porous media. However, the strong affinity of CEOR polyelectrolytes for clays is clearly evidenced by two sets of experiments using different approaches.

Fault clays formed in the North Anatolian Fault Zone at Gerede area, Turkey

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The North Anatolian Fault (NAF) is a major continental dextral transform fault zone that shapes the neotectonic evolution of Turkey and the eastern Mediterranean region. It is well known because of its extremely hazardous seismic activity and can be traced well along long distances because of its distinct morphological expression. Although the most attention has been given to its tectonic evolution, deep structure , seismic activity and consequent earthquake hazards, there are very few research focusing on the wall rock alteration mineralogy and the nature of the circulating hydrothermal fluids .

In this study hydrothermal alteration products of the Miocene age basaltic-andesitic volcanic wall rocks belonging to Galatean Volcanic Province on the western segment of the NAF zone are investigated, by focusing to the Ardıçlı Fault zone . This 6 m thick fault zone is exposed at a road cut along the Ankara-İstanbul Anatolian Motorway-04 located to the south of Gerede. Mineralogical and textural properties of the parent rock and clay samples were examined by optical microscopy in thin sections, XRD analysis of both whole rock samples and their clay fractions and SEM-EDX analysis. The hydothermal alteration of the wall rocks mainly produced heulandite-smectite-calcite mineral association. In addition, trace amounts of mixed-layer illite-smectite and pyrophyllite are also detected. Ca-rich mineral phase indicates the meteoric origin and basic character of the hydrothermal solutions. Lack of high illitization suggests that low temperatures dominated the fault environment. Based on textural relationships and mineral deformations, it can be suggested that heulandite-smectite mineral assembledge was formed prior to carbonate precipitation phase within the microfractures of this mineral asembledge , thus the reactivation of the fault was indicated.

Sorption Of Cu^{2+} Ions And Humic Acids From Aqueous Solutions By Modified Bentonite

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To improve the sorption characteristics of bentonites, they are modified using various techniques. One of these techniques is the saturation by Keggin-cations of metals and by humic acids (HA). But the modification by these methods can lead to both an improvement and a degradation of the sorption capacity of bentonites. The aim of the study was to identify regularities of sorption of Cu^{2+} ions and HA by bentonite, saturated with Na ions and modified by Keggin-cations of aluminum ("Al_{13}").

The object of the study was the bentonite fraction <1 µm from the Sarigyugh deposit (Republic of Armenia). Part of the fraction was saturated with sodium cations ("Na-bentonite"), the other part was saturated with "Al_{13}" ("HAl_{13}-bentonite"). Half of the latter one was then calcinated at 400°C ("Al_{13}-bentonite") and the other part was saturated with humic acids ("Al_{13}+HA-bentonite"). The obtained bentonite forms were studied by X-ray diffractometry (XRD). Sorption experiments with copper were carried out in the range of concentrations of $CuCl_2$ solutions of 0.025-0.5 mM/L at pH 4.5 and interaction time of 30 minutes. The concentrations of Cu in solutions were measured by flame atomic adsorption spectroscopy (AAS). Sorption experiments with HA were carried out in the range of HA carbon concentrations between 6 and 24 mM(C^{12})/L at pH from 3 to 7, ionic strength near 0,1 M/L (NaCl) and interaction time of 6 hours. The content of HA carbon in filtrate was analyzed by spectrophotometer. pH of zero point of charge (pH_{zpc}) of Na- and Al_{13}- bentonites was determined by potentiometric titration

The results of XRD analysis showed that the fine fraction of the bentonite consists almost entirely of montmorillonite; the introduction of the "Al_{13}" into the interlayer space of the montmorillonite leads to an increase of the d(001)-value from 12,4 to 18,5 Å. The d(001)-value of the montmorillonite in the Al_{13}-bentonite does not change after saturation with ethylene glycol (17,7 Å) and decreases slightly after calcination at 550°C (17,1 Å), thus the modified montmorillonite has a stable crystal lattice.

The results of sorption experiments showed that Na-bentonite adsorbs 2-6 times more Cu^{2+} (up to 88%) than HAl_{13}- and Al_{13}-bentonites (up to 17%) and the main mechanism of sorption on Na-bentonite is cation exchange. The creation of "pillared structures" in Al_{13}-bentonite led to an increase in the proportion of pH-dependent sorption sites and the predominance of pH-dependent charge, as evidenced by the intersection of the titration curves (pH_{zpc}=4,2); at pH 4.5 sorption sites have a significant positive charge, which prevents more intense sorption.

The Na-bentonite adsorbs 2 times more HA than Al_{13}-bentonite. At pH less than 4.2, the sorption centers of Al_{13}-bentonite are mainly protonated and do not participate in the sorption of HA, and with an increase of pH the deprotonated functional groups of HA are repelled from deprotonated sorption centers. After the treatment of Al_{13}-bentonite with HA, additional sorption sites occur on the surface of the organo-mineral complex and this contributes to an increase of the sorption of copper ions up to 90%.

Bionanocomposites as “green” alternatives for commercial food packaging materials

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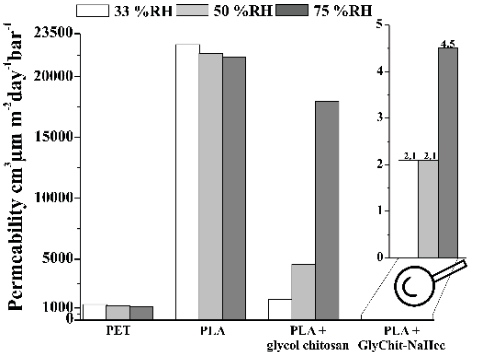

Fig. 1: Comparison of the oxygen permeabilities of commercial PET and PLA foils and foils with a bionanocomposite coating.

The ecological impacts of plastic and their awareness by the customers is still increasing and thereby biodegradable alternatives in the field of food packaging are of great importance. Nevertheless, inherent shortcomings like low barrier properties limit the best before date.[1] Therefore these barriers have to be improved for this application field. Biopolymers are known to swell at increasing relative humidities (r.h.) and therefore the barrier are insufficient for long shelf life packaging at relevant humidities. Neat PET represents the low performance standard in flexible food packaging with oxygen permeabilities of 1000 $\mathrm{cm^3\ \mu m\ m^{-2}\ day^{-1}\ bar^{-1}}$ whereas state of the art high performance packaging materials like laminates of ethylene vinyl alcohol copolymers and PE (EVOH/PE) or metalized PET typically warrant oxygen permeabilities < 50 $\mathrm{cm^3\ \mu m\ m^{-2}\ day^{-1}\ bar^{-1}}$.[2] The permeability of PLA as safe alternative (FDA) for PET is 20 times higher than that of PET and even more than two orders of magnitude higher than the above listed high performance materials.[3] The situation with all other biopolymers is nearly similar. Darder et al. first pointed out, that barrier fillers like clay are required to produce bionanocomposites.[4] This could be an innovative way to push biopolymers in the packaging market. Our group has shown that by applying high-aspect ratio synthetic clay (fluorohectorite) as filler in nanocomposites significant improvements in the range of several orders of magnitude can be achieved as compared to neat polymer matrices.[5] Furthermore, we showed with several different polymers that even environmentally benign waterborne polymer formulations show a barrier improvement by a factor of 10^4 even at a r.h. of 75 %. Such reduction levels correspond to potential extensions of best before dates for dry food like flour to more than 1000 days.[6] Furthermore, a PLA foil (25 µm) coated with a glycol chitosan-clay nanocomposite (1.4 µm, OTR= 0.17 $\mathrm{cm^3\ m^{-2}\ day^{-1}\ bar^{-1}}$ at 75 % r.h) was found to outperform state of the art high-performance materials like PVDC and metalized PET for O_2 barrier even at such harsh conditions. (**Fig. 1**) and further show anticolonization potential.[6]

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Cation exchange capacity (CEC) measurements of Opalinus clay: comparison of operational conditions

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CEC is a key parameter of clayey formations, such as Opalinus Clay (OPA) which is foreseen as host rock for a high level radioactive waste (HLRW) repository. Predicting the retention capacity and reactivity implies a good knowledge of the CEC of the clay rock, along with the in situ cation occupancy. The selection of a repository site for HLRW will involve the characterization of many samples. One has thus to define a simple method allowing fast and reliable determination of CEC. A large range of CEC methods exists, those using the highly selective metal dyes (e.g. Cu(trien) (Meier and Kahr, 1999), Ni(en)$_3$ (Baeyens and Bradbury, 1991), or CoHex (Rémy and Orsini, 1976)) are the most popular because of their simplicity (single extraction, possibility of colorimetric measurements of selective metal ion consumption etc.). Nevertheless, the presence of soluble phases (e.g. carbonate and sulphide minerals) complicates the interpretation of data on extracted cations. Moreover, operational conditions often vary from one research group to another: sample preparation, extraction time, aerobic/anaerobic conditions, liquid/solid ratio (L/S), or pre-saturation of extracting solution with calcite in order to limit carbonate dissolution. Instability of the selective metal ion in presence of reducing clayrock has been demonstrated in the case of CoHex (Hadi *et al.*, 2016). Whether similar artefacts hold regarding other selective metal ions remains an open question.

The present study focuses on the results from CEC intercomparison exercise (method and specific conditions) studying a single preserved OPA sample by three different methods (Cu(trien), (Ni(en)$_3$) and CoHex) and a range of operational conditions (contact time, L/S, pH).

Overall, the results showed that the L/S ratio clearly influences the extent of mineral dissolution, but has however no impact on the selective metal ion consumption. The most important parameters influencing the results are the pH of the extracting solution and contact time. Contact time should be at least two hours to ensure complete exchange, but no lower than two days to avoid partial precipitation of extracted Ca and Mg. The pH has a strong influence on the extent of mineral dissolution. If the initial pH is chosen high enough (>9.5), carbonate dissolution can be minimised. The identity of the selective metal ion has no influence regarding the amount of extracted cations, except for CoHex that appears to extract more K, Sr and Mg. Overconsumption of the selective ion is clearly observed in the case of CoHex method (due to side redox reactions with the preserved sample), but not in the case of Cu(trien) and Ni(en)$_3$.

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Synthesis and characterization of palygorskite modified with zinc oxide

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Palygorskite (Pal), also known as attapulgite in trade circles, is a hydrated phyllosilicate with a 2:1 structure elongated along the c axis. In this structure, the channels can be filled with water called zeolitic water, while their edges are covered with water molecules linked to octahedral cations (coordination water). The objective of this study is to synthesize nanocomposite samples of zinc oxide supported by purified palygorskite (Pur Pal) [1, 2] with a hydrolysis method. The nanocomposite was prepared by adding zinc chloride in sodium hydroxide solution. The reaction was allowed to proceed for two hours. The solution was washed away with distilled water several times. After washing, 1% of Pur Pal was added to the mixture obtained after the hydrolysis reaction under vigorous stirring for a few hours. The obtained sample (ZnO Pal), was dried at 80°C for 18 hours, and characterized by IR, UV, DRX and SEM. The X-ray diffraction shows the presence of zincite (ZnO), confirmed by the presence of the characteristic peaks at $2\theta = 32°, 35°, 37°, 47.5°$ and $57°$. SEM micrographs reveal the presence of zincite particles, and the palygorskite fibers were uniformly coated with ZnO nanoparticles (Fig.1). The resulting nanocomposite ZnO Pal will be tested in the future as an antibacterial.

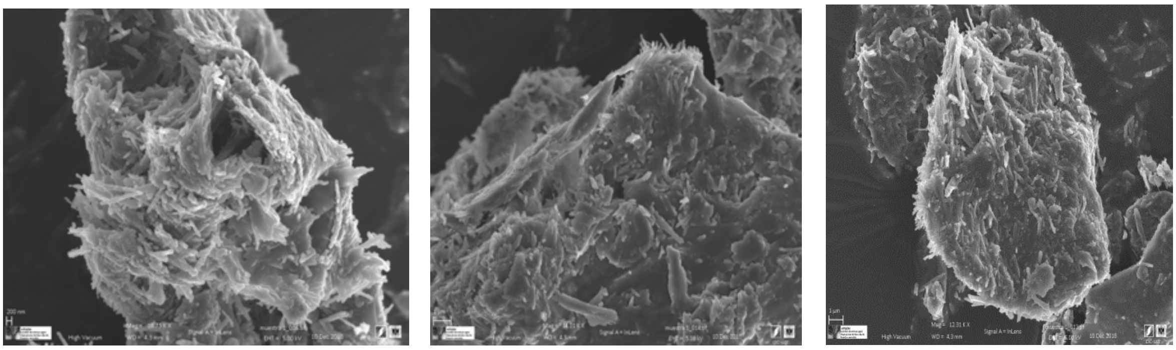

Fig.1. SEM images of samples ZnO Pal

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Oxidation of Carotene by Acid Treated Montmorillonite

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Many compounds undergo colour changes upon adsorption to clay minerals. The colour change of orange pigment carotene upon adsorption to clay surfaces is distinct, yet little is understood about what occurs chemically during this process.

Adsorption studies of β-carotene on to clay minerals were combined with ultra-high performance liquid chromatography mass spectrometry (UPLC-MS) to measure adsorbate composition as a function of time and mineral type. It was found that certain clay minerals possess the capability to oxidise carotene to a range of different carotenoids, each with slightly different colour, contributing to the change in clay appearance upon adsorption. This was suggested to be due to presence of Fe and/or acidic groups on the surface.

UPLC-MS techniques found that acid-treated montmorillonites convert carotene into carotenoids of mass 549.41 and 565.40 at room temperature. Quantification and identification of isomers was achieved using chemical standards and tandem MS data.

Effect of magnesite on the microstructural and mechanical properties of Cordierite-Mullite Ceramics prepared by tape casting process

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Mullite and cordierite are materials that have attracted considerable attention in recent decades [1,2]. The present work aimed at manufacturing textured cordierite-mullite ceramic materials from a stoichiometric mixture of an Algerian kaolinitic clay and magnesite as raw materials. A clay deposit of the Tamazert (Jijel, Algeria) was selected for this study thanks to its mineralogical composition and its suitability for industrial use. Tape-casting process was used to produce the green tapes in an aqueous system with optimized amount of dispersant (sodium hexametaphosphate), binder and plasticizer. Different magnesite ($MgCO_3$) contents, from 0 to 12 mass%, were added in order to determine the effective impact of this carbonate over the formation of cordierite and/or mullite upon sintering. The various green tapes were sintered at 1200°C with a dwelling time of 30 min to 3h. The green and sintered materials were characterized by thermodilatometry, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The biaxial flexural strength and mercury porosimetry measurements were performed onto the various specimens in order to investigate the evolution of their properties of use.

The results indicated that the increase of $MgCO_3$ content contributed to lower the linear shrinkage. From the XRD analysis, no significant effect of the $MgCO_3$ content and of the dwelling time was noted over the nature of the crystalline phases occurring at 1200°C. Nevertheless, the addition of 6 mass% of $MgCO_3$ contributed to enhance the densification of the kaolinitic clay and may increase the amount of cordierite and mullite phases. Indeed, the biaxial flexural strength values strongly depended on the sintering time, $MgCO_3$ addition, and the porosity. The morphological analysis of both polished and fractured samples (12 mass% $MgCO_3$) before and after sintering at 1200°C for 30 min and 3h, indicated a preferential organization of particles along the casting direction. As expected, it was noted a strong decrease of the total porosity with increasing sintering time (3h). However, the highest flexural strength values (109. 88 ± 49 MPa) was obtained for the specimens with 6 mass% of $MgCO_3$ content, exhibiting a total porosity of 26.3 % after sintering time at 1200°C for 3h. The as obtained ceramics appeared promising for further utilization as substrate, with high anisotropy in properties due to the textured microstructure.

Keywords: kaolinitic clay, magnesite, tape casting, Cordierite-Mullite

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How microbes break the cryptic manganese cycle to form manganese oxides

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The distribution of manganese (Mn) oxide deposits is variable throughout the geologic record and in modern marine sediments. Despite a wide diversity of aerobic microorganisms that can precipitate Mn oxides, the mechanisms of formation remain poorly understood. Further, the physiological basis for microbial Mn(II) oxidation remains an enigma.

We have recently revealed that Mn oxide formation by some fungal and bacterial species is a consequence of Mn(II) oxidation by the reactive oxygen species (ROS) superoxide ($O_2^{\bullet-}$). This superoxide production occurs extracellularly, via activity of transmembrane, outer membrane, or secreted proteins. These Mn oxides are highly reactive and induce further Mn oxide formation via autocatalytic oxidation of Mn(II) that leads to oxide ripening and ultimate loss in reactivity.

While we have shown that extracellular superoxide production is widespread in bacteria, this production does not necessarily confer the ability to produce Mn oxides. Indeed, the back-reaction between the products, Mn(III) and hydrogen peroxide (H_2O_2), formed upon Mn(II) and superoxide reaction inhibits Mn oxide formation. These findings indicate that at least two processes – the generation of superoxide and consumption of hydrogen peroxide – are requisite for superoxide-mediated Mn oxide formation.

Nevertheless, under controlled abiotic conditions, Mn oxides formed via ROS cycling remain as nanocrystalline phases that do not aggregate or ripen with time. We find high concentrations of organic carbon (OC), including enzymes involved in the superoxide production process, associated with the Mn oxides points. This association along with oxide growth morphologies point to a role for organic templates in the precipitation and aggregation of Mn oxides.

Together, we find that microbial mediated Mn oxide formation involves a complex network of biotic and abiotic reactions necessary for Mn(II) oxidation, Mn(III) stabilization, and Mn oxide precipitation and aggregation (see for example, Figure 1). Controls on each of these factors will therefore dictate the precipitation and distribution of Mn oxides within the environment. Within the ocean, targeting the controls on these three processes may allow for insight into the geographic variability often observed in Mn oxide and associated nutrient profiles along continental shelves and within coastal environments.

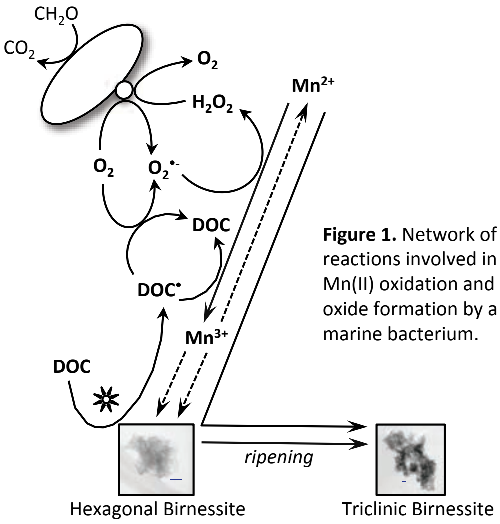

Figure 1. Network of reactions involved in Mn(II) oxidation and oxide formation by a marine bacterium.

Effects of transition metals on the adsorption of nucleotides onto clay mineral surfaces: implications for the origin of life

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Transition metals are a group of elements widely utilized by life for building components and biofunctions. Due to their trace amount in the modern surface waters, their effects on the overall interaction between mineral surfaces and aqueous species should be negligible, when it comes to life. However, on the prebiotic Earth, some transition metals, like Fe(II) and Mn(II), might have reached considerable levels in the early reducing and acidic surface waters as well as ultramafic hydrothermal fluids; thus, their effects on the surface interaction with minerals might not be neglected when considering that the interface between minerals and the building blocks of life could have played a role in the emergence of life.

Here, we designed batch adsorption experiments under both ambient and low-temperature hydrothermal conditions to test the effects of various transition metals (Zn, Ni, Mn) on the adsorption of nucleotides onto clay minerals. Our ambient experiment on the adsorption of nucleotides onto swelling clays (nontronite and montmorillonite) showed that the presence of transition metals could enhance the adsorption of nucleotides in a more efficient way than Ca, Mg, and Na. Our preliminary results on the adsorption of nucleotides onto swelling clays at elevated temperatures and pressures confirmed a more efficiently enhancing effect of transition metals on the adsorption of nucleotides onto swelling clays. We will conduct the same research on the non-swelling clays.

Enhanced adsorption amount of nucleotides and presumably other organics onto clay minerals might help ease the survival of those biomolecules against UV radiation and hydrothermal heating. In the meantime, the concentration of biomolecules onto mineral surfaces would also favor the polymerization process in the prebiotic ocean.

Decomposition of polycyclic aromatic hydrocarbons in the presence of hydrogen, carbon dioxide and ammonium gases with a clay mineral

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Most polycyclic aromatic hydrocarbons (PAHs) are harmful organic materials. Contact with them has to be avoided as they might be entered the body. PAHs might damage genes, and give us risks to the development of cancer and other hereditary diseases. PAHs are easily formed by incomplete combustion from household or natural forest fires. The formed PHAs transport worldwide by wind and rain, etc. Some of them are dissolved in water and spread into rivers and oceans. The ground, rivers and oceans will be contaminated by PAHs, and they might give some effects to animals and plants. Finally we may also have risks from consuming products. For that reason, we have to study to make PAHs harmless and useful. Clay minerals have characteristics like a catalytic activity to control the reaction of organic materials. The catalytic activity of clay minerals will advance a decomposition reaction of PAHs. Gas phases will assist the reaction of PAHs to make harmless or useful organic materials. We investigate the decomposition reaction of PAHs in the presence of hydrogen, carbon dioxide and ammonia gases with a clay mineral to make harmless and useful organic molecules.

We use pyrene (Pyr) as a PAH. The melting temperature of Pyr is 149°C. Natural kaolinite (Kn) is used as a clay mineral. It is delivered from Kanpaku, Japan. Ammonium hydrogen carbonate (NH_4HCO_3) is used. NH_4HCO_3 is decomposed at more than 60 °C, and ammonium (NH_3) and carbon dioxide (CO_2) gases are supplied. We use iron (Fe) and hydrochloric acid (HCl) to make hydrogen (H_2) gas. For the decomposition of Pyr, the mixture of 0.2 g of Pyr and 0.5 g of Kn, 1 g of Fe and 0.5 of NH_4HCO_3 were put in each vial. Those vials were set in a high-pressure reactor. To fill the reactor with H_2 gas, $1 cm^3$ of HCl ($1 mol \cdot dm^{-3}$) was poured in the Fe vial. Immediately, the lid of the high-pressure reactor was closed tightly. The high-pressure reactor was left at 80, 100 and 150 °C in an oven for 2 to 5 days. For the NMR analysis, $1 cm^3$ of chloroform-d_1 and heavy water (D_2O) were poured into the recovered vial with Pyr to extract products. After separation of chloroform-d_1 and D_2O, each solution was analyzed by ^1H NMR.

The products at three different temperatures are almost the same. There are a few benzene rings in the recovered sample. We could detect amino and hydroxyl group in the extraction by chloroform-d_1. From those results, some Pyr would be decomposed and the decomposed materials would react with NH_3 or H_2O in the system. When NH_4HCO_3 was absent in the system, carboxyl and hydroxyl group was detected in the recovered sample. In the case of Pyr with Kn, hydroxyl group was detected. When only Pyr was treated at those temperatures, most Pyr was not decomposed. In the case of the extraction by D_2O, we could not detect any functional group. We found that some solid Pyr was decomposed in the presence of Kn and those gases.

Enhance oil production throughout inhibition of fines migration using nano-drilling fluids

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Fines migration is the major reason for productivity decline known as formation damage in oil reservoirs. Nanofluids are good candidates for being injected into nearby wellbore regions because of their very small sizes for remediation purposes. In this study, a novel experimental procedure is utilized to study the use of different types and concentrations of nanoparticles to reduce fines migration in synthetic porous media. Three types of nanoparticles, MgO, SiO_2, and Al_2O_3, are used here as coating agents of the porous media grains to investigate the reduction of fines movement. In this study, we present new experiments and simple modeling of sand packed to observe such properties of nanoparticles. A zeta-potential test was used to examine changes in the potential of the pore surfaces. Additionally, a core displacement test (sand-pack) was conducted using injection of a nanofluid at different flow rates at chemical flooding test. The porous media were prepared with 250 g of sand with 18/30, 30/52 and 30/100 mesh size. The fines suspension was prepared of kaolin and quartz, the size of fines was less than 32 µm. this work aims to solve the fine migration and maximizing the oil production. The result well be presented later in the conference.

Deterministic inference of Representative Elementary Area of clay rock at the mesoscopic scale

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Clay rocks are the main geological caps to many hydrocarbon reservoirs as well as potential host rocks for high-level radioactive waste repositories in several industrial countries. These geological formations are heterogeneous at multiple scales and with regard to the complexity of their microstructure, the prediction of the engineering properties of shales is clearly a challenging task. Here, we will focus on the mesoscopic scale (typically in the sub-millimeter range) for which numerous theoretical studies have been devoted to the calculations of effective properties.

All the homogenization approaches used to estimate the effective properties of clay rocks are based on the paramount concept of Representative Elementary Volume (REV) (in 3D) or Representative Elementary Area (REA) (in 2D). A brief review shows that there exists a large variety of estimates of REA size (named L_{REA}) and with regard to clay rock, these estimates concern mainly petrographical or mineralogical parameters: porosity and mineral phases.

The objective of this communication is thus twofold. We would like to provide:

- New L_{REA} estimates obtained from two mineral maps acquired from two clay rocks extensively studied in the framework of deep disposal of radioactive waste: The Callovo-Oxfordian (COx) claystone from Meuse/Haute-Marne underground research laboratory (Eastern France) and Toarcian argillite from the experimental station of Tournemire (Southern France). These L_{REA} estimates have been calculated not only by classical "counting box" methods but also by statistical descriptors usually used to quantitatively describe microstructures (two-point probability function, lineal path function, percolation length and the range of variogram).
- A discussion of our different L_{REA} estimates and their associated methodologies which aims at identifying the most suitable method to infer in a practical viewpoint L_{REV} or L_{REA} of clay rock.

Our results show that (a) the two-point probability function and the range of variogram provide minima of REA size and (b) the L_{REA} estimates from the classical counting box method are ultimately inaccurate because they are very sensitive of an arbitrarily defined threshold. They confirm that the clay rocks under study are anisotropic (transverse isotropic) whose anisotropy results from the alignment of non-clay grains parallel to bedding. This anisotropy associated with aligned non-clay grains is added to the well-known anisotropy associated with the clay matrix.

Moreover, the two-point probability function calculated on the Tournemire map shows the existence a long-range order i.e., a macrostructure which clearly questions the concept of REA at this space scale.

Synthesis and characterisation of suspension of aggregated Illite particles with polysaccharide or Iron oxyhydroxide

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Many studies have shown the importance of the surface reactivity of the mineral and organo-mineral phases commonly found in natural systems (soils, aquatic suspended matter, sediments). In order to unravel mechanisms and processes controlling the distribution of metal elements in environmental media, and to avoid the complexity and heterogeneity of natural samples, simple and binary model systems have been developed and investigated [1]. However, such model samples supposed to mimic environmental particles should be pushed towards more complex assemblages, and their stability, reactivity should be deeply investigated. The main objective of our work is therefore to obtain a reproducible construction of aggregates using natural (Illite) or synthetic (Dextran, iron oxyhydroxide (HFO)) components that mimic the natural particles present in continental aquatic environments. In order to obtain reproducible and robust procedure of aggregate construction, different strategies were developed. The constituent ratios were selected in order to be as close as possible as those commonly encountered in the Moselle River watershed.

Two kinds of experiments were carried out:
- a first set of experiments was performed to build organo-clay aggregates on the basis of Dextran sorption onto Illite particles. The formation of Illite-Dextran aggregates was studied by Fourier Transform Infrared Spectroscopy in Transmission mode and in diffuse reflection mode to highlight the presence and where is located the Dextran, by measuring Turbidity to observe its stability over time and by Dynamic Light Scattering to follow particle aggregation. Different amounts of Dextran were added to the clay water suspensions and the stability of Dextran-Illite aggregates was followed with turbidity measurement.

- Illite-HFO-Dextran aggregates were obtained by the slow hydrolysis of iron nitrate in presence of Illite particles. The titration curve (OH/Fe as a function of pH) indicates that there is first a cationic exchange of Fe^{3+} on the surface of Illite minerals, followed by the hydrolysis of iron. Microscopic characterization of the final sample (after addition of Dextran) confirmed the presence of iron. FTIR spectra suggest that the presence of iron oxyhdroxide on illite particles does not drastically modify the sorption of Dextran molecules.

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Effect of Mg-silicate formation on hydrogen generation during low temperature serpentinization

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Low temperature serpentinization, a reaction between ultramafic rocks and water under ambient conditions, generates hydrogen near Earth's surface environments. This reaction has been considered to play important roles in the origin of life since hydrogen may have been important reducing gas for building blocks of life as well as early metabolisms. During serpentinization, hydrogen is generated by the reduction of water accompanied with oxidation of ferric ion in the primary minerals of ultramafic rocks such as olivine or pyroxene. However, the amount of hydrogen produced during low temperature serpentinization is controlled by various factors, which have not been well understood, particularly, the effect of the formation of secondary minerals. Therefore, we conducted a series of experiments using 10 ultramafic rock samples, from Japan (Horoman and Wakamatsu), Oman and Indonesia, including dunites and harzburgites subjected with different degrees of serpentinization during obduction. After mineral and chemical characterizations, experiments were conducted by reacting the samples with water under anaerobic conditions at 90°C, for 2 weeks. Gas, solid, and solution obtained from the experiments were then analyzed by GC-RGD, XRD, and ICP-AES, respectively.

The results show that the generated amount of hydrogen tends to decrease with increasing degree of serpentinization of the samples. Although highly serpentinized samples sometimes generated the highest amount of hydrogen, these results were poorly reproduced. Based on mineral characterization, this may have stemmed from the oxidation of trace minerals (e.g., Ni-Fe alloy) or their catalytic effects because these minerals were heterogeneously observed by microscopy in the serpentinites, in addition to the dissolution of Fe^{2+}-bearing primary minerals. Experiments were also conducted with some additives (e.g., MgO, SiO_2, and magnetite) to investigate the effect of solution chemistry and formation of secondary minerals on hydrogen generation. The results show that hydrogen was generated the most under Si-rich conditions. Solution chemistry suggests that, olivine and pyroxene likely dissolved with the Si-rich solution. This is consistent with the trend that harzburgites generate hydrogen more than dunite because harzburgite contains pyroxene, which dissolved much Si compared to olivine. Moreover, thermodynamic calculations suggest that amorphous Mg-silicate minerals (e.g., M-S-H), which are commonly precursors of serpentine, precipitated at high pH, controlling the solution chemistry including a decrease in pH. Because the dissolution rate of the primary minerals is greater at lower pH, the precipitation of Mg-silicate minerals may have promoted the dissolution cycle of the primary minerals and therefore generation of hydrogen, especially under Si-rich conditions.

Neutron scattering experiments to determine the structure and dynamics of interlayer H_2O in halloysite nanotubes.

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The structure and dynamics of the interlayer H_2O molecules in halloysite are poorly understood yet could be key to understanding why the mineral adopts a nanotubular form. Additionally, unique aspects of the crystal structure of halloysite amongst kaolins, such as the tendency towards $2M_1$ layer stacking, may be related to the presence of H_2O molecules in the interlayer, and their influence on the hydrogen bonding of the layer structure. Residual interlayer H_2O in 0.7 nm halloysite, the form that is commonly used in technological applications, is also likely to influence many of the surface interactions upon which many depend. Unlike other clay minerals, in which interlayer H_2O molecules are associated with cations, halloysite has no interlayer cations, and so presents a unique opportunity to study H_2O interaction with the surface of uncharged tetrahedral and octahedral sheets. To try to further elucidate the structure and dynamics of interlayer H_2O in halloysite nanotubes neutron scattering experiments have been performed (OSIRIS, NIMROD, TOSCA) on four different samples of fully hydrated 1 nm halloysite. Two samples are cylindrical halloysites from China and two are polygonal halloysites from the Dragon mine in Utah, USA.

There are numerous questions revolving around the nature of hydrogen bonding among H_2O molecules under (extreme) 2-dimensional confinement. Considering that the halloysite layer structure is well known (kaolinite) and the surface -OH localized, neutron scattering (OSIRIS) experiments exploiting the large incoherent scattering cross-section of H have been conducted to examine the interlayer water dynamics. Elastic scans were performed in the temperature range 5 K - 340 K to identify the onset of diffusive and rotational motions among the interlayer H_2O molecules. To investigate the dynamical motion at the transition temperature Quasi-elastic neutron scattering (QENS) experiments have been performed. Data analysis is being conducted in Mantid, to attempt to resolve localized rotational and the diffusive motion with increasing temperatures. Additionally, the samples have been prepared in four different H/D isotope ratios including null scattering (64:36 mole ratio) to obtain data (NIMROD) to determine the interlayer water structure. Data analysis is being conducted using Gudrun and Empirical Potential Structure Refinement (EPSR) – the latter being used to refine a simulation of water confined to powdered layered materials to the structural data from scattering. Various aspects of the data from the different experiments and its on-going analysis will be presented.

Atomistic views on smectite interlayers from molecular simulations and XRD profile modelling

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Hydration of clay mineral surfaces and surface bound ionic solutes is central to the physical state and properties of clays in natural and engineered environments and applications. This is especially true for swelling smectite clay minerals, which display substantial but intricate water-uptake, mainly governed by the clay mineral surface charge properties and interlayer cation composition.

Here we present our recent research efforts in comparing structural, thermodynamical and diffusion data from atomistic simulations with experimental XRD data of the corresponding ion-exchanged Wyoming montmorillonite clay and water-loadings, modelled with our new OneDXRD2C mixed-layering code. This is because several recent studies have shown that Molecular dynamics (MD) and Monte-Carlo (MC) simulations in combination with mixed layer modelling of *00l* powder XRD reflections can aid in the interpretation of experimental diffraction data, and vice versa [1]. This synergy between molecular simulations and XRD has significantly improved our understanding of the atomistic interlayer solute and water structure we need in order to correctly model other physical properties such as interlayer diffusion.

Still, certain forcefield dependent discrepancies between simulated and experimental structural data exists, often reported to be due to the position of the interlayer species which could significantly affect computed interlayer diffusion coefficients. By deconstructing the X-ray layer structure factors in terms of atom type, occupancy and position, we aim to demonstrate the governing factors explaining any such deviance between the simulated and modelled structural data. Specifically, we compute the structural data and main driving forces behind clay hydration for different combinations of mechanistic forcefields (CLAYFF and INTERFACE) and water models (SPC/SPC/E/TIP3P/TIP4P) commonly used in atomistic simulations of clay minerals [2,3]. Specifically, we compare predicted swelling states from swelling free energy (PMF) profiles from open-system umbrella sampling MD simulations and traditionally derived hydration immersion energies for mono-valent and divalent counter-ions of closed systems. The simulated structural data from the resulting stable hydration states are then scrutinized in view of the experimental XRD data, modelled by mixed-layer modelling in terms of interlayer loading and position of both the lattice and interlayer atoms.

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ATOM - Atomistic Topology Operations in Matlab: A general framework for construction and analysis of atomistic geochemical systems

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Different types of molecular modelling techniques are increasingly becoming popular in many different scientific and engineering disciplines. This is not only due to recent decades development of high-performance computing, but also thanks to increasingly user-friendly molecular modelling software. Nevertheless, since it is often the life science-related research community that have developed and designed molecular modelling software, other scientists like geochemists often find themselves lacking relevant data handling and analysis tools designed for their specific systems or problems. In this context, and especially for geochemists lacking comprehensive programming skills, Matlab offers an attractive solution to data handling and analysis - with its simple yet robust plotting tools, scripting language and display of variables and data in excel-like spreadsheets.

This work presents the **A**tomistic **T**opology **O**perations in **M**atlab[1] (*atom*) library – a collection of modular Matlab scripts, which comprise a general framework for construction and manipulating of atomistic systems, with the option of including topological and forcefield information. The purpose of the *atom* scripts is basically to simplify construction of complex and anisotropic multicomponent molecular systems, for instance hydrated multilayered clay particles with charge defects, and to perform certain types of trajectory analyses. The common theme for all the *atom* scripts is an indexed variable type (called *struct*) that holds all atoms and molecules different descriptors and properties. Due to the many different types of basic operations one can invoke on the *atom struct* using the different Matlab scripts, this general framework can easily be used to manipulate multi-molecule systems with explicit bonding and angle information, or be used to merge mineral slabs, ions and solvent without molecular overlap - into efficiently packed systems.

Apart from for import/exporting basic coordinate files (.xyz | .pdb | .cif | .gro) the *atom* library can also be used to output basic molecular topology files (.lmp | .itp | .psf) with bonding and angle information across the *PBC*. These files can then be used along the Clayff (Cygan et al 2004) or the INTERFACE (Heinz, 2005, 2013 - for certain systems/softwares) forcefields in molecular modelling software such as LAMMPS, Gromacs, NAMD2, RASPA2. Furthermore, a neighbor distance analysis can be performed by comparison to the *i)* Revised Shannon radii, or by *ii)* calculating the valence using the Bond Valence Method, or by *iii)* calculating basic XRD profiles.

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Fe valence state & distribution in the various size fractions of the Boom Clay

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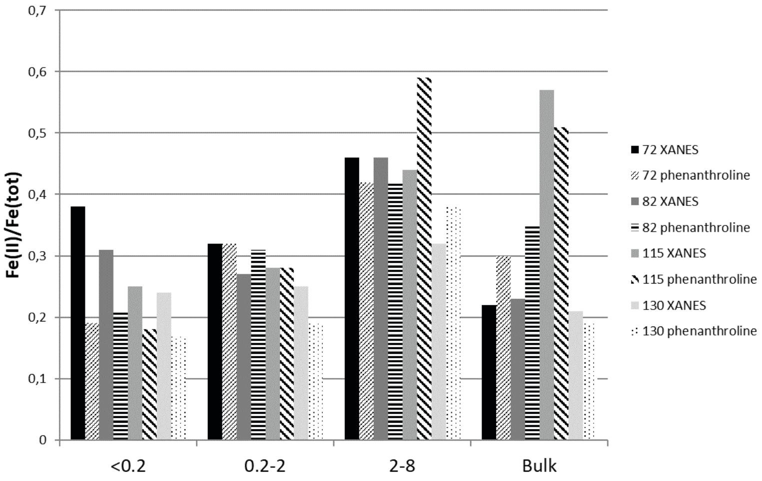
In the context of radioactive waste disposal in clay formations, the sorption of a number of redox sensitive radionuclides (e.g. U, Se, Tc) is controlled by the presence of Fe-containing minerals, mainly illite (Bruggeman et al., 2010), smectite (Guimaraes et al., 2016) and pyrite (Breynaert et al., 2010). In the repository lifetime, oxidizing conditions will prevail during the open drift phase enhanced by ventilation followed by recovery of reducing conditions after back-filling. Thus Fe-containing minerals will be subjected to redox cycles in the course of the repository operation.

In order to evaluate the sensitivity of different Fe containing minerals in the Boom Clay to changing redox conditions, firstly Fe^{2+}/Fe^{3+} partitioning was determined in various size fractions (<0.2, 0.2-2, 2-8 µm and bulk sample) spectrophotometrically (phenanthroline, (Harvey Jr et al., 1955) and with linear combination fitting of XANES spectra complemented by QXRD analysis. In general, a relatively good agreement was obtained between the two methods (see Figure below). The majority of Fe is present as Fe^{3+} in the octahedral sites of illite, illite-smectite and smectite, whereas the Fe^{2+} pool is predominantly controlled by Fe-Mg chlorite, Fe-Mg carbonate and pyrite. The increased Fe^{2+}/Fe_{tot} values in the 2-8 µm fraction of all samples can be attributed to the relative increase of chlorite content in this fraction. The second Fe^{2+}/Fe_{tot} maximum in the bulk 115 sample is explained by the presence of Fe-Mg carbonate in this specific sample.

The mediated electrochemical analysis is ongoing in order to assess electron accepting and electron donating capacities of the studied fractions simulating changes in the redox conditions.



Occurrence of mixed-layer minerals in temperate soils

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Mixed-layer minerals (MLMs) are common in soils developed under temperate climate. Determining the variability of MLMs crystal structure and their occurrence may offer the possibility to unravel their reactivity and the biogeochemical processes leading to their genesis. However, the identification of MLMs in soils and their quantification remain challenging due to i) the coexistence of several discrete clay minerals and MLMs; ii) the heterogeneous crystal structure of MLMs; and iii) the wide range of particle size distribution in the clay fraction (from tens of nanometers to few micrometers). Modelling X-ray diffraction profiles obtained from various size sub-fractions (<0.05, 0.05-0.1, 0.1-0.2 and 0.2-2 µm) has recently allowed to overcome these impediments. Four temperate soils involving different weathering processes were analyzed in different studies (Ferralitic Cambisol (Hubert et al., 2012), Aluminic Cambisol, (Viennet et al., 2015), Luvisol (Bakker et al., 2018) and a Neoluvisol (current work)). This work aims at showing the main differences and similarities in order to derive a general scheme of the soil clay mineralogy under temperate climate.

Tendencies obtained from the comparison of the four soils studied indicate that:

- MLMs are dominant and represent 70-82% in the bulk <2 µm fraction,
- Three-component MLMs (illite-smectite-chlorite) are widely observed and represent 27-76% in the bulk <2 µm fraction. Kaolinite-illite(-chlorite) are systematically present,
- The crystal structure of soil clay minerals tends to increase in heterogeneity or mixed-layering with decreasing particle size,
- The complexity of clay mineralogy is significant with eight to ten types of clay minerals. However several MLMs are similar in the four soils studied.
- The main differences of the clay mineralogy related to soil genesis are quantitative and involve the relative contributions of the different clay minerals present and the relative proportions of the different size sub-fractions.

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teaching clay science with today's technology

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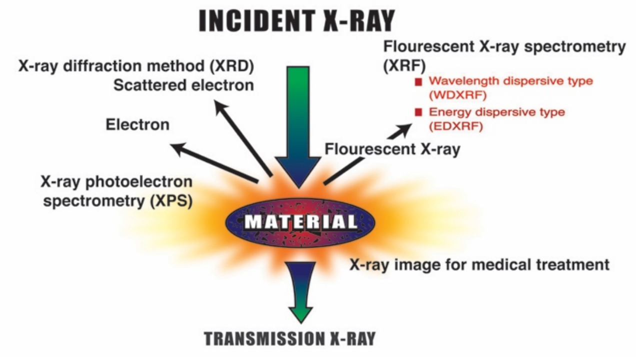
Since the earliest times, humans have had a close association with clay. From use as a building material, the primary component in pottery, for treating human digestive ailments to a multitude of industrial uses, clay is a key ingredient in the material world we live in. As a consequence, students of all ages should become aware of the occurrence, the acquisition and the nature of clay minerals. However, effective teaching today requires a proven solution that continuously evolves to meet our users' needs. Today's digital natives hunger for new educational approaches. Educators are more willing than ever to teach with technology, if it's powerful and easy to use.

Our educators and administrators need data to demonstrate student success. In order to deliver content digitally we need an effective learning management system (LMS). An effective LMS is easy-to-use, provides simple, but powerful workflows, enabling quick adoption by educators and students to create a better learning experience and increase engagement. Responsive and mobile-first design drive today's LMS experience ensuring educators and learners can connect anytime, anywhere, on any device. As teaching and learning continuously change, companies such as Blackboard Learn are pioneering advancements in teaching and learning and creating powerful analytics to drive learner success and institutional performance. The best learning management systems provide synchronous learning to foster engagement and real-time collaboration. With Blackboard Learn we are able to boost our technology adoption and achieve our broader goals.



The hyperlinked syllabus outlines the topics that are addressed in class and the Web Links and Course Materials pages have some resources that are used throughout the class. The class meets face-to-face but students who prefer to take it online may do so as long as they agree to attend the weekly laboratory sessions. Audio and video lecture capture can be done using in-house software called Echo360. Figures such as the attached X-ray image are used extensively in class along with videos and links to external clay-related sites.

Students are required to prepare and present clay-related reports in class at the end of the term. Topics typically range from geology to anthropology to archaeology to civil engineering to cosmetics to pet litter to food items.

The Role of Interlayer Cations for CO_2 Capture in a Smectite Clay

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Experiments and simulations have shown that CO_2 (like H_2O) intercalate in smectite nano-lamellar clays, both in the supercritical ($scCO_2$)[1], and in the gaseous/liquid phase[2]. Understanding how clay swells and adsorbs CO_2 is vital for CCS and potential capturing applications, e.g. filtering of combustion gases.

Our group has demonstrated that CO_2 intercalates into dry synthetic Fluorohectorite (Fh) clay with Na^+, Ni^{2+} or Li^+ as interlayer cations. We found that Li-Fh clay retain CO_2 (0.23 ton of captured-CO2/m3-clay) up to a temperature of 35°C, at ambient pressure, and that the captured CO_2 can be released by heating above this temperature [3]. Ni-Fh demonstrate an exceptionally high CO_2 adsorption capacity [5] compared to other materials. Furthermore, Ni-Fh and Li-Fh show much faster intercalation kinetics than the Na-Fh case, which possibly is related to the ionic radii, and the polarizability of the CO_2 molecule.

Recently, we have also studied (Cs-, Ca-, Ba-) Fh clay [6] in a capillary based custom-made high-pressure cell using synchrotron XRD. We confirm that the kinetics of the adsorption depends on the specific cation, clay layer charge, temperatures and pressure. Our recent studies show crystalline swelling of Ni-Fh within seconds in response to CO_2 exposure, and we find that neither Cs-Fh, Ca-Fh and Ba-Fh show any sign of crystalline swelling when exposed CO_2. Further, using this cell and synchrotron XRD, we have investigated CO_2 capture by Ni-Fh for three different clay layer charges, 0.3, 0.5, 0.7 per formula unit ($Si_4O_{10}F_2$) respectively. We find that Ni-Fh display crystalline swelling at 5-10 bar (0.3 layer charge), 10-15 bar (0.5 layer charge) and 30 bar (0.7 layer charge) at room temperature.

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Utilization of zeolitic but unique microchannels within layers of a layered silicate, Magadiite

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Development of microporous materials such as pillared clays and zeolites, with better properties and new functions, is important, while yet challenging, in many important applications including photoreactions and optics. Owing to their ubiquity in nature and/or low cost, combined with high thermal and chemical stability, layered silicates such as layered clay minerals have a strong historical background in the field of porous materials (or scaffolds for designing porous materials).[1] Magadiite is a naturally occurring layered silicate, which was found at Lake Magadi, Kenya in 1967[2] and is nowadays one of the most frequently studied layered silicates as porous materials.[1] In terms of large-scale production, magadiite is attractive because it can be facilely prepared by hydrothermal reactions. However, its properties were still mysterious because the crystal structure had not been solved yet. Here we succeed in determining the structure of magadiite for the first time and report on the presence of unexpected zeolitic, but unique, micropores within the layers (Figure 1).[3] We also report on the use of magadiite as an additive to boost photocatalytic organic synthetic reactions by TiO_2.[3,4] Furthermore, we will present the exfoliation of magadiite to enhance the adsorption properties via the intralayer microchannels.

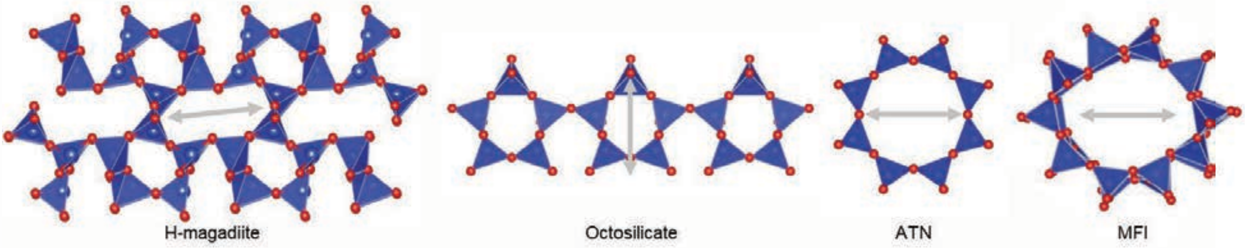

Figure 1. Singe layers of magadiite (its ptotonated form) and octosilicate, and 8-membered- and 10-membered-ring channels of ATN-type zeolite and MFI-type zeolite, respectively. The length of arrows is identical, meaning the unique shape/size of 8-membered-ring channels of magadiite.

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Development of a chemo-mechanical model of a bentonite-sand sealing component

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Swelling clay seal cores will be used for the closure of the future deep geological disposal facility for radioactive waste in France, named Cigéo (fig. 1-a). Their main safety functions rely upon the development and stability of swelling pressure that is transferred to the surrounding materials. To predict long-term changes in the swelling pressure, thermo-hydro-mechanical models are typically used. This work is focused on the physico-chemical processes at the interface between the sealing component and the surrounding materials (concrete support bases, concrete liner, and the surrounding Callovo-Oxfordian claystone). The effects of chemically-induced swelling pressure changes at full scale are explored here. The swelling clay-based material is considered as composed of a mix of MX-80 bentonite and siliceous sand.

A 2D axisymmetric coupled chemo-mechanical model of the sealing system has been developed and implemented in iCP (Nardi *et al.*, 2014), considering water-saturated and isothermal conditions. The model accounts not only for reactive transport processes of the interaction between the different materials, but also for the mechanical response of the system under such geochemical changes. The mechanical behaviour of bentonite is based on the Barcelona Basic Model (Alonso *et al.*, 1990). The chemo-mechanical couplings considered in the model include: (1) montmorillonite dissolution, (2) mineral precipitation/dissolution, (3) porewater salinity, and (4) composition of interlayer water (cation exchange reactions). These couplings relate chemical changes with the mechanical behaviour, mainly affecting the void ratio, material stiffness, total suction values and swelling pressure development. The model has been used to assess the chemo-mechanical evolution of the system over 10,000 years as a result of the geochemical alteration of the sealing component (fig. 1-b).

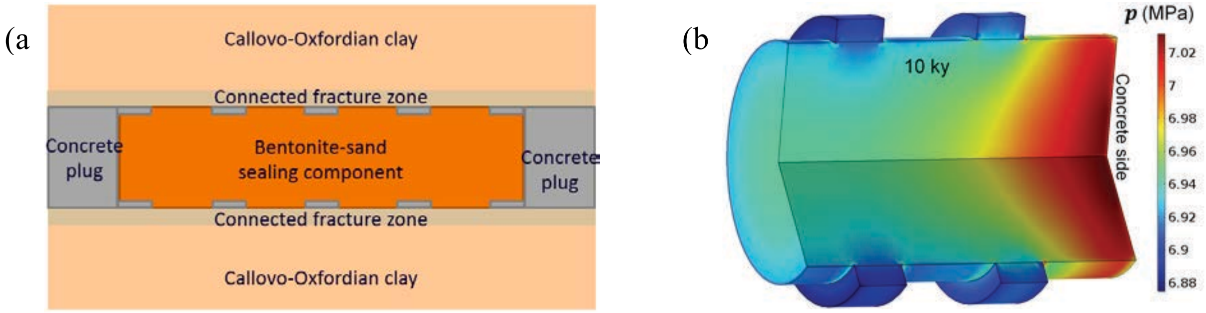

***Figure 6. (a)** General concept of a sealing component for Cigéo. **(b)** bentonite swelling pressure at 10,000 years.*

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Modelling radionuclide diffusion through compacted bentonite in a nuclear waste repository vault

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The Swedish Nuclear Fuel and Waste Management Company (SKB) plans to dispose of long-lived low and intermediate level waste in a deep geological repository, named SFL. One of the vaults relies on a bentonite backfill for radionuclide confinement. It is generally accepted that reactive transport in compacted bentonite is dominated by diffusion, but the mechanistic description of this process is not as well-established. In this work, five different models for anion diffusion in compacted bentonite, both empirical and mechanistic, have been used to estimate the long-term release of $^{36}Cl^-$ radionuclides from the repository. In general, the different modelling approaches yield comparable results, except for the multi-porosity model, which predicts a substantially higher flux (Figure 3). The results and main assumptions are thoroughly discussed.

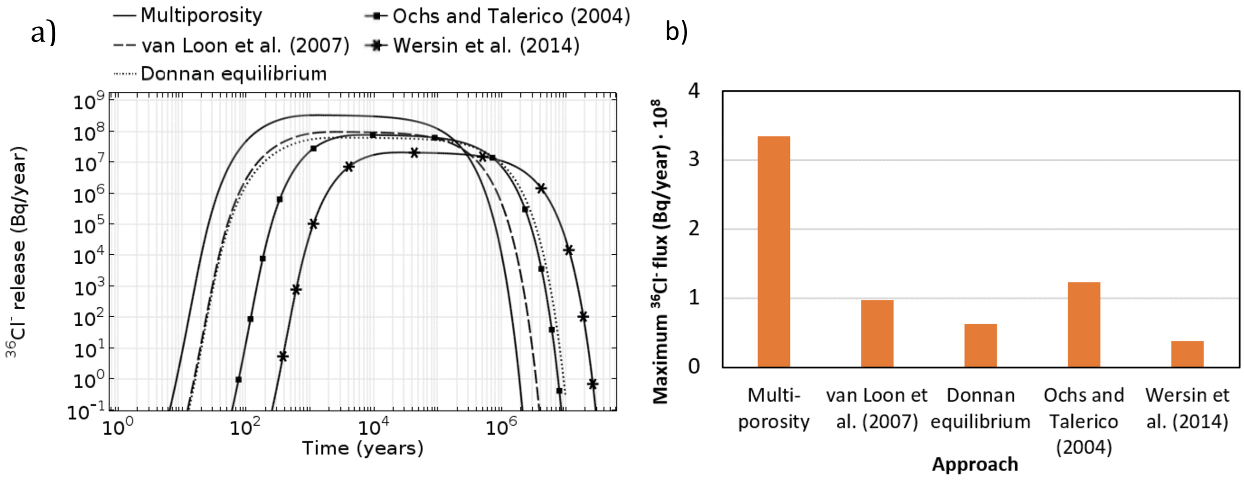

Figure 3. a) Evolution of total $^{36}Cl^-$ release from the vault and b) maximum $^{36}Cl^-$ fluxes obtained using the different modelling approaches.

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Evolution of a bentonite barrier initially inhomogeneous upon hydration

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The overall objective of the Beacon (Bentonite Mechanical Evolution) project is to evaluate the performance of inhomogeneous bentonite barriers in geological repositories for high-level radioactive waste. Although the bentonite buffer shows a natural tendency towards homogenisation, long-term observations have revealed that a degree of heterogeneity persists. In the framework of this project CIEMAT is carrying out a series of tests in cells to evaluate one of the sources of bentonite heterogeneity: the combination in the same barrier of pellets and blocks of compacted bentonite, whose dry densities and structures noticeably differ. The aim of these investigations is to obtain qualitative and quantitative information about the evolution, at laboratory scale, of initially inhomogeneous bentonite (pellets/blocks) upon hydration.

Two types of cells are being used: a large-scale oedometer (LSO, 10x10 cm) and a transparent cell (TC). In both kinds of cells the lower half is filled with FEBEX bentonite pellets (smaller than 9.5 mm in particle size) with an average dry density close to 1.30 g/cm^3. The upper part of the cell is filled with a FEBEX bentonite block compacted to a dry density of 1.60 g/cm^3. Hydration under a very low injection pressure takes place through the pellets side. The water intake over time is measured, as well as the axial pressure in the LSO (Figure 1, left). Factors that could modify the homogenisation process, such as the water intake rate, are being analysed.

The TC cell test is a custom-built square cell consisting of a transparent methacrylate chamber reinforced with steels frames, designed to record and analyse textural changes inside the cell caused by hydration. Photos are periodically taken to observe textural changes, particle displacements, etc (Figure 1, centre and right). Postmortem analyses allow checking the final state of the material in terms of dry density, water content and pore size distribution.

Figure 4 : Evolution of axial pressure in LSO and textural observations in TC during saturation of pellets/powder mixture

Relation between Corrosion Behavior of Steel Rod and Bentonite Particle Size

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1. Introduction

Geological disposal is the most realistic method for disposal of high-level radioactive waste1). In one proposed method, a combination of bentonite and carbon steel is used in waste containers. Carbon steel overpacks, or waste containers, must be designed to be effective for 1000 years. However, corrosion can affect the containers' protection properties. Many researcher have studied methods of filling the containers with bentonite. Vibration and spray-type methods are the main methods considered1). However, there are some variations in the quality achieved by these methods2), such as unbalanced particle size distribution. Furthermore, the corrosion behavior of carbon steel must be changed. This is the most important factor in ensuring long-term stability of geological disposal3). The total area of water film on the carbon steel varies in proportion to bentonite particle size, and this controls steel corrosion behavior. We investigated the corrosion behavior of steel in bentonite from the viewpoint of particle size. We tested four bentonite samples with different particle sizes.

2. Experimental method

We classified KUNIGEL, into four bentonite particle sizes (0.85mm or less, 0.85-2.00mm, 2.00-4.75mm, 4.75- 9.00mm). First, a container of diameter 30mm was filled with bentonite to 45mm height. We then inserted a steel rod (C:0.80~0.85% ϕ1mm×45mm) into the container to simulate an overpack. We connected the steel rod as working electrode, Pt, as a counter electrode and Ag/AgCl to a potentiostat as a reference electrode. Measurement conditions of polarization were: scan speed 1mV/s and scan range ±250mV from natural potential.

3. Results and Discussion

Under the conditions of Fig.1, mixed potential $E=(2rn/S_0)E_1+\{(S_0-2rn)/S_0\}E_2$…(1). E_2 is negligible for a partially formed water. $2R\times n=S_0$ (total length of carbon steel)…(2). From equations (1) and (2), $E=(2rn/2Rn)E_1$…(3) where, r and E_1 are given. Thus, E is a function of R. Figure 2 shows the correlation between measured potential E and R^{-1}. The broken line is obtained by the least squares method of the experimental result. The relation between measured potential E and R^{-1} is linear. Therefore equation (1) is applicable to our results, i.e., the corrosion potential of steel in bentonite is proportional to the inverse of particle diameter.

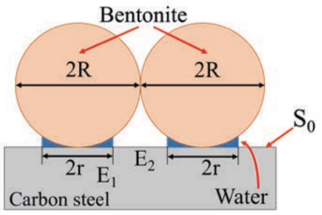

Fig. 1 Model of steel and bentonite interface we

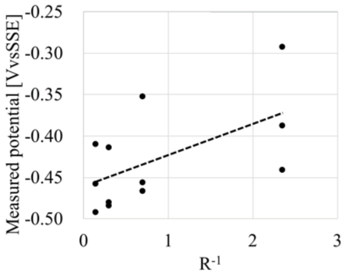

Fig. 2 Relation between corrosion potential and particle size

4. Conclusion

The corrosion potential of steel in bentonite is proportional to the inverse of particle diameter.

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Roman amphoras from an Iron Age settlement at the Danube

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Remnants of an Iron Age (Dacian) fortified settlement, dated to the 1st c. BC-1st c. AD, were explored at Divici-Grad on the Danube (todays Romania). The settlement is located on the northernbank of the Danube gorges (also called 'The Iron Gates') and was active in the time when the Romans intensified the control at the Danube through the establishment of a secure line along the Iron Gates. The first Roman military structures in the area date back to the first half of the 1st c. AD. The written proofs as well as the fortifications show a period of conflicts between the Romans and their neighbors, primarily the Dacians. The necessity of a fortification well agrees with the ancient literary sources which hand down a period of conflict betweenDacians and Romans. Highly fragmented wine amphoras were found at Divici-Grad. Based on typology, the amphoras were linked to three main production areas, *i.e.*Aegean, Pontic and Italic. The present study addresses a set of amphoras resembling the Dressel IIB type (widely produced in Campania, southern Italy). The combination of the typological analysis with polarized light optical microscopy, X-ray powder diffraction, cold field emissions canning electron microscopy coupled with energy dispersive X-ray spectroscopy and electron microprobe analysis aims to obtain data on the amphoras composition and provenance, in order to reconstruct trade routes of imports at the northeastern limes of the Roman empire.

The results show a Ca-rich ceramic paste, with frequent fragments of pyroxene (augite), plagioclase and amphibole. K-feldspar, quartz and muscovite are rarer. Well-preserved tests of foraminifera as well as shell fragments are characteristic. Lithoclasts are represented by fragments of quartzite, muscovite schist, weathered and fresh andesite, dolerite, granitic rock, limestone, sandstone, chert and argillitic rock fragments. The matrix is low birefringent. Porous glassy material is also common. The compositional features of the ceramic sherds suggest the use of a carbonatic clay as the main raw material. The lithoclasts are mainly represented by rocks of volcanic origin, although a minoritary metamorphic component is also present. Combining all data achieved so far, it is possibile to indicate the Vesuvian territory (Campania) as the most likely area of production of these amphoras. The present results would then testify for a long-scale trade of amphoras and related content from the Tyrrenian Sea to the boundaries of the Roman Empire.

Acknowledgement. The study was financed through the project UEFISCDI/CNCS PN-III-P4-ID-PCE-2016-0229. C.I. acknowledges subsidy by the Russian Government to support the Program of competitive growth of Kazan Federal University.

Multi-analytical approach of the composition and provenance of ancient ceramics

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The mineralogical methods started to be applied in studying the ancient ceramics only in the 30's of the last century with the aim to help the archaeologists to find answers to the old questions addressing the source and type of the raw materials and the technological constraints for producing the pottery. As the ceramic material is generally little altered over thousands of years of burial, it offers information about the economic, cultural and social context of an ancient society.

The ceramics is the first artificial material ever produced by man and consists of a complex and porous mixture of crystalline and amorphous phases. It offers an excellent field to study high-T low-P anthropogenic metamorphism. The initial mixture of mudstone(s) and various mineral and organic tempering materials transforms upon firing at a temperature generally between 700 ºC and 950 ºC, into a puzzle of micro-domains. The estimation of the firing temperature is based on the microstructural thermal changes of the matrix and the formation of new phases. The latter are regarded as both temperature- and raw materials-markers.

Old and new analytical methods are currently used in studying ancient ceramics from Romania, such as optical microscopy, X-Ray diffraction, electron microprobe, cold field emission scanning electron microscopy and field emission gun electron microprobe. They help in investigating to a high-resolution the physical details and the chemistry of ceramics. The methods provide insights into the degree of sintering and vitrification process, the thermal alteration of some components, and the shape and composition of firing phases. A perfect visualization of the tiny phases composing the matrix is enabled as well. As the results are influenced also by the quality of the thin sections, the ion-etching technique (Ar ion-beam) is used for the final stage of polishing. Case studies of ancient pottery found in Romania are presented.

Acknowledgements. The study was financed by the Excellence Research Program (Romanian Ministry of Research and Innovation through the UEFISCDI/CNCS project PN-III-P4-ID-PCE-2016-0229. C.I. acknowledges support of the Russian Government Program of Competitive Growth of Kazan Federal University.

Experimental fossilization of biomolecules and micro-organisms in clays

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The oldest fossil record gives us valuable information on the first steps of history of life on Earth (Briggs and Summons, 2014). Unfortunately, these are microfossils, only composed of organic matter, which underwent many transformations during the geological history of their host rocks, making their identification very difficult. Although many analytical techniques can be used to describe their structure and chemical composition down to the submicrometer scale, a precise understanding of biomolecule fossilization processes is critical to properly decode the ancient fossil record. In this aim, we develop an experimental approach to document the evolution of organo-mineral assemblages during thermal diagenesis while identifying the key thermodynamic parameters involved in the degradation processes. As the starting organic materials, we use either RNA or *E. coli* cells, which we fossilize in the lab within a gel of phyllosilicate composition and submit to hydrothermal conditions at 200°C. The microscopy and spectroscopy characterization of the residues reveals (i) the significant role of the mineral matrix and the influence of the amount of water on the intensity of degradation of biogenic chemical signatures, and (ii) the influence of the presence of organic compounds on the crystallization of mineral phases. These results offer new perspectives for the search for the oldest traces of life on Earth and highlight the need to characterize organic and mineral phases conjointly to properly discuss the biogenicity of "putative" Archean microfossils.

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Valorization of Tunisian clays in the ceramics field

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The ceramics sector in Tunisia includes 49 brick manufacturing plants, 101 artisanal bricks plants, 15 earthenware factories, 7 sanitary units and 3 units of refractory products. The consumption of clay is about 9 million tons per year distributed among the brick (6 million tons), earthenware, sanitary, refractory and artisanal pottery sectors. The Tunisian sector mines the sedimentary clay levels extending from the Triassic to the Pliocene and imports almost 149 thousand tons of clay per year, to meet this demand.

We have carried out research from the South to the North of Tunisia covering the entire stratigraphic series (Jamoussi, 2001, Fakhfakh et al., 2007, Hajjaji et al., 2010, Hachani 2011, Moussi et al., 2011).

The clay levels of the sedimentary series which contain illite, kaolinite, halloysite and which are likely to be used in ceramics are: clays of the Triassic of the Saharan platform, clays of the Lower Cretaceous over all Tunisia, clays of the Oligocene and Eocene of northern Tunisia and some clays of the Mio-Pliocene of northern Tunisia.

Laboratory and semi-industrial technological tests were carried out on the clays in order to decipher their ceramic potential. These analyses show that the Paleocene, Eocene and Oligocene clays give very satisfactory results in the production of bricks. The Triassic and Lower Cretaceous clays are used for the manufacture of ceramic tiles. Some of them have given good results in both the production of bricks and the manufacture of ceramic tiles. Some kaolinitic clays from Northwestern Tunisia yielded satisfactory results for the manufacture of refractory bricks. We have also been able to manufacture Light Weight Aggregates with Tunisian clays with or without correction and sometimes with the use of industrial waste.

The number of jobs generated in Tunisia in the ceramics sector is about 13500 jobs. This number could be improved if the Tunisian clays are better valorised.

Sorption an textile dye to clay modified with phosphonium surfactants

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Montmorillonite, a natural mineral, is becoming widely used as an alternative material in areas where sorptive, catalytic and rheological applications are required. High ion exchange capacity and surface area and more importantly its relatively cheap price make it an attractive adsorbent. With a chemical modification, the inorganic exchangeable cations of clay can be replaced by organic containing alkyl groups and phosphonium central atom. By this way, the surface properties of the clay are changed from hydrophilic to increasingly hydrophobic. As a result, the modified organoclay becomes a powerful adsorbent for toxic organics. One of the major problem concerning textile wastewaters is coloured effluent. Though not particularly toxic, dyes have an adverse aesthetic effect because they are visible pollutants. The main pollution source of textile wastewater comes from dyeing processes, with the degree of colouration being dependent on the colour/shade dyed and the type of dye used.

The present work is aimed to study the adsorption capacity and mechanism of removal of industrial anionic textile dye Acid Red by organobentonite. The organoclay adsorbent used was prepared by modification of purified Wyoming montmorillonite with the phosphonium surfactants P16, P28, P32, P40 containing the same central P atom and four various alkyl chains.

The layer spacing of the organophosphonium smectites was well preserved during water washings, indicating stability of surfactant molecules in the interlayer galleries. The phoshonium surfactant treatment introduced more than 95% of the CEC of the smectite. The phosphonium organoclays with long alkyl chains effectively removed aromatic textile azo dye from water solution while untreated smectite did not adsorb these molecules. The enhanced adsorption of the aromatic compounds is attributed to the length or number of aliphatic segments (C8-C16) of largest surfactants.

Acknowledgement: APVV 15-0741, APVV15-0347, VEGA 2/0141/17

Intercalation of montmorillonite with functionalized surfactant

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The structurally unique clay-intercalable 9,10-dihydroxy-octadecyltrimethylammonium (OH-ODTMA) cationic surfactant has been synthesized in two steps from commercially available oleylamine. Sodium montmorillonite (Na-MT) was modified via a cation exchange reaction using three different octadecyltrimethylamonium (ODTMA)-based organic cations. Basal spacings, surfactant configuration, interlamellar structure and thermal stability of the resulting organo-montmorillonites were characterized using X-ray diffraction (XRD), infrared spectroscopy (IR), thermogravimetric (TG) analysis and nuclear magnetic resonance (NMR) techniques. The 13C MAS NMR study demonstrated the coexistence of ordered (all-trans) and disordered (gauche) chain conformations. Deconvolution of the NMR spectra indicated that the conformational ordering of surfactant molecules within the gallery of montmorillonite strongly depended on their orientation, the presence of functional groups and temperature. Compared to ODTMA-MT, the amount of gauche conformers was significantly higher in montmorillonite intercalated with OH-ODTMA cation as well as in its synthetic precursor, oleyltrimethylammonium cation. Changes in the organic cations ordering were confirmed by FT-IR with a distinct frequency shift of the CH stretching and overtone bands. The novel alkylammonium surfactant functionalized with two OH groups in the middle of the backbone represents a prospective ingredient for organoclay-polyurethane nanocomposites.

Acknowledgement: APVV 15-0741, APVV 15-0347, VEGA 2/0141/17

The effect of the relative permittivity, the counterion charge ratio and the temperature on the structural properties and swelling of montmorillonite

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The thermodynamical and structural properties of charged colloids are strongly affected by the valency of the counterions, the solvent, as well as the temperature. With monovalent counterions, the electrostatic interaction between the particles is repulsive, whereas for multivalent counterions, the interaction can be attractive due to ion-ion correlation forces.

Here we will present results regarding the structural properties, and the intracrystalline swelling of the natural clay minerals Na^+-, and Ca^{2+}-montmorillonite as an effect of the relative permittivity of the solvent, the counterion charge ratio, and the temperature. For this purpose, we have used the experimental techniques; small angle X-ray scattering, and osmotic pressure measurements, in combination with the continuum model utilizing coarse-grained molecular dynamics simulations.

It was found that it is possible to tune the electrostatic interactions to obtain a transition from a repulsive to an attractive system for Na^+-montmorillonite by decreasing the relative permittivity of the solvent, or increasing the divalent counterion charge ratio, i.e. exchanging the counterions successively with Ca^{2+}. The transition arises from the enhanced attractive ion-ion correlation forces, where for the decrease of the relative permittivity is due to an increase in Bjerrum length. For the Ca^{2+}-montmorillonite, a non-monotonic behavior of the intracrystalline swelling was captured experimentally when decreasing the relative permittivity of the solvent. First, an increase in osmotic pressure, and in *d*-spacing was found, indicating that short-ranged interactions dominate the system. Then, the osmotic pressure, and *d*-spacing decreased below the initial system, implying that the ion-ion correlation forces are of importance. Moreover, it was found that the attractive electrostatic ion-ion correlation forces were enhanced with temperature.

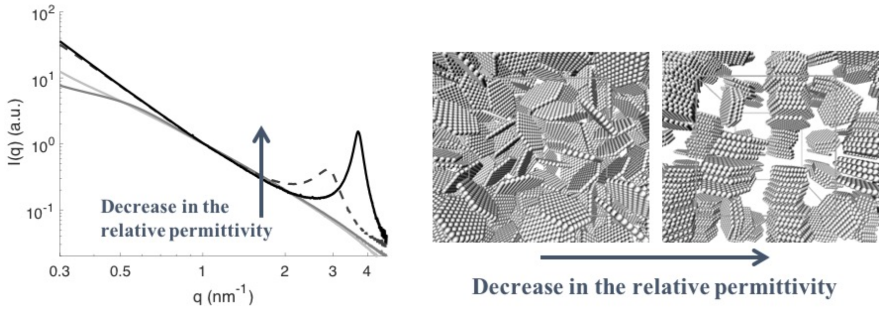

Figure 1: Scattering intensities, and simulation snapshots for Na-montmorillonite.

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Encapsulation of doxorubicin into polymer modified layered double hydroxide for effective cellular drug delivery

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Doxorubicin (Dox) is one of the widely utilized anticancer drug; however, its cardiotoxicity[1] has been raised as a weak point. In order to overcome the drawback, in this study, we suggest encapsulation of Dox in layered double hydroxide (LDH), which is known to deliver encapsulated moiety to cancer cells specifically[2]. As Dox and LDH both have positive charge, we first modified the interlayer space of LDH with anionic moiety poly(acrylic acid) (PAA) through ion-exchange route. Then, PAA-LDH was treated with Dox solution for encapsulation. The X-ray diffraction patterns of LDH, PAA-LDH and Dox-PAA-LDH showed (003) peak with respective d-spacing of 8.28, 11.02 and 11.96 Å, suggesting the consecutive intercalation of PAA and Dox. Furthermore, the fourier transform infrared spectroscopy and elemental analyses exhibited the intact structure of Dox was well preserved in Dox-PAA-LDH with loading capacity of 31.95 wt/wt%. Dynamic light scattering measurement indicated that the hydrodynamic radius of Dox-PAA-LDH was ~174.3 nm of which size is advantageous in clathrin-mediated endocytosis of LDH carrier toward cancer cells[3]. The anticancer activity of Dox-PAA-LDH was evaluated against human lung adenocarcinoma cell line (A549) and human osteosarcoma cell lines (MG-63) being compared with Dox, LDH and PAA-LDH. The 50% inhibitory concentration of Dox and Dox-PAA-LDH was determined 0.53 and 0.17 μg-Dox/mL, respectively, against MG-63 and 0.91 and 0.33 μg-Dox/mL, respectively, against A549. On the other hand, both LDH and PAA-LDH did not show significant suppression of cell viability for both cell lines. These results strongly suggested that the encapsulation of Dox into LDH enhanced cancer cell specificity of drug and cellular uptake.

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Contribution to the zeolite deposits in Mangatarem, Pangasinan, Philippines

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A zeolite deposit in Mangatarem, Pangasinan, Philippines is approximately 40 kilometers thick and interbedded with bentonite. The zeolites in Mangatarem contain two types of zeolite, namely: mordenite and clinoptilolite. The Aksitero Formation, a rock unit within Mangatarem, is characterized to have more mordenite than clinoptilolite. Several authors have studied the area presenting different results and having disagreements on how the zeolites in Mangatarem were formed. Previous authors regarded that the process through which the zeolites in Aksitero Formation formed due to burial diagenesis. Some regarded that zeolites were formed due to the reaction of smectite with hyperalkaline groundwater. Though, there is no detailed study on the quantitative mineralogy and petrography of zeolites in Mangatarem. This study aims to: examine, in more detail, the mineralogical, petrographical and morphological characteristics of the zeolite deposits in Mangatarem. Mineralogical, petrological and geochemical properties will be determined by X-ray diffraction, optical microscopy, scanning electron microscopy and energy dispersive spectrometry. The results of this study intend to give new insights and better understanding of the geology and conditions on how the zeolite deposits in Mangatarem were formed.

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Unravel the famous halloysite structural charge and interlayered cations from X-ray absorption spectroscopy investigations

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The halloysite revival occurred with halloysite nanotubes (HNT) which offer an attractive natural cylindrical material that could be obtained at a fraction of the cost of synthesized nanomaterials such as carbon nanotubes. Halloysite is a dioctahedral 1:1 clay mineral commonly found in both weathered rocks and soils. Halloysite differs from kaolinite by (i) its morphology (tubes or spheroids versus platy one), and (i) a driving force that attracts water into the interlayer space. However, halloysite (10 Å) irreversibly loses its interlayer water easily giving rise to halloysite (7 Å) on standing in dry air, vacuum, or upon heating. The halloysite (10 Å) exhibits higher cationic exchange capacity (CEC) than the 7 Å-dehydrated form. It was hypothesized that HNTs may carry a negative charge which could be counterbalanced by exchangeable cations shielded by the intercalated water. While halloysitic soils may present a high CEC of 10 to 40 $\text{cmol}_c\ \text{kg}^{-1}$, and a high selectivity for poorly hydrated cations, such as K^+ and Cs^+, the hypothesis or alternative explanations have never been validated up to now.

In this context, we aimed at unraveling the structural charge of different representative halloysites from various environments (soils and quarries from all around the world) to understand the ability of halloysite to fix cations. For this purpose, we investigated the atomic coordination and the local environment of Al, Si, Fe atoms, corresponding to structural network of halloysite and the one of K ions as interlayer probe, performing *in situ* X-ray Absorption Near Edge Structure measurements (XANES) at the K-edge of each element at LUCIA beamline (SOLEIL synchrotron). XANES experiments were coupled with others analytical technics such as X-ray diffraction, infrared spectroscopy and transmission electron microscopy... The results will then be discussed in relation to the origin, morphology and physicochemical properties of halloysites.

Cobalt impregnated smectites (raw and acid activated) as catalysts in organic dye oxidation process in the presence of peroxymonosulfate generated radicals

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Smectite based Co catalysts were prepared using the wetness impregnation method and applied as activators of potassium peroxymonosulfate as the source of sulfate radicals and tested in the degradation of Acid Orange 10 (AO10) in aqueous solution. Starting smectite clay (Bogovina, Serbia) was submitted to acid activation which resulted in enhanced textural properties [1].

The starting smectite (S) and acid activated (S_A) were impregnated with predefined amounts of $Co(NO_3)_2$ which corresponded to 1.0 or 0.5 times the value of CEC. The impregnation process was followed by calcination at 450 °C during 6 h. The obtained catalysts were denoted according to the type of activation and Co^{2+} loading as: 1.0Co/S, 0.5Co/S, 1.0Co/S_A and 0.5Co/S_A. The chemical and phase composition of the catalysts were determined using XRF and XRD method, respectively. Textural properties were monitored using the low temperature N_2 physisorption method. Potassium peroxymonosulfate (Oxone® i.e. $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$) was used as the source of sulfate radicals generated by cobalt incorporated into smectite structure of Co/S and Co/S_A. The influence of cobalt content and acid modification on the efficiency of the decolorization of dye solutions was investigated. The decolorization of AO10 was monitored using UV–Vis spectrophotometry at λ_{max}=478 nm.

All catalyst efficiently decolorized investigated dye within 4 h. The decrease of absorbance at the characteristic wavelength was tested with different kinetic models and the exponential equation showed the best fit indicating the first order kinetics for investigated catalytic systems. The increase of cobalt content had higher impact on decolorization rate than the development of porous structure achieved by acid activation.

Acknowledgment: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No. III 45001).

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Geotechnical Characterization of Zeolite Deposits in Mangatarem, Pangasinan, Philippines

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The clinoptilolite and mordenite are the two types of zeolites found in Mangatarem, province of Pangasinan, Philippines which thickness ranges from 20 to 40 meters. These two are the most effective zeolites with adsorption capacity and commercial value. Due to the wide distribution and the unique properties of these zeolites, these have been mined and used in several industries and became notable in geotechnical engineering. The thermal behavior of the Philippine natural zeolites has been investigated. However, the characterization of geotechnical properties of zeolites has not been studied. This study aims to assess the engineering geological properties of zeolite particularly the pH, grain size, plasticity, swelling indices, compaction and specific gravity, compressibility, and shear strength. X-ray diffraction (XRD) and scanning electron microscope (SEM) were also utilized to understand its composition and microstructure.

Mineralogy, geochemistry, and genesis of bentonites in Upper Cretaceous Bereketli Member of the Reşadiye Formation, Reşadiye (Tokat), Turkey

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The depression zone tectonically-controlled by the North Anatolian fault, hosted chemically weathered Upper Cretaceous volcano-sedimentary units. The weathering of trachyte, trachyandesite, rhyolite, rhyodacite, and pyroclastics resulted in formation of bentonites in the Reşadiye (Tokat) region. These bentonites have an economic importance for the drilling, molding, and paper industries. The characteristics of these bentonites were examined using polarized-light microscopy, X-ray powder diffractometry, scanning electron microscopy, infrared spectrum, differential thermal analyses and thermal gravimetry, and chemical analyses. Smectite is seen as both massive grains and as coarse smectite crystals found in dissolution voids and desiccation fractures. These coarse smectite crystals are associated with clinoptilolite-heulandite and micritic calcite crystals. In this association, smectite was formed by *in situ* precipitation under closed hydrologic system during diagenesis. Smectite was observed in contact with relict of weathered–feldspars, mica, and devitrified glass shards. It was likely formed by a dissolution of volcanic source rocks followed by precipitation under alkaline conditions. The composition of smectite clay fractions showed both montmorillonitic and beidellitic character based on the tetrahedral charge/octahedral charge ratio, with average structural formulae of:
$(\mathrm{Si}_{8.10}\mathrm{Al}_{0.02})(\mathrm{Al}_{2.86}\mathrm{Fe}_{0.39}\mathrm{Mg}_{0.47}\mathrm{Mn}_{0.0002}\mathrm{Ti}_{0.04})(\mathrm{Ca}_{0.12}\mathrm{Na}_{0.38}\mathrm{K}_{0.05})$ and
$(\mathrm{Si}_{7.21}\mathrm{Al}_{0.79})(\mathrm{Al}_{2.57}\mathrm{Fe}_{0.92}\mathrm{Mg}_{0.71}\mathrm{Mn}_{0.01}\mathrm{Ti}_{0.09})(\mathrm{Ca}_{0.17}\mathrm{Na}_{0.03}\mathrm{K}_{0.10})$, respectively.
The positive correlation of Zr/Ni ratio versus Zr/Co ratio and Zr/Sm ratio versus SiO_2 in the claystone, tuff/tuffite, and clay fraction samples showed the increased Zr with increasing abundance of smectite in bentonite deposits and related volcanic source units. The negative correlation of Al_2O_3 versus SiO_2, each of Fe_2O_3+TiO_2 and Mg versus SiO_2, and positive correlation each of Na_2O, K_2O, Sr, Nb, Zr/Sm, Dy/Yb with SiO_2; Rb+Ba versus Na_2O+K_2O; Zr/Sm versus SiO_2, and enhance of LREE/MREE+HREE ratio, and a negative Eu anomaly, were consistent with the fractionation of plagioclase, K-feldspar, hornblende and devitrification of volcanic glass in altered volcanic materials during weathering process of the host rocks. The enrichment from 20.67 to 28.08 V-SMOW in $\delta^{18}O$ and the depletion from -73.67 to -82.61 V-SMOW in δD of montmorillonite and beidellite, suggest precipitation under influence of early diagenetic processes following the chemical weathering process under the appropriate climatic conditions.

Preparation of gallate / layered double hydroxide composite and its application to environmental purification

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Layered double hydroxide (LDH) has an anion exchange ability and reconstruction function, and it is widely used materials such as plastic filler, environmental purification material, and antacid agent. In addition, there are many researches on complexing of various organic substances by the anion exchange ability of LDH. There are also many researches such as improvement of stability of interlayer materials and confinement effect between interlayer. On the other hand, gallic acid (GA) is an herbal medicine present in plants' insects and is well known as a typical phenol carboxylic acid. Recently, several studies on the GA / LDH composite have been reported1-2). The authors also reported on the synthesis of GA / LDH composite3). In this paper, we investigated the preparation of GA / LDH composite mainly by reconstruction method and investigated the environmental purification application of the obtained composite.

Mg-Al-CO_3 type LDH prepared by coprecipitation method was used as a starting material. Gallic acid / monohydrate of reagent was used as a target material. Since GA has a greater solubility in ethanol than water, sodium gallate was precipitated by adding sodium hydroxide to a GA ethanol solution, followed by solid-liquid separation, washing and drying. Obtained sodium gallate was also used as a target material. Thermally decomposed LDH heat-treated at 500°C for 24 h was used in the reconstruction method. Thermally decomposed LDH was added to 100 mL of a predetermined concentration of GA and sodium gallate solutions and reacted at room temperature for 24 h. After the reaction, the solid component was separated with a centrifugation, washed with deionized water and dried to obtain the GA / LDH composite.

XRD patterns of obtained GA / LDH composites are shown in Fig.1. GA / LDH composite prepared using higher concentrated solutions showed larger basal spacing. About GA / LDH composite prepared with 10 mM solution, the introduced amount of gallate was estimated as 80% of the ion exchange equivalent. Results on environmental purification using this composite will be reported on the day.

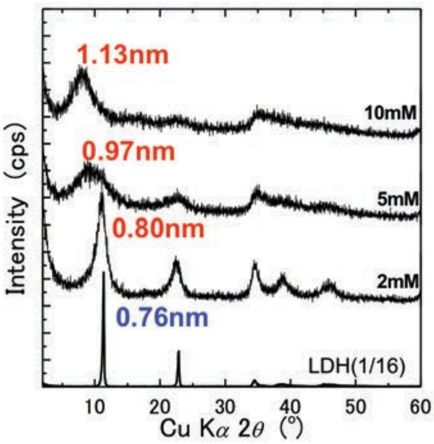

Fig.1 XRD patterns of GA/LDHs prepared using sodium gallate solution.

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Linking the geochemical composition of lake sediments to DNA sorption and preservation

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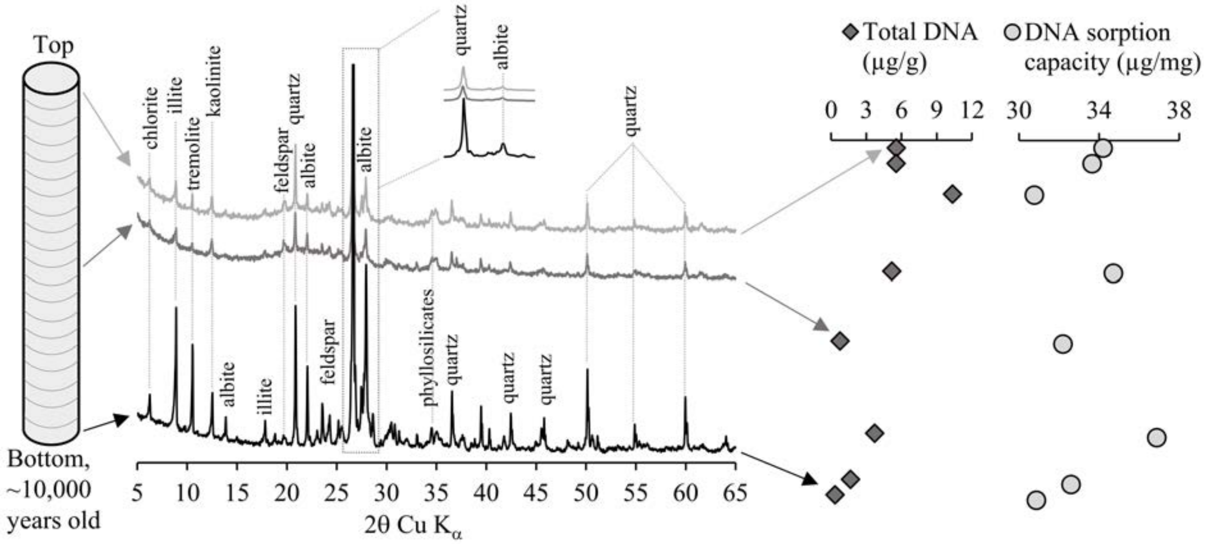
Lake sediments constitute natural archives that contain biological and chemical records from local regions. Since sediments were shown to preserve DNA fragments for tens and even thousands of years[1,2], these sedimentary records can in principle reveal ancient biotic activities, such as species colonization and abundance. Even though the sorption of DNA molecules and nucleotides onto well-defined minerals, especially clays, has been reported in the literature [3,4], the link between the geochemical features of freshwater sediments and DNA sorption and preservation is rarely discussed. Therefore, the aim of this research is to understand the geochemical aspects that are responsible for the binding and preservation of ancient DNA (aDNA) in lake sediments. For this reason, a sediment core was collected from the Hotagen Lake in central Sweden. The mineralogical, chemical, and physicochemical composition were determined for selected sediment layers throughout the core, as well as the corresponding total DNA content and the DNA sorption capacity. Even though the sediment layers showed common clays and other minerals, such as chlorite, illite, kaolinite, and albite, their abundance is different. Similarly, the chemical contents (such as Si, Al, Mg, and K), organic matter, and physicochemical parameters, such as CEC, were different for the sediment layers. Preliminary results did not show a common trend between sorption capacity and the total DNA content for the sediment layers. Therefore, we follow the change in mineralogy, chemical composition, and physicochemical parameters in the lake sediments and link them to the sorption and preservation of DNA. Furthermore, this connection gives insight on the conservation of aDNA on one hand, and the evolution of life on the other.



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Evaluation of Milos' bentonites with respect to aflatoxin adsorption and governing mechanisms of clay surface / aflatoxin molecule interaction

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Bentonite rich in montmorillonite is an effective adsorbent of mycotoxins. This feature of montmorillonite is used to inactivate mycotoxins in feedstuff by adding a certain clay amount to it. Clay particles adsorbs toxins' molecules in the digestive track of the animal. Bentonite is the dominant mineral adsorbent against aflatoxin molecule (AfB1) while its efficiency against the rest of mycotoxins (FUM, DON, OTA, ZEA, T2) varies very much depending on a)its microstructure and b)on the surface modification which has previously undergone. Bentonites of various origins and of different surface treatment present different adsorption efficacy.

The objective is to evaluate bentonites from Milos island-Greece for AfB1 adsorption and illustrate the governing mechanisms. Samples were characterized with analytical methods: XRD, Layer Charge density (LCD), Electrical Charge deficiency origin (ECDO), total CEC, Exchangeable cations concentration, XRF and BET method. Among many raw samples a certain number was intentionally selected so as to have the maximum possible variation in terms of mineralogical characteristics, chemical composition and typical smectite clay features. Bentonites were then classified as low-, medium- and high- in respect to AfB1 adsorption. A strong correlation between LCD, ECDO and AfB1 adsorption was found. Low LCD smectites with unit layer charge not higher than 0.36 and octahedral charge origin > 80% appear to have high binding capacity. High smectite content (XRD) results also to high AfB1 adsorption. Exchangeable cations are binding sites of AfB1 molecule. Different cations of different valence and hydration films around them, occupy different volume into smectite interlayer space. Valence and radius of hydrated predominant exchangeable cation are key factors affecting binding capacity and, thus, the mechanism governing the clay surface / aflatoxin molecule interaction. Naturally occurring bentonites have varying CEC values as well as different exchangeable cation concentrations. We found that CEC value and exchangeable cation concentration in smectite interlayer space (along with LCD and ECDO) are predictors of bentonite's adsorption capacity. Accordingly soda ash activation degree affects capacity since it determines the type the predominant exchangeable cation.

Since stereochemical environment in close proximity of montmorillonite's surface plays a key role we concluded that 3D size, shape and polarity of AfB1 molecule as well as of other mycotoxins' molecules affect interactions between those toxic compounds and dispersed clay particles. Various thermal and chemical treatment techniques of bentonites, which modify this environment can increase its binding capacity of AfB1 or other mycotoxins.

Bentonite low permeability barrier in highly ionic strength environment: interaction with silica

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Sealing properties of bentonite are well known and recognized, thus, it is extensively used as a barrier for geosynthetic clay liners (GCL) and later even for nuclear waste disposal facilities. In GCL a long term low permeability is a demand. Apart from acting as a barrier that inhibits the permeation of liquids through the liner, bentonite is also flexible, self-healing and a low cost solution, with all these characteristics being very important for the application. Another technical request is bentonite of GCL to perform well in highly ionic strength liquid environments, providing impermeable lining barrier and caps for landfill and industrial waste containment, and replacing traditional Compacted Clay Liners CCLs of higher thickness. Higher performance is related to lower hydraulic conductivity

Bentonite is characterized by its great ability to absorb water molecules (8-9 times its dry mass) and swell its volume up to 15-20 times. When water starts entering the interlayer space a rigid network of relatively immobilized molecules is formed and no more water can pass through the entrance of the interlayer. This makes bentonite impermeable or, in other words, gives a hydraulic conductivity less than 10^{-9} m/s. However, it is well known that in the presence of soluble salts bentonite loses part of its ability to hydrate and retain an impermeable structure. Studies on the direction of preserving bentonite properties in highly ionic strength solution have been made and the problem so far is approached with the addition of organic compounds such as cellulose. A more innovative and viable approach has been stated in literature where through the addition of a component containing free silica or other silicon compound, bentonite can preserve its sealing properties in highly alkaline environment, by precipitation of new siliceous phases within the pore space of bentonite.

In order to validate theory of secondary precipitation Micrasil™, an Imerys' micronized natural amorphous silica source, was used in combination with a low hydraulic conductivity bentonite and tested in various ionic strength solutions, at a pH ranging from 5 to 12.5. The use of amorphous silica does not improve bentonite performance. In all cases the water hydration of bentonite / Micrasil™ mixtures was reduced correspondingly to the Micrasil™ replacement. However, there was a minor improvement by 16% in the hydration ability of bentonite against an alkaline solution containing readily available silica from Micrasil™. In conclusion, the practical significance of adding a siliceous solid source to bentonite is limited, as the effect is negligible or negative, nevertheless the impact of silica on bentonite with respect to its hydration is a valid observation, and further scientific proofs are necessary in order to be elucidated.

Liquid crystal phase of clay nanosheet dispersed in *N*, *N*-dimethylformaide / water mixture

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Anisotropic colloids of rod- or plate-like particles have been interested in condensed matter physics field because of their unique properties such as liquid crystallinity (LC) and unusual rheological properties. Especially, inorganic nanosheets that are obtained by exfoliation of layered materials are highlighted as ultimately anisotropic nanoparticle[1-2]. Among various nanosheets, layered clay minerals are important materials for many industrial applications such as paint, cosmetics, and plastics.[3] In those applications, dispersion in non-aqueous solvents are required; however, it is generally difficult to prepare good dispersion of fully-exfoliated nanosheets in non-aqueous solvents and, therefore, the property of those colloids have hardly been investigated. The non-aqueous colloidal systems are also curious form the fundamental point of view because there have been few detailed studies for those system. Here we demonstrate successful preparation of the colloidal sols of a fluorinated layered clay mineral, fluorohectorite, dispersed in *N*,*N*-dimethylformamide (DMF)/water mixture. We investigated liquid crystallinity, structure of the colloidal sols, and rheological property.

Regardless of the solvent composition, textures and colors due to birefringent of LC phases were observed by polarized microscopy above the same critical concentration, indicating that the nanosheets are well-dispersed in the mixed solvents. In the LC colloids, swollen lamellar-like structures with the basal spacing of up to ca. 100 nm were identified by small-angle X-ray scattering. With the increase of DMF content, the basal spacing increased significantly, indicating that the DMF facilitated the repulsive interaction between the nanosheets. The dependence of viscosity of the colloid on DMF content showed an unexpected trend. It increased with the increase of DMF content below ca. 50 wt% of DMF but it decreased afterwards.

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About the Critical Coagulation Concentration of Allophane and dioctahedral Smectite

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Clay minerals can be dispersed in water (aqueous solutions) if the ionic strength is below the critical coagulation concentration (ccc). Mixtures of clay minerals and water in which the clay minerals settle are called suspensions. The term "dispersion" is used if no separation of both phases is observed, at least not within several hours. Increasing ionic strength is known to destabilize dispersions, leading to a coagulated system. In case of dioctahedral smectites, phosphate addition leads to significant increase of the ccc because heterocoagulation, which is based on the interaction between positively charged edges and negatively charged faces, is prevented. Coagulation caused by increasing the ionic strength is caused by a compression of the diffuse ionic double layer, which in turn depends on the surface functional groups and surface charges. The most important functional groups of both allophane and dioctahedral smectite are aluminol groups. Allophane primary particles, however, are spherical hence exhibiting a more or less uniform surface. The surface characterisitics of smectite edge surfaces and smectite basal surfaces, on the other hand, differ, causing different coagulation behavior. Allophane is much more difficult to disperse than dioctahedral smectite.. It tends to coagulate, even at low ionic strength. Dispersion of allophane is only possible at low ionic strength and pH 4 (or less). Below pH 4.5 aluminol groups are positively charged hence leading to repulsion of primary allophane particles. Smectites' aluminol groups are located at the edges only. The repulsive forces between the edges of smectites (small part of the total surface area), however, are less significant than the attractive forces between the positively charged edges and the negatively charged basal surfaces (larger part of the total surface area). This so called heterocoagulation led to a much lower ccc of smectites (around 10 mmol/L NaCl) at low pH compared to pH > 7 (20 – 30 mmol/L). Even more stable dispersions were obtained at pH around 10 (ccc about 50 mmol/L NaCl). Special behavior was observed for Wyoming bentonites at pH > 7. Dispersions made out of Wyoming bentonites were stable even up to > 100 mmol/L. This phenomenon, however, cannot be explained, yet. Comparing the ccc of 38 bentonites with their basic parameters suggests that the portion of tetrahedral charge has an effect on the ccc in that higher charge leads to lower ccc. The Wyoming bentonites on the other hand prove, that other parameters are also important (Kaufhold et al., 2018).

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Optical manipulation of oxide nanosheets

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On-demand and local manipulation of exfoliated oxide nanosheets, including clay nanosheets, in colloidal dispersions enables a variety of novel applications of nanosheet-based materials. We have realized local and on-demand orientation of colloidal fluorohectorite and hexaniobate ($K_4Nb_6O_{17}$) nanosheets by irradiation of a focused laser beam (Tominaga et al., 2018a, b; Nagashita et al., 2018; Higashi et al., 2018).

Colloidal samples of nanosheets used for optical manipulation were injected into a 100 µm thick thin-layer glass cell. The cell was set on the stage of a microscope. A linearly polarized continuous-wave laser beam emitting at 532 nm was focused at the center of the cell (50 µm from the cell-sample interface) using an objective lens.

Microscope images of a fluorohectorite colloid with a concentration of 0.01 g L^{-1} before and during irradiation with the linearly polarized laser beam are shown in Figure 1. With the irradiation of a 50 mW of the laser beam, the nanosheet was immediately trapped at the focal point. After 12 s of continuous laser irradiation, the fluorohectorite nanosheet started tilting toward the direction perpendicular to the cell surface. After 14 s, the fluorohectorite nanosheet was stationarily oriented in this direction. Then, the oriented nanosheet started to rotate its edge with respect to the laser propagation direction. Finally, the nanosheet edge was oriented parallel to the polarization direction of the incident laser beam. The nanosheet stably trapped with this orientation manner during laser irradiation (after 20 s). Due to a large refractive index, a niobate nanosheet was optically manipulated similarly even by relatively weak optical power 5 mW of the laser beam.

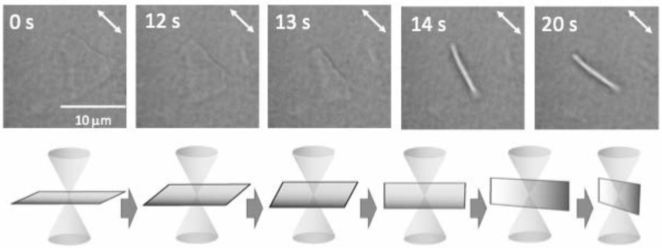

Figure 1. Microscope images of a fluorohectorite nanosheet before and during laser irradiation. The schematic representation is also shown. The white arrow indicates the polarization direction.

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Effect of solution type and temperature on the strengthening of laterite (Cameroon) based geomaterials: Rheological and micro calorimetry analyses

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The aim of this work was to investigate the effect of acid and alkaline solutions on the setting time, rheological behaviour and heat release of two calcined laterites (iron-rich laterite (LAI600) and lateritic clay (LAC600)) highly available in Cameroon (at room temperature (18 ± 3°C)). Two solutions were used for the geomaterials synthesis. The specimens were cured at room temperature (18 ± 3°C) and 40°C. Results showed that in alkaline solution the setting of activated LAI600 was shorter compared to that of LAC600. This could be due to the high content of iron phase which may react with hydroxide ions (HO^-) to form $Fe(OH)_3$ gel allowing the lower setting. The isothermal calorimeter was adopted to evaluate the heat evolution of both activated laterite based geomaterials. Both hardener and temperature influenced significantly the duration of exothermal consolidation peaks. From the measurements, the partial dissolution of LAI600 occurred rapidly compared to LAC600 and the formation of binding phases could be detected by the end of the decrease of exothermal peaks with time. It was also noticed that the released energy tended to increase during the activation when increasing the temperature from 20 to 40°C. Hence the increase of temperature likely favoured the faster dissolution accompanied by higher energy. For the rheological data the shear stress within the linear viscoelastic region was higher for LAI600 pastes than LAC600 pastes when acid or alkaline solutions were used. This could be due to the formation of Fe_2SiO_4, $FePO_4$ or $AlPO_4$ gels arising from the interactions between Fe^{3+} or Fe^{2+} provided from LAI600 and Si^{4+} and PO_4^{3-} ions provided from alkaline and acid solutions respectively with the time. Understanding and controlling the rheological behaviour, setting time and reactivity of acid or alkali activated laterite based geomaterials will determine whether they can be implemented at high scale. Therefore a systematic study needs to be carried out in details by evaluating the different factors that can affect these parameters in order to develop more resistant and sustainable geomaterials from laterites.

Fault zones, graphite, and anomalous celadonite/nontronite alteration in deeply weathered high-grade metamorphic rocks of southern Eyre Peninsula, South Australia

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Anomalous alteration, in the form of nontronite and/or celadonite as veins and patches, occurs within and adjacent to prominent shear zones in weathered, graphite-rich schist and gneiss of Paleoproterozoic high-grade metamorphic rocks exposed at the Uley graphite mine and in coastal cliffs at Sleaford Bay on southern Eyre Peninsula. The celadonite is a product of biotite alteration. Two distinct nontronites are present at the Uley mine and formed by alteration of biotite and amphibole (ferro-hornblende), the source of CMS special clays NAu-1 and NAu-2, respectively. The alteration was interpreted to reflect low temperature hydrothermal fluid activity. The basis for interpretation was the increase in alteration intensity in zones of brittle fracture, persistence of nontronite and celadonite with depth, and effect in modifying overprinting kaolinization, which extends to ~60 m depth (Keeling et al. 2000). The timing of nontronite/celadonite alteration was speculated as late-post Kimban orogeny (c. 1730-1690 Ma), during late-stage igneous activity and fracturing accompanying exhumation of the granulite facies rocks.

Subsequent dating of celadonite by K-Ar method, together with oxygen isotope data, indicated that supergene processes were most likely responsible for celadonite formation. Separated fine fractions of celadonite from Sleaford Bay were dated at c. 48-46 Ma (early Eocene); Uley mine celadonite formed at c. 21-15 Ma (early Miocene). Oxygen $\delta^{18}O$ values averaged 21.8 per mil relative to V-SMOW.

An alternative explanation for the formation of celadonite/nontronite alteration from biotite considered the role of graphite and fault zones in modifying the local environment during chemical weathering and oxidation. Under redox conditions, conductive graphitic bodies focus the flow of negative charge towards the zone of oxidation leading to increased consumption of oxidizing agents in the area near the top of the conductor. Graphite smeared along fault zones enhances the effect through increased connectivity and higher electrical conduction. A self potential (SP) anomaly of -300 mV was measured at the Uley mine. This is sufficient to stabilize Fe^{2+} at pH <8 and thereby limit the formation of $Fe(OH)_3$. The combination of a relatively reduced environment and high salinity could maintain Fe^{2+} and facilitate formation of celadonite and nontronite, during weathering processes that ultimately result in partial or complete oxidation to Fe^{3+}.

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Earthen construction in future urban area

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Major component of raw earth construction, natural and reusable material, clays have amazing properties. They act as a binder in earthen materials and have enabled the building of cities since the beginning of the Neolithic revolution. However, their high sensitivity to the environment impacts the durability of clay-rich materials such as earthen ones. Alluvium is a project supported by the I-Site FUTURE from the Paris Est University, and brings together economists, architects, researchers of historical sites as well as engineers to develop, test and apply at different scales reinforced earthen materials. The properties improvement is obtained by the addition of biopolymers or surfactants. Our project aims to demonstrate the potential of earthen construction in future urban area as well as in the conservation of a traditional built cultural heritage.

At microscopic scale (particle scale), the interactions between pure clays minerals and additives such as bio-polymers, polymers or surfactants are studied to understand the process that ensures the strengthening or the lowering of the water sensitivity of the material. Colloidal modelling helps understanding this process whose effects are studied at the mesoscopic scale (or brick scale) via the transfer properties in porous medium and mechanics (especially swelling-shrinkage). Then, the results will be upscaled to natural clay-rich soils from Parisian basin. The project aims particularly at reusing local excavated soils and to develop maintenance techniques adapted to earthen materials, thus promoting the local circular economy. The durability of newly developed and formulated materials with additives will be evaluated by applying wet-dry cycles.

Finally, a demonstrator at the building scale will validate the processes implemented by practitioners and the energy efficiency of reinforced earthen building. A socio-economic approach will evaluate the impacts both on the local economy, on the quality of habitat (especially its consumption of energy) and on a wider scale, the quality of life for inhabitants.

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Mineral characterization of Pakistan's indigenous clays for their potential use as aflatoxin adsorbent

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Pakistan has large clay deposits of medium to high grade with high potential for various industrial, biological, agricultural, and health applications. Yet, limited studies have been conducted on the mineralogy details of these clay reserves, which hindered their exploitation for specified uses. Forty-two active mines of Pakistan's clays/bentonites reserves were investigated for their mineralogy to identify their potential use as aflatoxin binder.

The mineral phases in the clays were identified through X-ray diffraction analysis, structural characteristics through Fourier transform infrared (FTIR) band positions, particle size distribution through laser diffraction, aflatoxin adsorptive effectiveness through Langmuir adsorption isotherms, and charge estimation through cation exchange capacity determination.

Based on the dominance of the respective minerals determined through XRD of the bulk samples, six clay mineral groups were identified and named as smectite-vermiculite, smectite, super expanding/interstratified smectite, smectite-chlorite, palygorskite-smectite, and kaolinite having 32, 26, 16, 12, 10 and 5% of total samples, respectively. Smectite dominance was evident at each mined site with other minor mineral constituents such as mica, kaolinite, and quartz, indicating their genesis as of sedimentary origin. Dioctahedral nature of montmorillonite and dominance of Al at octahedral sites was described by the 915 cm^{-1} bands in most smectites. Fewer smectites had ferrous at the octahedral position through isomorphic substitution; however, Mg substitution was also identified at 840 cm^{-1}. Palygorskite characteristic band at 1190 cm^{-1} assigned to Si-O-Si bonding related to inversion of apical O in alternating ribbons was also present. The super expanding/interstratified smectites and the palygorskite-smectite mixture had the higher (50-65%) particle volume fractions while smectite, smectite-chlorite and smectite-vermiculite had particle size fraction 20-35% below 2 µm. Organic carbon content was below 0.2% in most of the clay repositories, except for the interstratified smectite group which had slightly higher (0.6%), and suited their use as aflatoxin adsorbent. Aflatoxin adsorption capacity estimated through Langmuir adsorption model indicated the optimistic potential use of indigenous clays as aflatoxin binders. Smectite dominance had a positive correlation to aflatoxin adsorption. The aflatoxin binding capacities was in the order: smectite > smectite-vermiculite > smectite-chlorite > super expanding/interstratified-smectite > palygorskite-smectite > kaolinite.

Calcium bentonites had greater adsorption capacity and isomorphic substitution of ferrous in the octahedral sheet enhanced bonding of aflatoxin to clays. Use of indigenous clays as aflatoxin binder at an affordable price in high potential feed industry of Pakistan could not only reduce import of binders but also reduce the incidence of aflatoxicosis.

A new model of mass transport in clays and its experimental verification

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A new model of transport processes in deformable shrinking-swelling clayey rocks is proposed. The model is designed for coupled description of rheological and mass transport properties of shrinking-swelling clayey rocks. Model is founded on classical methods of physical-chemical poromechanics and mass exchange theory between water in transport pores and clay minerals in various kinds of clayey rocks. The main advantage of the model is concluded in using of proper storage equation in non-equilibrium mass-exchange processes model (*Khramchenkov et al, 2016*). Equations of the models are:

1) The mass balance equation:

$$\mathrm{div}\mathbf{q} + \partial\theta/\partial t = \xi,\ \xi = \lambda(\theta_\infty - \theta)^\omega;\ \lambda, \omega = \mathrm{const} \tag{1}$$

Here θ – dilation, $\mathbf{q} = -\frac{k}{\mu}\nabla p,\ k = \frac{k_0 m^3}{(1-m)^2},\ k_0 = \mathrm{const}$ – Darcy law for water flux, *k* – permeability, *m* – porosity, μ – viscosity, *p* – pressure, ξ – shrinkage-swelling function. For θ_∞ we have $RTq/[V_0(1+\theta_\infty) - V_s] = W$, where *R* – gas constant, *T* – temperature, *q* – cation exchange capacity, V_0 – initial volume, V_s – volume of solid phase, *W* – total load.

2) Equation for connection of dilation and porosity

$$\frac{\partial m}{\partial t} = (1-m)\frac{\partial\theta}{\partial t} - \frac{1-m}{V_s}\frac{\partial V_s}{\partial t},\ \frac{1-m}{V_s}\frac{\partial V_s}{\partial t} = \xi \tag{2}$$

3) Equation for deformation description:

$$\theta = \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = \mathrm{div}\mathbf{U} \tag{3}$$

4) Rheological correlations:

$$\left(K + \frac{G}{3}\right)\left(\nabla(\mathrm{div}\mathbf{U})\right) + G\left(\Delta\mathbf{U}\right) = \nabla(p + (\rho_s + \rho_w)gz). \tag{4}$$

Here *K*, *G* – elastic coefficients of porous matrix, $\mathbf{U}$ – displacement vector, ρ_s and ρ_w – density of solid phase and water correspondingly.

Features of the model, which are important for explaining of hydro-mechanical and mass transport clay's behavior, were examined. It is shown that in one-dimensional case the model of flow in swelling clay layer can be reduced to the Fisher–KPP equation. The solution of the equation was used for determination of parameters of the process for experimental studies. Obtained numerical solution is in close agreement with the experimental data.

Khramchenkov E.; Khramchenkov M. (**2016**) Int. J. of Rock Mechanics&Mining Sci. 86, 1 –4.

Nanoscopic structures and chemistry of mixed-layer biotite-vermiculite in the weathering profile in Abukuma granitic rocks in the eastern part of Fukushima, Japan

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The present study is dedicated for the mineralogical investigation on “weathered biotite”, which is considered as a major material fixing radioactive cesium in granitic soils mainly covering contaminated area formed by the Fukushima nuclear accident in 2011[1]. Biotite in granitic rocks commonly transforms by weathering to vermiculite and other secondary minerals via various alteration stages. Although tremendous works on the mechanism of biotite alteration have been conducted in the past, the characteristics of the mixed-layer structures of biotite-vermiculite and heterogenous chemical features of weathered biotite are still unclear. In the present study, complex structures and chemical compositions of the weathered biotite collected from a weathering profile of granodiorite rock in Fukushima Prefecture, Japan, have been examined by means of several nanoscopic methods combining with bulk analyses.

Based on mineralogical and chemical analysis, three stages of biotite alteration within a weathering profile were deduced as below: (1) Biotite altered to lamination of almost unweathered biotite packets (~ several micrometers thick) and those with biotite-vermiculite interstratification, showing a significant release of K from biotite and incorporation of Ca into biotite from the external solution. Unlike interlayer cations (K, Na, Ca), contents of the 2:1 layer of biotite such as Si, Al, Fe, Mg, Ti were almost the same as those in the fresh biotite. Secondary minerals were hardly found. (2) A partially ordered interstratified structures gradually increased instead of segregated one with the formation of Fe-bearing kaolinite around cleavages. The contents of kaolinite and iron hydroxide gradually increased as the progress of weathering. Chemical analysis showed non-stoichiometric decrease of Mg, Fe and K, and increase of Al and Si. The former change was derived from cation ejection from biotite structure, while the latter was probably due to the formation of fine packets of kaolinite within micro-cleavages. Ca-vermiculite gradually disappeared as the progress of weathering, instead Mg-vermiculite gradually became dominant. (3) Vermiculite-layers increased in the mixed-layer structures of biotite-vermiculite. The significant increase in volume of Fe-bearing kaolinite around the edge of the grain caused “fanned out” texture from the edge. The decrease of Ti was observed as well as Mg, Fe and K, and the released Ti formed TiO_2 particles around the cleavages.

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Investigation of phosphate removal efficacy of layered double hydroxide and their hybrid with magnetic nanoparticles

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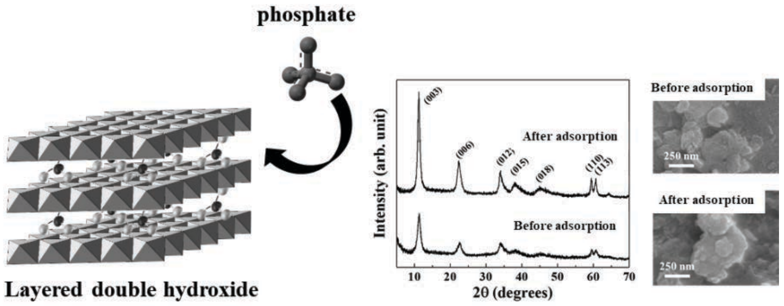
Phosphorus in the form of phosphate is an essential nutrient for plants, which is most often obtained by mining. However, phosphate rocks are predicted to be depleted within the next century. For this reason, recovery of phosphate from other sources such as phosphate rich wastewater is currently being investigated, using various adsorbents such as activated alumina, calcite, zirconium hydroxide, activated carbon, iron oxide and layered double hydroxide (LDH). Among those adsorbents, the use pf LDH for phosphate recovery is often studied due to their favorable properties, e.g., high biocompatibility, high adsorption capacity, and high affinity for orthophosphate.

First, MgFe-LDHs were prepared with two different metal ratios (2:1 and 3:1) and two different interlayer anions (Cl^- and NO_3^-) through the conventional coprecipitation method. The powder X-ray diffractograms of the prepared MgFe-LDHs showed the typical hydrotalcite-like structure without impurities. Also, the physicochemical properties were verified with FT-IR, SEM, zeta-potentiometer, and dynamic light scattering. The phosphate adsorption efficacy of the prepared MgFe-LDHs were evaluated as a function of phosphate concentration, time, and pH.

Based on the adsorption efficacy of MgFe-LDHs, LDH and magnetic nanoparticles (MNPs) hybrid materials were designed as recyclable adsorbents for magnetic separation of the LDHs after phosphate adsorption. First, MNPs were synthesized by simple coprecipitation method and then their surface was coated with SiO_2 for hybridization. The prepared MNPs show high magnetic saturation value and could be separated by a permanent magnet. Then suspension of SiO_2 coated MNP and LDH were simply mixed for hybridization. The phosphate adsorption efficiency of prepared hybrid was investigated with different phosphate concentration and various time points.



Surface roughness dependent cellular uptake behavior of layered double hydroxide nanoparticle

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Cellular uptake behavior of layered double hydroxides (LDHs) depending on surface property was compared in human lung adenocarcinoma (A549) cell culture line. LDHs with rough and smooth surface were prepared by ion-exchange and reconstruction route, respectively. For effective tracing and quantification, anionic fluorescein dye (AFD, fluorescence indicator) and 1-butanesulfonate (BS, pillar) were co-intercalated into interlayer of LDH during synthesis. X-ray diffraction patterns and fourier transformed-infrared spectra of pristine LDHs (MgAl-NO_3-LDH and MgAl-CO_3-LDH) and AFD-BS-LDH (FLDH) prepared by ion-exchange (FLDH-I) and reconstruction (FLDH-R) revealed that AFD and BS was co-incorporated with d-spacing ~ 1.58 nm. Through scanning electron microscopy and dynamic light scattring, we confirmed that the pristine LDHs and both FLDH hybrids have plate-like shape with ~ 180 nm size and that the particle size and morphology was remained after intercalation AFD and BS. The zeta-potential result indicated that both FLDH hybrids have positive surface charge. From the atomic force microscopy analysis, the surface roughness (Ra) values of FLDH-I and FLDH-R hybrids were determined 0.564 nm and 1.437 nm, respectively, indicating different surface roughness. The cytotoxicity of both FLDH hybrids were evaluated with trypan blue assay against A549 cell which revealed that FLDH-I and FLDH-R hybrids was biocompatible up to 200 µg/mL. From fluoresence-activated cell sorter analysis, we confirmed that the FLDH-I was 1.5 times more internalized into A549 cell than FLDH-R. Different cellular uptake behavior of FLDHs could be expalined by the protein-LDH interaction. Human serum albumin adsorption was 2.5 times more on FLDH-I than FLDH-R, and the protein corona would faciliate cellular uptake.

Reduction assisted exfoliation of ferric containing layered double hydroxide

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Exfoliation of layered double hydroxide has long been suggested to obtain two dimensional precursor for materials fabrication. Due to the relatively high charge density, exfoliation of layered double hydroxide was not easily carried out in aqueous media; the most widely utilized method is to suspend layered double hydroxide in formamide which is toxic and hard to remove. In this study, we exfoliated layered double hydroxide in aqueous media by controlling layer charge. First, layered double hydroxide with chemical formula of $Mg^{2+}{}_2Fe^{3+}(OH)_6(CO_3)_{0.5}$ was prepared by conventional co-precipitation method. Then the slurry was suspended in deioized water with 1 mg/mL concentration. Treatment of the suspension with sodium borohydride under moderate temperature redced ferric to ferrous, which was simply checked by change in color of suspension from reddish brown (ferric) to dark green (ferrous). The optimum condition for reduction was 10 equivalent of sodium borohydride compared with ferric in layered double hydroxide, 90°C reaction temperature and at least 15 min time. According to and 10 eq. The atomic force microscopy revealed that the particle thickness of layered double hydroxide was ~55 nm and ~ 0.5 nm before and after reduction, respectively. Selected area electron diffraction pattern obtained by transmission electron microscopy indictaed that the spot pattern was more scattered after redution, revealing the random orientation thin layers. These results implied that the layered double hydroxide could be exfoliated by decrease in charge density thanks to the reduction of lattice ferric to ferrous.

Smectite-methane interactions: in situ high T and P XRD, IR, and ^{13}C NMR studies

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Clay minerals are important components of shales and other tight gas reservoirs, and improving CH_4 production from them requires detailed, molecular scale understanding of the structural environments and dynamical and energetic behavior of their interaction with methane and other fluid species. It is now known that methane can enter the interlayer galleries of smectite clays driven by passive, space filling interactions. We present here i*n situ* X-ray diffraction and ^{13}C MAS NMR and IR spectroscopic data obtained at $P_{fluid} = 90$ bar and T = 323 K (equivalent to ~1 km depth) showing that the structural charge and exchangeable cation have significant effects on methane interaction with smectite clays. Data were collected for San Bernardino hectorite (Clay Minerals Society SHCa-1, 55% F^- for OH^- substitution, structural charge = - 0.72), a commercial, synthetic 100% OH^- hectorite (laponite, structural charge = - 0.36) and a synthetic 100% F^- hectorite (Corning corporation; structural charge = - 1.12) exchanged with Cs^+, tetramethyl ammonium (TMA^+), and Ca^{2+}. Differences in the intensities of the forbidden v_1 IR band near 2900 cm^{-1} representing surface-associated CH_4 shows that the extent of CH_4 association with the clay decreases dramatically with increasing structural charge of the clay and the relative humidity (R.H.) of the supercritical CH_4 and that this association is generally larger with Ca^{2+} than with Cs^+ and TMA^+. The intensities of the ^{13}C MAS NMR resonances for clay-associated CH_4 parallel these changes. The ^{13}C MAS NMR spectra contain resonances for CH_4 in the interlayer galleries, in bulk fluid, and exchanging between these two environments on an ~300 ms timescale. These results, thus, demonstrate the effectiveness of this methods to directly probe the CH_4 structural environments and exchange dynamics. Interlayer CH_4 has NMR chemical shifts between -4 ppm and -7 ppm, with the shift becoming more negative with decreasing accessible interlayer volume, reflecting changes in basal spacing and the lateral pore dimensions parallel to the clay basal surfaces as a result of changes in the hydration state. The results are in good agreement with previous results for clays and nano-porous model compounds such as silicas. The observation of multiple resonances for interlayer $^{13}CH_4$ in laponite, which has a very small particle size, but not for the other hectorites suggests the presence of dynamic basal spacing fluctuations with wavelengths greater than at least ~10 nm that affect the behavior of larger, natural clay particles.

Chemical trapping of CO_2 by smectite clays under supercritical conditions

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The chemical interaction between CO_2 and minerals in reservoir and cap rocks to produce carbonate minerals is of significant interest in geological C-sequestration and enhanced oil and gas production, but little is known about CO_2 reactions with clays and other minerals in shales and other common sedimentary rocks under relevant supercritical fluid conditions. We present here the results of *in situ* high-pressure and temperature (P_{fluid} = 90 bar, T = 323 K) NMR, IR, and XRD experiments that demonstrate two chemical processes by which clay-CO_2 interactions lead to carbonate mineral formation. One mechanism involves precipitation of carbonate phases by reaction with the exchangeable cation and the other involves dissolution of the clay structure and precipitation of carbonate or bicarbonate phases. Both mechanisms require formation of HCO_3^- and/or CO_3^{2-} ions by reaction of CO_2 with an aqueous fluid. The experiments were done with a commercial, high surface area hydroxy hectorite (laponite) exchanged with Cs^+, tetramethyl ammonium (TMA^+) and Ca^{2+}, and with San Bernardino hectorite (Clay Minerals Society SHCa-1) exchanged with Pb^{2+}. For the three laponites exposed to both nominally vacuum dry conditions (~ 4-6 H_2O molecules/exchangeable cation) and to 100% relative humidity ^{13}C MAS NMR shows formation of HCO_3^-, with mobility of this ion increasing with increasing R.H. For Ca-laponite reaction with exchangeable Ca^{2+} results in the precipitation of amorphous Ca-carbonate in the nominally vacuum dried sample and aragonite, vaterite and calcite in the 100% R.H. sample. At 100% R.H., dissolution of the clay structure to release Mg^{2+} from the octahedral sheet, probably by attack on the broken edges of the clay layers, results in the precipitation of amorphous Mg-carbonate. All these reactions took place in the high T and P NMR rotors within a few hours, suggesting that such reactions could occur for clays with larger particle sizes on the multi-year time scale relevant to reservoir conditions. For the Pb-hectorite, the *in situ* XRD shows precipitation of cerussite at ~78% R.H. of the $scCO_2$, high enough to form a bilayer hydrate. ATR IR shows the formation of CO_3^{2-} ion at R.H.s < 10%. High-angle annular dark field scanning transmission electron microscopy shows removal of the Pb^{2+} from the interlayers and precipitation of cerussite on the clay surfaces. ^1H NMR spectroscopy shows that the removal of Pb^{2+} from the interlayers is balanced by hydronium ion (H_3O^+) formed by reaction of CO_2 in the water film to form CO_3^{2-}.

Improving the preparation method and structural description of illite-smectite interstratifications for X-ray powder diffraction analysis

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The preparation of powder samples is one of the most critical steps in quantitative X-ray diffraction (XRD) analysis (Kleeberg et al., 2008). One challenge in preparing clay rich samples is to avoid preferred orientation of the clay particles. Traditionally, oriented specimens are used to characterize clay minerals with diagnostic tests, to differentiate (for example) swelling clay minerals from non-swelling ones. On the other hand, textured specimens are insufficient for quantification because of the unknown phase-specific degree of orientation. The goal of this study is to improve the differentiation of interstratified illite-smectite (I/S) clay minerals even in texture-free X-ray diffractograms. Therefore, the spray-drying method of Hillier (1999) was used in combination with glycerol intercalation for a stable expansion of smectitic layers in one step within the production of powder samples. Furthermore, modified three-dimensional structural models including glycerol solvated interlayers were applied for a successful quantification via the Rietveld method using the recursive description.

Samples of I/S with different degrees of ordering and amounts of smectitic layers were investigated. Liquid glycerol was added to the sample-ethanol-suspensions direct after McCrone micronizing and then sprayed. Glycerol solvation was completed within a few minutes at room temperature and spherules of the sample particles were formed after spray-drying and characterized by XRD. The amount of added glycerol is the critical factor. If insufficient glycerol was added, no complete intercalation occurred, if too much was added, the sprayed spherules stuck together, which hampered any further preparation significantly. For all investigated samples a range of amount of glycerol revealing stable intercalations in the diffraction patterns was found. For the structural description in the Rietveld approach, the glycerol molecule was integrated in the interlayer space of published structural models (Ufer et al., 2012) via the interpreter language using BGMN (Bergmann et al., 1998). These modified three-dimensional structural models are in general suitable and successful Rietveld applications of these structures will be presented.

This study was financed by the European Social Fund (ESF) and the Development Bank of Saxony (SAB) (grant number 100316839).

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Effects of pH values and polyborate anions on boron coprecipitation with calcium carbonate

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Calcium carbonate is one of the ubiquitous precipitates in nature. Precipitated calcium carbonates (PCC) in drainage sediments often work as a scavenger for boron by incorporated into the carbonate structure. Polyborate anions exist both in spring and industrial effluents with a high boron concentration. However, the knowledge about coprecipitation characteristics of boron species, especially polyborate anions, with calcium carbonate is limited. The objectives of this study were to characterize the PCC as affected by different pH values and boron concentrations, and to investigate the effect of boron species on the coprecipitation with PCC.

Based on the coprecipitation experiments using a pH-stat system, the PCC contained the highest boron at pH10 when the solution had relatively low concentrations (1~35 mmol-B/L). Unlike pH10 and pH12, a rapid increase of boron inclusion in PCC occurred at pH8 more than 20 mmol-B/L, indicating that polyborate anions enhanced the amount of boron coprecipitation. The mixture of vaterite and calcite was observed in the solution without boron, whereas only the calcite was formed with increasing the boron concentration. The crystal size of PCC significantly changed small when the solution had high concentration at pH10 and 12, which showed that boric acid molecule has no influence to PCC crystal growth. X-ray absorption spectroscopy (XAS) analyses determined the dominance of boron on the surface rather than inside of the PCC crystal. The XAS results implied boron accumulation on the PCC surface in moderately alkaline pH values. These findings are valuable for making predictions on the boron removal related to PCC from the effluents.

Visualization of Clays at the Atomic Scale

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Structures of clay minerals, most of which belong to the phyllosilicate group, are often enigmatic owing to the existence of polytypes/stacking disorder, mixed-layer structures, and other various inhomogeneity. Because most of such structural variations or disorder in phyllosilicates are of one-dimensional character, direct imaging of atomic columns using electron microscopy is most effective with the incident beam parallel to the layers. However, at least in the author's recognition, structure analysis of clay minerals by imaging close to the atomic scale is not as common as expected in spite of its importance. There are several reasons for this but we should continue and encourage such challenges for the further progress of clay science. As demonstrated in recent decades by a number of clay mineralogists operating electron microscopes, high-resolution transmission electron microscopy (HRTEM) with a point resolution of ~ 2 Å has unraveled complicated structures of clay minerals. For example, we successfully explained mysterious features in powder XRD patterns and the mechanism of clay formation. Fortunately, the progress of electron microscopy does not cease and new technologies appears every year owing to the various demands from material sciences. Now we should make efforts to introduce these into clay science to solve a number of remaining problems in this field.

In the first-half of my lecture, I would like to introduce several examples of the accomplishments of HRTEM to present-day clay mineralogy. They include the complete determination of the stacking sequence in long-period polytypes or heavily disordered samples from two images of the same area along two independent directions. Also the elucidation of the origin of stacking disorder in beam-sensitive clays like kaolinite, halloysite, pyrophyllite, etc. from sufficiently high-quality structure images and the determination of a novel 2:1 layer by comparison between experimental and simulated images, etc. by using conventional TEM. Annular-dark-field (ADF) imaging by STEM has an advantage over phase contrast imaging by TEM, in that the contrast can be corresponded unambiguously to heavy atomic columns and heavy atoms can be easily distinguished in the structure. For instance, we can search for cesium ions incorporated in vermiculite by ion-exchange at the atomic scale.

In the second-half of my lecture, I would like to discuss promising, state-of-the-art techniques for solving remaining problems in clay science. Cancelation of spherical aberration by Cs-corrector has improved the point resolution of TEM or STEM close to or beyond 1 Å. This is very useful for the complete resolution of cation columns in the clay structures, although we are still concerned with radiation damage. Beside such high resolution, or by the sacrifice of resolution to some extent, we can obtain a wider gap for the specimen in the pole piece, by which we may make environment-controlled observations, for example, high-resolution imaging without dehydration of clay samples. New generations of recording media, represented by C-MOS or direct detection cameras, will definitely overcome the limitation of imaging of clay structures by radiation damage. On the other hand, although it is not relevant to structure imaging, improvement of X-ray detection efficiency by more than one order in recent energy dispersive X-ray spectroscopy (EDS) will open a new window for the analysis of fine clays.

Acicular chamosite in the coal mined in southern China, as potential cause of lung cancer in the area

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In Xuan Wei and its neighboring counties of southern China, lung cancer rates tend to be higher in places where local coal is mined and utilized for household heating. This coal contains mineral component of ca. 25 wt.%, which mainly consists of quartz, calcite and Fe-chlorite (chamosite). We suspected that chamosite released during coal burning is a potential cause of the lung disease of the residents, and characterized the mineral and its structural changes after heating or combustion.

Acicular chamosite and quartz are embedded parallel in coal, probably according to the texture of original plant tissues. The cross section of the acicula in coal is in an irregular form of ~ 10 μm in size. The composition of the chamosite is $(Fe^{2+}_{3.98}Mg_{0.68}Al_{1.35})(Si_{2.65}Al_{1.35})O_{10}(OH)_8$. The complete absence of ferric iron was confirmed by Mössbauer spectroscopy. High-resolution transmission electron microscopy (HRTEM) indicated that the chamosite consists of interstratification of 14 Å chlorite layer and 7 Å berthierine layer, with the dominance of the 14 Å layer. This interstratification significantly decreases the intensity of the 14 Å basal reflection of chamosite in the X-ray diffraction pattern. When the chamosite in the coal was heated at 550°C for one hour, the interlayer region was dehydroxylated and adopted the "two-layer" structure proposed by Guggenheim and Zhan (1999). Mössbauer spectroscopy indicated that 27% of iron was oxidized by the heating. On the other hand, when the chamosite was heated at the same temperature for 5 hours with more complete coal combustion, almost all of the iron was oxidized. In this case, probably the silicate layers remained mostly intact accommodating ferric iron, but a part of them was resolved to form nanoparticulates of maghemite (γ-Fe_2O_3).

Surface Hydrophobicity and Energetics at Mica-Water Interfaces

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Phyllosilicate-water interfaces are relevant to a variety of geochemical processes such as heterogeneous nucleation and subsurface transport. The intrinsic chemical heterogeneity of phyllosilicates (i.e. cationic and anionic substitution) can give rise to diverse crystal structures and surface physicochemical properties such as hydrophobicity, which in turn determines the nature of interfacial reactions.

This study aims at examining the effects of fluorine/hydroxyl substitution on the hydrophobicity of the basal surface of phlogopite in the presence of various counterions (K^+, Na^+ and Cs^+). The surface properties of phlogopite mica are closely related to minerals of the clay group: they share a two dimensional structure with interlayer cations and a hydrophilic behavior dictated both by the presence of hydroxyl groups and hydrated cations. Surface hydration processes were monitored in situ using near-ambient pressure X-ray photoelectron spectroscopy and interfacial water properties were probed by X-ray reflectivity, which was further combined with classical molecular dynamics simulations to obtain energetics of hydration. Results suggest that the surface hydrophobicity is particularly well manifested at or above 1 monolayer coverage of water and may be mostly enthalpy-driven. At lower coverage, on the other hand, entropic contribution to water adsorption is non-negligible and reflects the type of counterions. This study overall provides molecular basis for surface hydrophobicity, applicable to the microscopic details, energetics and kinetics of various reactions occurring at the phyllosilicate-water interfaces.

Influence of acid and alkali treatment on physical and surface charge properties of clayey soils

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Most of the surface related phenomena in the case of fine-grained soil are attributed to their unique surface charge properties and specific surface area. The temporal variations in soil behavior, to some extent, can be credited to the changes in these properties. Among the multitude of factors that affect the charge and surface area of clay minerals, the inherent system chemistry occupies the cardinal position. The impact is more profound when the chemistry change is manifested in terms of the system pH. The pH plays a significant role by modifying the edge charges of clay minerals and facilitating mineral dissolution. Hence there is a need to address the variations in physical and charge properties of fine-grained soils treated over a range of acidic as well as alkaline conditions.

In the present study, three soils (two soils commercially procured and one natural soil) exhibiting distinct mineralogical compositions are subjected to different pH environment over a range of 2 to 13. The soil-solutions prepared at a definite liquid to solid ratio are adjusted to the required pH value by adding measured quantities of 0.1M HCl/0.1M NaOH. The studies are conducted over a range of interaction time, varying from 1 to 96 hours. The treated soils are then analyzed for their physical property modification in terms of specific surface area. Further, modifications in surface morphology are evaluated from a scanning electron microscope (SEM) imaging. Changes in the surface charge properties are assessed in terms of zeta potential measurements. Studies show significant variations in total surface area, probably because of the dissolution of clay minerals. This observation is further substantiated by the morphological analysis with SEM imaging. The zeta potential measurements on soils indicate noticeable variation upon acid/alkali treatment, which is partially ascribed to the modifications in the pH-dependant edge charges and partially due to the clay mineral dissolution. The mineralogical modifications upon acid treatment are reflected in the FTIR analysis. The results provide valuable insight into the role of pH in a clay-electrolyte system upon surface related phenomena such as species adsorption, fabric modification etc.

Sorption of $^{131}I^-$, $^{36}Cl^-$ and $^{99m}TcO_4^-$ Anions by ZnAl and MgAl Layered Double Hydroxides

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Synthetic sorbents are studied for sorbing environmental pollutants such as inorganic oxyanions (NO_3^-, SO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, CrO_4^{2-} etc.) and single anions (F^-, Cl^-, Br^-, I^-) as well as their radioactive nuclides. These species can be sorbed by anion exchange. Removing radioactive impurities from waters is a rather complex problem, the sorbent should be resistant to heat and radiation. Hydrotalcite or calcined hydrotalcite type layered double hydroxides may be suitable for this purpose. Primarily, hydrotalcite has been used because it has positive layer charge, thus acting as an anion exchanger [1] and resistant to high thermal effects. This also makes it possible to treat the cooling water of nuclear reactors. There are also other layered double hydroxides such as zinc and aluminum-containing double hydroxides (ZnAl LDH) that can be produced in the laboratory, and the positive layer charge allows the anions to be sorbed.

Mg-Al-CO_3 calcined hydrotalcite (TA LDH) and ZnAl layered double hydroxide (ZnAl LDH) were prepared. The successful preparation was proved by XRD measurement. These synthetized LDHs' sorption capabilities were examined using ^{131}I, ^{36}Cl and ^{99m}Tc radionuclides by gamma spectrometry and liquid scintillation measurement. The experimental data showed an efficient uptake of $^{131}I^-$. However, in case of $^{36}Cl^-$ for ZnAl LDH, sorption capability was heavily influenced by the competition of non-radioactive Cl^- ions in the environment. Positive results were obtained using TA LDH. The $^{99m}TcO_4^-$ sorption experiments indicated that ZnAl LDH is capable of removing 12% of $^{99m}TcO_4^-$ ions from the sample, which is good to sorb at all compering with literature data.

Acknowledgments:
This study was financed by the EU and co-financed by the European Regional Development [GINOP-2.3.2-15-2016-00008]; the Hungarian National Research, Development, and Innovation Office [NKFIH K 120265].

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Hydrotalcite-like hosts intercalated with atorvastatin

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Hydrotalcite-like compounds are often used as host structures for intercalation of anionic species. These materials intercalated with pharmaceutically active ingredients attract increasing attention as drug carriers and drug delivery systems in medical applications as intercalation of the API can considerably affect its release from a solid dosage form. Atorvastatin is a synthetic medication used for treatment of dyslipidemia and prevention of cardiovascular disease. It is usually supplied in the form of calcium salt almost insoluble in water but soluble in some organic solvents.

The hydrotalcite-like precursors in nitrate form were prepared by coprecipitation of Mg and Al nitrates under nitrogen and then treated for 120 h at 140 °C under hydrothermal conditions; the products with various Mg/Al molar ratios (2, 3, and 4) were obtained. The intercalation of atorvastatin was carried out by delamination/reassembling procedure [1], when colloidal dispersions of Mg-Al-NO_3 precursors delaminated in formamide were added to the solution of atorvastatin in ethanol.

Intercalation of atorvastatin into the hosts interlayer was indicated by powder XRD; the d_{003} basal spacing of the intercalated products considerably increased in comparison with the Mg-Al-NO_3 precursors (from about 0.8 – 0.9 to 3.0 – 3.4 nm). Content of atorvastatin in the intercalated products was determined by UV-vis spectrophotometry and varied approximately between 30 and 35 wt. % in dependence on the Mg/Al molar ratio in the host structure. Molecular simulations were used to model arrangement of the atorvastatin molecules in the interlayer. Interaction of carboxyl group of atorvastatin with hydroxide sheets via the hydroxyl groups of the positively charged sites of Al-containing octahedra, as well as interactions between neighboring atorvastatin molecules can be expected.

The back release of intercalated atorvastatin was examined by dissolution tests carried out in phosphate buffer (pH of 6.5) simulating an intestinal fluid. Capsules containing a mixture of starch with powdered atorvastatin (calcium salt) or atorvastatin intercalated in hydrotalcite-like hosts were compared; enhanced release of atorvastatin from capsules containing intercalated products was found.

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Structure of glycerol-Mg-smectites/vermiculites complex based on molecular dynamics and implementation of the model for XRD modelling

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Vermiculites are operationally distinguished from smectites upon Mg-saturation and solvation with glycerol. Smectites expands to 18 Å forming two-layer complex, while vermiculites to 14.5 Å forming one-layer intercalate. Among vermiculites there is also dependence on layer charge: low charge vermiculites (e.g. 0.6 phuc) will form two-layer complex, while these with higher charge (e.g. 0.8 phuc) will create mainly one-layer structure. Additionally, distribution of layer charges within one population of crystallites can lead to mixed-layered one-/two-glycerol layers complexes.

In spite of significance of this structure there is however no model of one- and two-layer glycerol-Mg-smectite/vermiculite complex implemented in programs used for XRD modelling. The aim of this study was therefore to provide new and adjustable models of this intercalate based on the molecular dynamics (MD) calculations.

In MD simulations, montmorillonite with charges: 0.3, 0.5 and 0.75 phuc were considered. A wide range of glycerol and water contents in the simulated structure was considered. The complex shows two readily distinguishable platoes at c.a. 15 and 18 Å, corresponding to one- and two- layer complex, respectively. There is no significant dependence of basal spacing on charge for the same amount of water and glycerol.

For all the simulations, the average atomic density profiles along the z direction were calculated. Subsets corresponding to certain basal spacings (platoes) were chosen as representative for one- and two-layers intercalates. The electronic density profiles of glycerol, water and Mg^{2+} ions were fitted with Gaussian functions. The aim was to minimize the number of functions and to achieve a maximally simple but yet flexible model of the interlayer structures.

It was also possible to determine the relationship between position of the atomic distributions and the basal spacing. All the relationships were implemented in the Sybilla program. Using the new model of the complex it was possible to fit a series of Mg-montmorillonites with different layer charges. The limitation of the new model is due to the fact that distributions of water and glycerol molecules in the interlayer space are quite similar. Therefore, during minimalization procedure, glycerol and water molecules in the interlayer space are not treated fully separately.

Visualization DNA-montmorillonite complexes with atomic-force microscopy

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Development of clay-based gene and protein drug delivery systems remains challenging due to high potential of clays in bio technology and medicine [1]. In present work we have visualized and characterized DNA-montmorillonite complexes at different ionic strengths of the solution of divalent cations using atomic force microscopy (AFM).

In contrast to the integral methods of studying the sorption of DNA on clay, the AFM method allows us to study this process at the molecular level. It has been shown that the DNA molecule in such complexes is in the extended rather than condensed state. We have demonstrated that only small part of a molecule binds to montmorillonite, whereas its major fraction has remained unbound. These complexes can be used to store genetic material, concentrate DNA from solution and increase the efficiency of the PCR reaction.

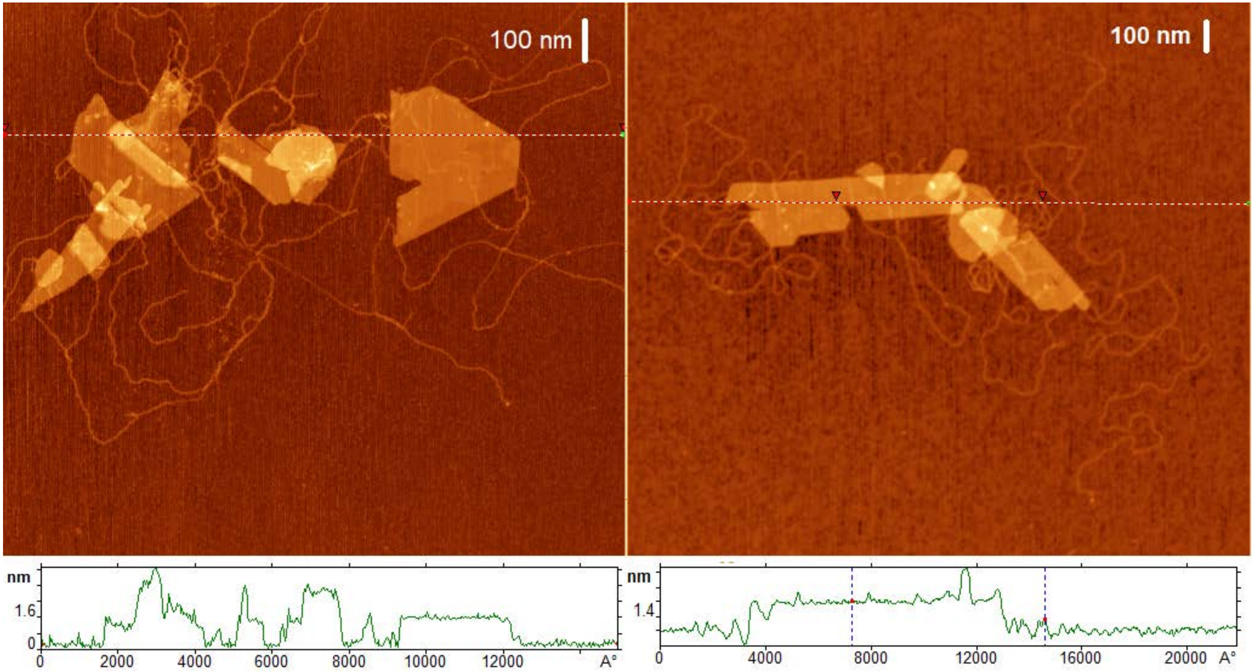

Figure 1. AFM-images of DNA-montmorillonite complexes with their profiles along the dotted line.

This work was supported by the Russian Science Foundation, project №17-75-30064.

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Identification of montmorillonite particle edge orientations by atomic-force microscopy

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Crystallographically different montmorillonite particle edges have different reactivity. Accurate realistic modeling of transport properties and adsorption at clay mineral surfaces remains challenging because of the qualitative and quantitative differences in the structure and composition of adsorption sites on the basal surfaces of clay particles and on their edges. We used atomic force microscopy (AFM) to visualize and quantitatively characterize the geometry and size distribution of montmorillonite particles with determination of the crystallographic orientation of their edges. Fourier peaks of AFM-images, obtained at the ultra-scale, were decoded using atomistic molecular dynamics simulations.

The experimental and modeling results confirm, that the most stable edge surfaces of montmorillonite are perpendicular to the crystallographic directions [010] and [110].

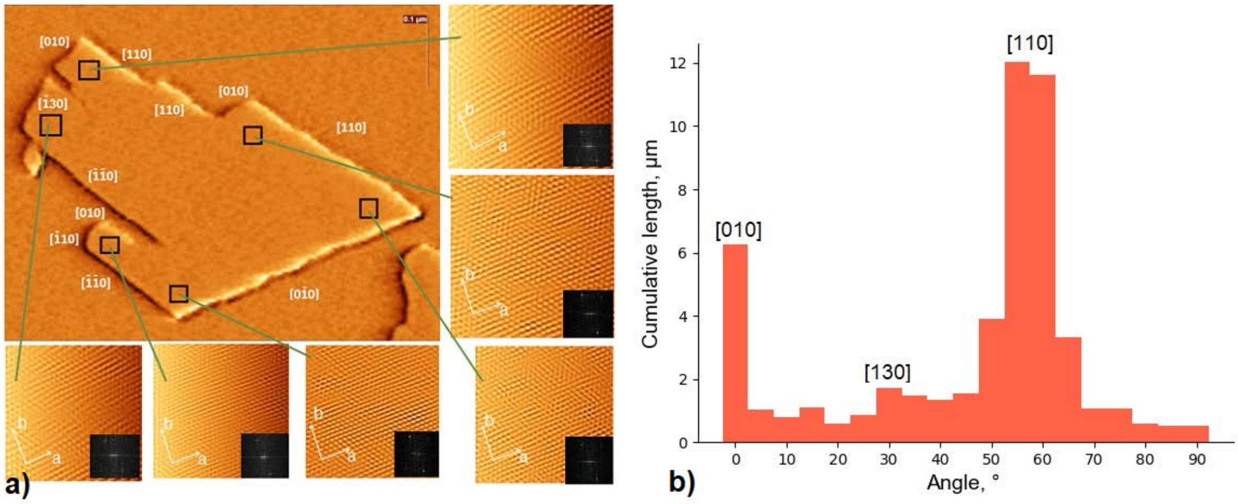

Figure 1. a) AFM-images of montmorillonite particles and their ultrastructure; b) the histogram of different edge distribution

An energy model for studying of size parameters and chemical composition features of hydrosilicate nanoscrolls

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This abstract considers energy model of single- and multi-walled hydrosilicate nanoscrolls with chrysotile, halloysite and imogolite structure, which is focused on determination of preferable size parameters of these particles. Energy effect of scrolling is a difference between energies of scrolled and flat state of the hydrosilicate layer. In turn, the energy of each state consists of three principle components: strain, surface and adhesion energy. Adhesion and surface energies are proportional to the area of contact between adjacent turns and to the full surface area, correspondingly. Strain energy is proportional to squared difference of current and stress-free curvatures. The latter depends on crystal structure and ionic radii of constituting cations. It can be calculated by analysis of diffraction data or structure optimization.

Involving same formalism, the following cases will be considered: preferable size parameters of imogolite, chrysotile and halloysite cross-sections [1]; synthesis and modelling of finite size multi-walled chrysotile and pecoraite nanoscrolls [2]; Mg and Ni cations distribution along the length of conical nanotube [3] and its experimental observation in multi-walled Mg-Ni-hydrosilicate nanoscrolls using STEM/EDS [4]; presence of cations like $Fe^{2+/3+}$ and $Co^{2+/3+}$.

The research was partially supported by the Russian Science Foundation grant 16-13-10252.

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Quantum chemical modelling of Fe(III) and Fe(II) in 2:1 dioctahedral smectites

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Due to their versatile properties such as low permeability, plasticity, and swelling, clays are used as technical barriers for waste repositories. Clay minerals, the main constituents of clays, show a strong ability to sorb and exchange cations. These properties of clay minerals, and therefore of clays, depend on their structure and chemical composition.

In our study we investigate relationships between the structure of clay minerals and their composition, specifically the Fe(III)/Fe(II) content, by means of the computational density functional theory approach. We applied a periodic plane-wave based band structure method together with the projector-augmented wave approach as implemented in the software VASP, complemented by two types of corrections, (*i*) a self-interaction correction (DFT+U) to enable an adequate localization of the d electrons of iron as well as (*ii*) van der Waals corrections (D3 approach). We considered a Fe content of up to 25 % in dry and solvated (interlayer water) smectite models with a layer charge of -0.25 and -0.5 *e* per formula unit.

The interaction of two octahedral Fe substitutions is repulsive in all model smectites studied. The repulsion gets stronger for reduced Fe. Octahedral Fe(III) prefers sites distant from charged octahedral Mg(II) substitutions, but close to charged tetrahedral Al(III) substitutions. Depending on the type of charged substitution, octahedral or tetrahedral, we determined an energy preference for cis- or trans-vacant lattice structures, respectively. A larger Fe(III) content increases the preference for the trans-vacant structure. Thus, with growing iron content, our models predict that the ratio of trans- to cis-vacant structures as well as the fraction of tetrahedral charge increases, in agreement with known empirical correlations [1].

Energy variations calculated for Fe(II) substitutions at various sites are more pronounced, compared to Fe(III). However, consistent energies could be calculated only when interlayer Na^+ was at least partially solvated by interlayer water. Octahedral Fe(II) strongly prefers sites distant from both octahedral and tetrahedral charged substitutions. Estimated standard reduction potentials for Fe(III/II) depend on the smectite model and on the Fe position with respect to octahedral and tetrahedral substitutions. Interlayer water was shown to play a crucial role when estimating reduction potentials.

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Structural features of montmorillonites as a key for understanding the stability of bentonite buffer for isolation of radioactive waste

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The most modern concepts for the isolation of radioactive waste, especially high-level waste, are based on the use of a multi-barrier system in which bentonite is a one of the important components of engineering safety barriers. Currently, the Russian Federation is considering a concept for the construction of a deep disposal facility for radioactive waste in the Nizhne-Kansky massif (Krasnoyarsk region). The construction of the Underground Research Laboratory (Exploratory Rock Laboratory In Krasnoyarsk region - ERLIK) has already begun and full-scale experiments are planned to begin in 2021

In this regard, the identification of structural criteria and stability of montmorillonite in aggressive conditions will allow to make predictions of the evolution of the properties of engineering barriers for the near and far prospects with higher accuracy. This work presents the results of an experimental study of changes in the composition, structure and properties of bentonites from industrial deposits in Russia and the near abroad (Kazakhstan, Azerbaijan), which are considered promising for the isolation of radioactive waste.

The experiments were carried out under acidic (in the presence of HNO_3 solutions) and alkaline (KOH) conditions at room (~ 25 ° C) and high (90 ° C) temperatures during various time intervals (from 1 hour to 1 year). As a research methods were used: XRD, FTIR, DTG/TG, XRF, ICP-MS, Sbet, pore size and volume, grain size, adsorption (including radionuclides).

The conducted studies led to the conclusion that one of the most important structural criteria for the stability of montmorillonites under such conditions is the predominance of cis or trans-vacant octahedra. All studied montmorillonites with a predominance of trans-vacant octahedra showed low resistance to thermochemical treatments compared to montmorillonites with a predominance of cis-vacant octahedra. This criterion turned out to be more pronounced than the actual number of isomorphic substitutions of Al, Mg or Fe.

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Kaolin clay alleviates toxicity of graphene oxide in aqueous environments

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Graphene oxide based materials are intensively gaining popularity among researchers. The wider application areas and increased level of production, however, suggest an increased risk of environmental exposure to graphene oxide, including aqueous habitats. Graphene oxide is a toxic material. In particular, aqueous organisms, both marine and freshwater can be severely affected via graphene oxide exposure. Therefore, it is challenging to envisage a safe and effective approach to alleviating graphene oxide toxicity in aqueous ecosystems. In this research we report for the first time the effective remediation of graphene oxide toxicity by kaolin clay particles.

We evaluated the remediation of graphene oxide toxicity by kaolin particles using *Paramecium caudatum* as an *in vivo* model. We have applied a set of toxicity evaluation test to demonstrate the effects of equal concentrations of kaolin on remediation of graphene oxide toxicity on survival and growth rate, chemotaxis, galvanotaxis, DNA complexation and food vacuole formation.

Here were reported for the first time the interesting and potentially important fact, the effective alleviation of graphene oxide toxicity by kaolin nanoclay. We found that kaolin coagulates with graphene oxide in water, producing relatively large complexes. This reduces the adverse effects of graphene oxide on *P. caudatums* protozoans, increasing survival and growth rate, normalising chemotaxis and galvanotaxis, improving food digestion and reducing macronucleus deformities. Within the range of concentrations studied, 90−100% of graphene oxide was coagulated by kaolin. Importantly, the toxicity of graphene oxide coagulated with kaolin is reduced without removal of the aggregated particles from the environment.

Overall, our results suggest that kaolin nanoclay, a cheap and environmentally friendly material, may find applications in environmental remediation of graphene-related materials.

Acknowledgments: This work was funded by RFBR according to the research project № 18-29-25057.

Clay-gouge bearing faults in the Norwegian basement: K-Ar geochronology and insights into strain localization, mineralogy and temperature conditions

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The Norwegian basement is old, heavily fractured and has undergone differential exhumation during several stages of rifting and continental margin development, making it an ideal natural laboratory to study the architecture and evolution of deformation structures across crustal levels, from ductile shear zones to brittle faults. During the last decade, several studies combining K-Ar illite geochronology with structural and mineralogical analyses have provided new insights not only into the regional tectonic history, but also into strain localization within faults during reactivation, the mineralogy of fault rocks and the temperature conditions of fault zones.

In a regional tectonic perspective, most K-Ar ages obtained from brittle structures along the Norwegian margin correlate to Permian and Jurassic rifting in the North Sea and North Atlantic, while younger rift episodes and the eventual break-up of the North Atlantic are underrepresented. Many faults show signs of repeated reactivation over 100s of million years, and detailed K-Ar dating of larger faults reveals that such reactivation is often localized along distinct levels within an already weak fault core. Thus, several generations of illite can be found in some of the faults.

The mineralogy of the sampled fault gouges depends on the host rocks. In Norway, magmatic and metamorphic rocks dominate, and the fault gouge compositions are thus markedly different from faults hosted in sedimentary rocks. Feldspar, hornblende and muscovite are frequent K-bearing contaminants that need to be considered when interpreting K-Ar dates. However, studies of exhumed Paleozoic-early Mesozoic faults have shown that the deeper and hotter parts of faults may also contain neocrystallized $2M_1$ illite. Thus, the assumption that all $2M_1$ illite/muscovite is inherited ('detrital') does not hold. Independent Ar/Ar ages of host rock muscovite may be required to identify either higher temperature faulting or contamination from the host rock.

Temperature estimates from both fault gouges (illite crystallinity, illite polytypes, chlorite geothermometry) and host rocks (thermochronology) suggest that illite or illite/smectite mixed-layer clays grew in faults over a wide range of temperatures from > 200°C to < 100°C, often at temperatures in excess of the ambient temperature of the host rock. In addition to illite, many faults contain abundant smectite or illite/smectite with very low illite contents that may have grown at even lower temperatures during Cenozoic fault reactivation. Due to very low K-contents, this last reactivation can easily escape radiometric dating attempts.

How to properly describe mass gain in dehydroxylated clay mienrals?

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Rehydroxylation (RHX) is the reformation of OH groups lost by a clay mineral during prior dehydroxylation. RHX has been applied in archeometry to determine the age of ancient ceramics (Wilson et al., 2009). Mass gained by ceramics due to RHX is proportional to the fourth root of time elapsed since firing. Mass gain vs (time)$^{0.25}$ curves often show departure from linearity for small (time)$^{0.25}$ values (Figure 1), which was explained by mass gain occurring before the ceramics had reached thermal equilibrium with its environment. The departure can be corrected by introducing time offset, giving rise to the equation (Barrett, 2013): $\Delta m=\alpha(T)(t-t_0)^{0.25}$, where Δm is mass gain due to rehydroxylation, $\alpha(T)$ is RHX rate constant, t is elapsed time and t_0 is time offset.

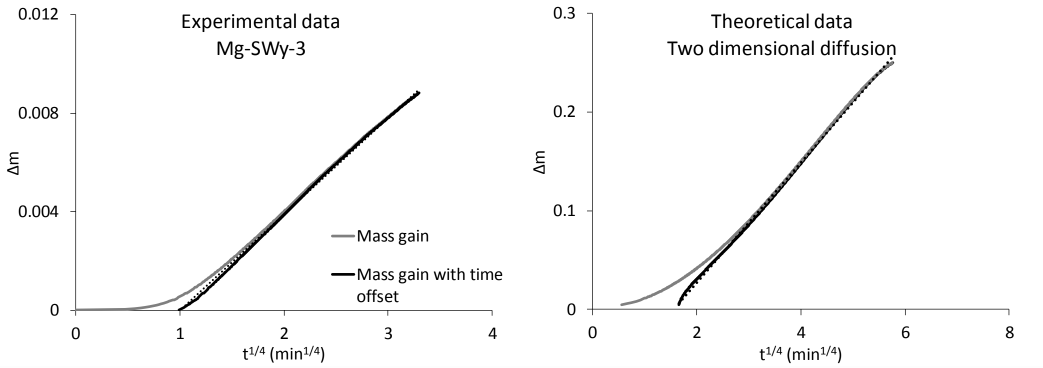

Figure 1. Experimental (left) and theoretical (right) fractional mass gain data for rehydroxylation reaction plotted against the fourth root of time with and without time offset.

A thermogravimetric (TG) study of dehydroxylation and rehydroxylation aimed at providing a kinetic description of these reactions was conducted. Smectite rehydroxylation and rehydration tests were performed on pure smectite reference samples SWy-3 (*cis*-vacant) and SCa-3 (*trans*-vacant) by connecting a humidity generator to the TG analyzer. In addition, we tested theoretical kinetic data generated by various solid state kinetic reaction models.

We conclude that the fourth root of time model correctly describes not only rehydroxylation, but rehydration and dehydroxylation reactions as well. Theoretical tests revealed that the departure from (time)$^{0.25}$ linearity in the early stages of the reaction may be due to the fact that the reaction follows other than the fourth root of time model. In such a case, time offset can be used to mathematically correct for this departure, however it has no physical meaning (Figure 1).

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ACKNOWLEDGEMENTS:
This study was financed by the Polish National Science Centre grant OPUS13 25/B/ST10/01675.

Properties of hydrothermally modified rocks of the Pauzhetskoye field

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Transformations of volcanic rocks within thermal fields lead to the formation of a near-surface horizon of hydrothermal clay soils up to several meters thick. The base of the clay stratum represented by fractured and brecciated, intensely argilized andesite lavas, which can be classified as metasomatic breccias. Below occur the andesites, which have undergone transformations to varying degrees. Studies have shown that hydrothermal exposure firstly results to transformation of volcanic glass, and then secondary changes develop in phenocrysts in the following order: plagioclases, pyroxenes, amphiboles, potassium feldspar. For hydrothermal clay soils, the content of clay minerals is more than 50%, in some samples it reaches 95%. Clay minerals are represented by kaolinite, mixed-layer kaolinite-smectites and smectite group minerals, mainly montmorillonite. Despite the complete transformation of the mineral composition of the original volcanic rocks, pseudomorphs, due to the inherited structure, are characteristic of the formed clay soils. Such a structure determines the nature of deformation and destruction during the strength and deformation tests of clay soils. Iron and silica minerals precipitated from the solution through cracks form a "framework", due to which these soils do not become fluid, despite full water saturation.

Particles and aggregates with a size of less than 0.005 mm prevail in the particle size distribution; their content for most samples is about 60-70%. In this case, up to 60% may fall on particles whose size does not exceed 0.001 mm.

At the same time, in the microaggregate composition, aggregates with a size of 0.01-0.1 mm prevail, the content of which can reach 80%

The soils that were formed as a result of hydrothermal transformations are characterized by extremely low indicators of strength and deformation properties. At that time, as the initial rocks are characterized by the values of the strength for uniaxial compression up to 120 MPa, the hydrothermal formed clay soils are characterized by values not exceeding 180 kPa.

To study the deformation properties of clay soils were carried out compression tests. They can be characterized as highly compressible: the compressibility coefficient reaches 10 MPa^{-1}.

In the natural state of the soil are at temperatures up to 100 °C, which affects their properties. However, the effect of temperature on the strength and deformation properties is ambiguous. On the one hand, a decrease in the viscosity of cohesive water leads to a decrease in the strength of coagulation contacts, on the other hand, as a result of a decrease in the thickness of electrical double layer, the number of particles directly in contact with each other increases. Thus, the overall effect of temperature on properties may be different.

Clay hybridized with nanoparticles for removal of antibiotics in water usage cycle

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The growing use of antibiotics induces the emergence of micropollutants in the environment, especially in water. To overcome this problem, we focused our work on the synthesis of clay-based nanocomposites materials dedicated to the removal of such contaminants from effluents. Five priority substances have been selected, based on relevance and recalcitrance criteria, that are doxycyclin, carbamazepin, ciprofloxacin, danofloxacin and sulfaméthoxazole.

Both adsorption and degradation mechanisms were addressed in our approach. Metallic oxide nanoparticles SiO_2 or Fe_2O_3 were associated with Na-montmorillonite clay so as to obtain a porous hybrid structure that increased the adsorption capacity (Figure 1). In addition, laccase enzymes were grafted on the hybrid material in order to exploit bio-catalytic degradation of the pollutant.

The obtained nanocomposites were characterized and their behavior in water was studied. Their reactivity for pollutant adsorption or degradation was tested in synthetic water as well as in real complex effluents in order to test their selectivity. The results were compared to conventional treatments using activated carbon and evaluated in term of benefit/cost balance.

Results will be presented that illustrate the efficient pollutant adsorption and degradation by the hybrid nanocomposite synthesized SiO_2 / montmorillonte / laccase.

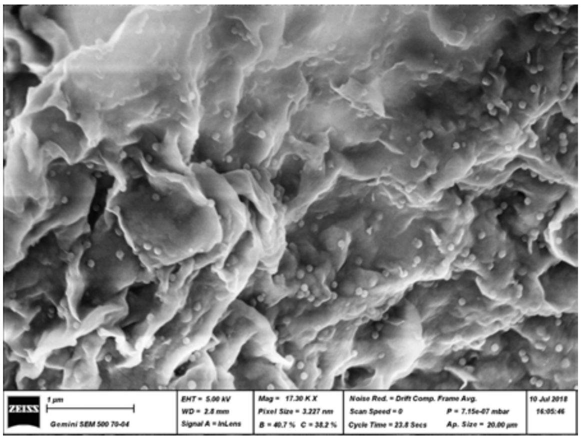

Figure 5 hybrid nanocomposite made of motmorillonite and silica nanoparticles observed by SEM. Sclae bar = 1 µm

Use of clay minerals as indicators of the paleoenvironments of Ediacaran multicellular life in the Doushantuo Formation (South China)

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In the crystal structure of clay minerals fluorine (F) readily substitutes for hydroxyl groups, thus its concentration in clays appears to have the potential to reflect depositional conditions. Although rarely studied because of their scarcity, authigenic clay minerals forming in open ocean sediments lack levels of F enrichment seen in alkaline lake clays. This work focuses on the use of the F content as a tool for testing the hypothesis that certain sections of the Doushantuo Formation were deposited in non-marine settings (Bristow, 2009). These sedimentary deposits, rich in clay minerals, have experienced little alteration during burial and are host to some of the earliest animal fossils in the geological record. This makes the Doushantuo Formation an ideal place for investigating the types of environments in which early animals lived and were preserved.

Mg-F smectites have been synthesized using the sol-gel method modified from Decarreau (1985). The experiments have been performed by aging gels at different temperatures ranging 25, 50, 100, 150 °C in an oven for periods of 50-120 days, in solutions with [F] of ~ 10, 20, 50, 100 and 500 mg/l, concentrations that cover the range observed in ocean water and in alkaline lakes. Final solid phase products have been characterized by X-ray diffraction (XRD), and VIS-NIR and Raman spectroscopies. The partition coefficients of F into synthesized clays have been measured and applied to the chemical data obtained from the best-preserved saponite clay minerals of the Doushantuo Formation, and the demonstrably marine Hunnberg and Svanbergfjellet Formations from Svalbard.

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Incorporation of ZnO into clay volcanic (sericite-clinochlore) by impregnation Method for photo-degradation of the methylene blue dye under solar

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Water contamination is a major problem, and water quality is now a major environmental issue [1].Dyes are extensively used for many industries, including the textile, paper, plastic, wood and food industries [2]. Clay minerals are considered as promising supports due to their interesting inherent properties, namely their adsorption capacity,and their ability to be bounded to chemical compounds [3]. The principle of this study is focus attention to the photo-degradation of methylene bleu (MB) under solar on modified clay the Ain Ourka (Algeria) (CA) with oxide de zinc (ZnO-CAC) by impregnated method compared with calcined (CAC) and a raw clay (CAR). These samples are characterized by several analytical methods, XRD, TGA-DTG, BET and SEM. First, we tested our catalysts on adsorption and photo-degradation under solar irradiation in the presence of H_2O_2 as oxidant. The results of XRD show that these clays contain four phases, Sericite 2M1, Clinochlore, quartz and presence of a new phase for the modified clay named zincite (ZnO). The measured cation exchange capacity (CEC) is 9 meq/100g and the BET analysis shows the increase of surface area for these clays, from 9 to 30 m2 g-1. The results show also that the catalysts have a better affinity than the adsorption kinetics follows better fitted by the pseudo-second-order, as well as the adsorption capacity considerable. The results show that the effect of H_2O_2 does not influence the adsorption rate. On the other hand, it increases the catalytic reactivity. The best reactivity was noticed for the ZnO-CAC with a 14% adsorption rate and a catalytic reactivity of 77%.

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Fe_2O_3/Clay as useful heterogeneous Fenton catalyst for the elimination of Congo Red

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Water contamination is a major problem, and water quality is now a major environmental issue [1].Dyes are extensively used for many industries, including the textile, paper, plastic, wood and food industries [2]. Clay minerals are considered as promising supports due to their interesting inherent properties, namely their adsorption capacity, and their ability to be bounded to chemical compounds [3].Fenton technology is a well known process and has been reported as an effective alternative for the treatment of the industrial wastewater containing non-biodegradable organic pollutants. Fenton reagents involve the generation of hydroxyl radicals via homogeneous reaction between hydrogen peroxide and ferrous ion [4]. Volcanic clay from Aïn Ouarka south west of Algeria (CA) was applied to remove malachite green (MG). This material was purified (CAP) and characterized by different techniques such as Brunauer, Emmett and Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD),thermal analytical techniques (ATG-ATD) and Fourier Transform Infrared Spectroscopy (FT-IR). The cation exchange capacity (CEC) was also determined. This clay was modified with F_2O_3 by impregnation (Fe-CAP). The applicability of iron-CAP as a heterogeneous Fenton-type catalyst for the elimination of the RC dye as a model pollutant has been investigated. The influence of operating parameters such as different mass of catalyst, initial concentration of H_2O_2, and initial pH. The Fe–CAP has been proved to be a superior heterogeneous catalyst for elimination of RC in an aqueous solution. The best operation parameters for the Fenton oxidation of RC were 5 wt.% of iron ions loading, 0.66 g/L of catalyst dosage, and 39.1 m.mol of H_2O_2 for 71 μmol /L initial RC concentration at an initial pH 2.5 with 27 ◦C temperature. Under these conditions, 90% decolorization efficiency of RC in aqueous solution was achieved within 60 min of reaction time.

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High-temperature phases in fireclays by spontaneous coal combustion process

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Spontaneous coal combustion occurs when the rate of heat generated by the organic matter oxidation exceeds the rate of heat dissipation in coal deposits [1]. This process produces the melting of the surrounding clays with the generation of an Al-Si rich vitreous phase. Subsequently, high-temperature phases crystalize from the vitreous phase. These new minerals are interesting due to the similarity with those formed during ceramic process, used in the manufactured of stoneware and ceramic floor, as well as in refractory ceramics [2].

Fireclays samples from the lower Cretaceous coal deposits in Ariño (Teruel, NE Spain) were studied to describe mineral and textural transformations produced during the spontaneous combustion of coal, using XRD, optical microscopy and FESEM. The precursor clays of the fireclays are composed by organic matter, kaolinite, illite and minor proportions of quartz, K-feldspar, siderite, pyrite and Ti and Fe oxides [3]. This research shows that fireclays are composed by vitreous phase, mullite, hematite, hercynite, cristobalite, quartz, pyroxenes, cordierite, pyrite and calcium oxides.

Mullite showed a Si/Al ratio of 1.21, which is higher than the theoretical one (0.35) indicating that this mullite is Si-richer than those formed from Al-rich clays during ceramic firing [2]. EDS/FESEM analyses show a trend from hematite to hercynite composition indicating compositional variations at sample scale. These variations are reflected in XRD patterns, which evidence d-spacing differences in hercynite (8.208, 8.196 and 8.168 Å). This suggests structural variations that can be related to the Al and Fe content in hercynite depending on its texture: exsolution lamellae within hematite (5.9% Al and 48.1% Fe), exsolution lamellae within cordierite (11.4% Al and 40.8% Fe) and replacement textures with hematite as well as scattered hercynite crystals (24.2% Al and 27.8% Fe).

Three pyroxene-type compositions were found: diopside-type, ferrosilite-type and a Ca-Al-rich pyroxene with an intermediate composition among diopside, fassaite and esseneite. Comparing with the theoretical compositions, the analysed pyroxenes are non-stoichiometric.

The presence of these non-stoichiometric phases in the fireclays could be explained by the temperature reached and the relatively short duration of the spontaneous combustion in the studied area, which could not be the ideal conditions to allow crystals reaching the theoretical composition.

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Mineralogical and textural characterization of the Barremian lateritic paleosols of the Oliete sub basin (Lower Cretaceous, NE Spain)

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The Lower Cretaceous (Barremian) Blesa Fm (Iberian Range, NE Spain) constitutes a synrift, mainly continental, unit that overlies Jurassic shallow-marine limestones. Its lowermost part is characterized by greyish and ocherish to reddish marls/clays with local root traces, continental vertebrate bones and iron pisoids, suggesting lateritic soil development on the Jurassic substratum [1].

This study presents the results of the XRD and optical and electron microscopy analyses (both pisoids and clay matix) of 26 samples from six outcrops of pisolitic clays near the localities of Alacón and Obón (Teruel). They consist of 2 to 3.5 m-thick ocherish-violaceous clayey levels with abundant rounded mm- to cm-sized, dark and compact pisoids. Interlayered lacustrine limestones (0.4 to 2 m in thickness) are also present, some of them containing pisoids with similar size to those found in the pisolitic clays.

The XRD and optical and electron microscopy indicate that the clay matrix is formed by abundant microsparitic carbonate cements, silicates and Fe oxides and oxihydroxides. Among the silicates, the most abundant are kaolinite and quartz. Most of the samples contain goethite and hematite and occasionally minor proportions of K-feldspar, maghemite, ferrihydrite, ilmenite, rutile, anatase and diaspore. Pisoids are formed by a core and an outer concentric-layered cortex about 40 to 400 µm in thickness. The cortex and the core contain hematite, goethite, maghemite, ferrihydrite, ilmenite, anatase, rutile, kaolinite, quartz and microsparitic carbonate cement. Occasionally, the core contains micro-ooids with a similar mineralogical composition.

The mineral association (kaolinite + Fe oxides and oxihydroxides) in the study materials agrees with that expected for lateritic soils that usually are formed under humid and warm conditions. The textural features of the microsparitic carbonate cement indicate that it is probably diagenetic and thus with no genetic relationship with the paleosols. A decrease in the kaolinite content and its crystallinity from bottom to top of the paleosols levels has been observed by XRD. Furthermore, the lowermost parts of the studied interval only contain kaolinite as clay mineral, whereas the variety of clays (kaolinite, illite, smectite and chlorite) increases upwards. This could be indicating that chemical weathering was more intense in the lower part of the sequence than in the upper one.

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How good are clay minerals for biopolymers formation?

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The role for which clay minerals have most often be tested in origins of life studies is the formation of biopolymers from small biological molecules. Classical studies by Lahav[1] or Bujdák and Rode[2] have been devoted a long time ago to the condensation of amino acids to oligopeptides in the presence of montmorillonite (Mt), and the formation of long RNA strands from activated nucleotides on Mt has drawn a lot of interest.[3]

However, these studies had a heuristic character: the formation of "interesting" polymers was recorded but little insight was gained as to the nature of the interaction between the clay minerals and the biomolecules, and how they influenced the reactivity of the latter. Here we want to summarize the recent results we obtained with several clay minerals (montmorillonite, nontronite, laponite, hectorite, saponite, kaolinite) and biomolecules susceptible to condensation reactions (glycine, alanine, leucine, glutamic acid, nucleotides and their precursors), and discuss the interactions that are established between these partners -chiefly ion exchange with intercalation, hydrogen bonding to edge groups. Data obtained from thermogravimetric analysis (TG), vibrational spectroscopy, solid-state NMR, MS and macroscopic adsorption (isotherms) allow to identify the state of the adsorbed molecules and follow their reactivity *in situ*.

The first conclusion that can be drawn from a large number of studies is the diversity of observed behaviors. While condensation of biomolecules to polymers is promoted in some cases, molecules in the interlayers tend to be protected against reaction, often stable to rather high temperatures; reactions catalyzed by the clay may include degradation e.g. by decarboxylation in the case of amino acids.

In view of these results, the reactivity of clay minerals may be compared to that of other minerals such as silica or alumina on the basis of the nature of their catalytically active surface sites.

We will offer a critical reappraisal of the literature on clay-based prebiotic systems, and of their relevance for origins-of-life scenarios.

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The reaction of decylphosphonic acid and imogolite yields a composite material of residual imogolite and lamellar phase.

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Imogolite ($(HO)_3Al_2O_3SiOH$) is a natural clay mineral of nano-tubular structure and is a promising candidate in the fields of polymer reinforcement, catalysis, etc. Having a hydrophilic exterior, imogolite needs to be functionalized to explore potential applications in hydrophobic environments. The phosphonic acid moiety is the most used and described grafting agent for the gibbsite-like outer surface and shows strong reactivity with imogolite. The resulting product shows differing properties from the starting material, strongly suggesting that the tube exterior has been modified. However, the integrity of the tubular structure was never demonstrated and there is still a need for experimental evidence of imogolite with a corona of grafted, brush like phosphonic acid.

By combining different experimental techniques (SAXS, IR, MAS NMR, SEM and TEM), we shed light on the fate of imogolite in the reaction between imogolite and decylphosphonic acid. The formed product is dispersible in toluene and stabilizes water in oil emulsions, but we found no evidence for decylphosphonic acid grafted imogolite. Instead, we observed the formation of a lamellar phase at the expense of the tubular structure. The lamellar phase forms a composite material with imogolite. We explain the exhibited reactivity by the surface chemistry of imogolite and describe the unusual interfacial properties of this hybrid compound.

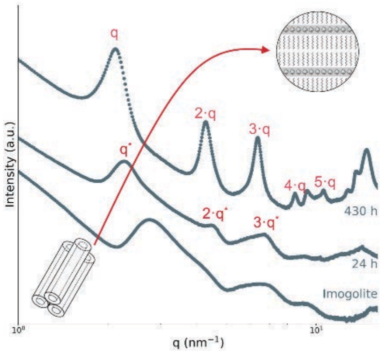

Figure 1. SAXS patterns of imogolite and the reaction product with decylphosphonic acid.

X-ray diffraction full-profile modelling as a tool to assess evolution of soil clay mineralogy arising from agronomic practices: Insights from the Morrow Plots experimental fields

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Potassium is an essential plant nutrient, with roles in photosynthesis, water regulation and disease resistance. In soils, 95-99 % of potassium is commonly contained in the crystal structure of K-feldspars and micas such as muscovite and biotite. Under natural conditions, release of this structural K is strongly dependent on the nature of the soil parent material and the rate of climate-induced weathering. Nevertheless, the ability of plants to extract non-exchangeable K has been observed and rapid mineralogical changes, such as the vermiculitization of micaceous minerals following plant growth on clay substrate, have been reported in the rhizosphere of plant roots.

Long-term field experiments such as the Morrow Plots, established on the Urbana-Champaign campus in 1876, offer a unique chance to look at the effect of continuous plant growth on the evolution of clay minerals in natural soils. The present talk will report on the use of full-pattern X-ray diffraction (XRD) modelling to obtain a comprehensive mineralogical description of the Morrow Plots in different clay sub-fractions (2-0.2, 0.2-0.05, and <0.05 µm) and to compare and contrast, quantitatively, the effects of 110 years (1904-2014) of continuous plant-growth under different agronomic practices on the status and potassium content of soil clay minerals.

Discrete phases prevail in coarser clay sub-fractions but are absent in finer ones. The contribution of mixed layers that compose the dominant fine clay sub-fractions is essentially overlooked in the XRD of the bulk <2.0 µm clay fraction because of its weakly modulated and faint diffraction signature. In addition, this distinctive signature requires both sample and data specific processing to validate structure models hypothesized for these highly-disordered interstratified contributions with vanishingly small particle size.

Present day mineralogical differences in the Morrow plots are limited to a statistically insignificant increase of illite and smectite layers in continuous corn plots compared to crop rotation ones. The increase of the relative proportion of <0.05 µm sub-fractions of all subplots regardless of agronomic treatment between 1957 and 2014 is accompanied by an increase of the cation exchange capacity, suggesting that the latter increase is due to the higher proportion of expandable mixed-layers in the <0.05 µm sub-fraction.

The absence of mineralogical contrast as a function of agronomical practices will be compared to previous reports on the clay mineralogy of the Morrow Plots and its origin discussed in the light of literature data on potassium extraction from micas. Implications for soil evolution under continuous cultivation will also be discussed.

Hydrothermal synthesis of trioctahedral smectites with an extended compositional range

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Smectites are often used as a major component of engineered barriers for the storage of municipal, industrial, or radioactive waste. These clays have excellent plasticity and allow self-healing of the cracks formed during drying. They also have very low permeability, which makes it possible to control the diffusion of pollutants into the soil and groundwater. The crystalline structure of trioctahedral smectites consists of two tetrahedral (T) siliceous sheets between which an octahedral (O) magnesian sheet is present. The whole forms a TOT or 2:1 layer. Both the occurrence of isomorphic substitutions in tetrahedral or in octahedral sheets and the presence of vacant sites in (tri)octahedral sheets induce a permanent negative layer charge, which is compensated for by the presence of exchangeable cations in smectite interlayers. Cation hydration controls in turn the hydration and swelling of these structures.

The present poster reports on a protocol allowing the synthesis of trioctahedral magnesian smectites covering an extended compositional range: saponites with tetrahedral layer charge deficit, hectorites with octahedral charge deficit, and stevensites with octahedral vacancies. In all cases, the actual amount of layer charge may be varied from low-charge (~0.6-0.8 charge per $O_{20}(OH)_4$) to high-charge (~1.4-1.6 charge per $O_{20}(OH)_4$) smectites or even to mica composition (2.0 charge per $O_{20}(OH)_4$) preserving however hydration of interlayer cations. High-temperature (~400°C) hydrothermal synthesis leads to well-crystallized products allowing detailed crystal-chemical investigations.

The resulting set of accessible compositions makes it possible to investigate the influence of smectite crystal chemistry (location and amount of layer charge deficit) on their properties. This ability will be exemplified with the structure and dynamics of interlayer species.

Crystal structure of defective lamellar minerals and their X-ray identification: Implications for reactivity

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Layered minerals and materials are ubiquitous and characterized by the frequent occurrence of stacking defects that are key to their reactivity. These defects range from local defects such as isomorphous substitutions, layer vacancies, or atomic displacements, to random or well-defined stacking faults induced by non-periodic layer rotations, translations or twinning, and to mixed layering resulting from the coexistence within a given crystal of layers having different structure, thickness, or interlayer displacement. The occurrence of stacking faults in lamellar structures is favoured by the energetic similarity of the different stacking modes, owing to the weak interactions between adjacent layers. In addition, layered materials and minerals often exhibit minute crystal sizes that may be considered as an additional type of defect because of the induced disruption of the three-dimensional crystal periodicity.

To determine, control, or predict mineral / material reactivity a detailed structural characterization of layered structures, including structure defects, is thus essential, and X-ray diffraction (XRD) has been the preferred method of investigation for this purpose. However, as a result of their non-periodicity or their reduced periodicity, the diffraction maxima recorded from these compounds do not strictly obey Bragg's law, thus hampering the use of conventional diffraction approaches. Profiles and intensities of diffraction maxima are affected by the nature, content, and distribution of structure defects, however, thus allowing the determination of these parameters with diffraction techniques and specific algorithms have been developed.

From the results of a few examples, this presentation will outline how our understanding of defective structures and mixed layers has improved over the last decade or so and describe some of the new perspectives opened by this improvement, with special emphasis on the induced reactivity.

Water mobility and its influence in the capture and retention of CO_2 in the interlayer space of Fluorohectorite clay minerals

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As a result of their swelling properties and platelet structures, clays are materials with a number of traditional, applications such as recovery of heavy metals and encapsulation of bioactive molecules, but also newer applications as capture and retention of CO_2. Thus understanding the driving forces for water uptake and loss as a function of interlayer cation is of great interest to improve and control their extensive use. In this study we have focused our attention on the synthetic smectite fluoro-hectorite (Fh). Previous studies have shown that the interlayer cation in LiFHt and NaFHt can be easily replaced by the bioactive molecule Ciprofloxacin [1, 2], while in the case of LiFHt, CO_2 capture is also facilitated [3, 4]. The interest in NiFHt stems from the fact that the presence of different forms of Ni-hydrates complexes might hinder CO_2 release. It is hypothesized that interactions of these hydrates with CO_2 are the driving mechanisms for CO_2 binding, as any residual H_2O will affect the kinetics of CO_2 intercalation (and retention) [3].

Considering that quasi-elastic neutron scattering (QENS) (i) allows accessing water dynamics in the time scale of ps, and therefore giving access to distinct diffusive motions of intercalated water in clay minerals under different conditions, and (ii) that preceding QENS studies of montmorillonite (Mt) have indicated that the cation controls water uptake and mobility in the interlayer region [5], we have performed QENS experiments on LiFHt, NaFHt and NiFHt aiming to contrast how interlayer water diffusion in FHt is affected by variations of relative humidity and interlayer cation.

In this talk we will describe the clear dissimilarities in water uptake and loss in these samples, reflected by the differences in the residence time, which gives direct insight into how the cation changes the H-bond network of water. We will also show that LiFHt not only holds more interparticle water, but also retains interlayer and cationic water more strongly than NaFHt or NiFHt. At the end of the presentation we will make a connection between hydration state and dynamical behavior of CO_2 intercalation (retention).

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Cesium sorption on Ca-vermiculite: comparison with Ca-illite and Ca-smectite behavior

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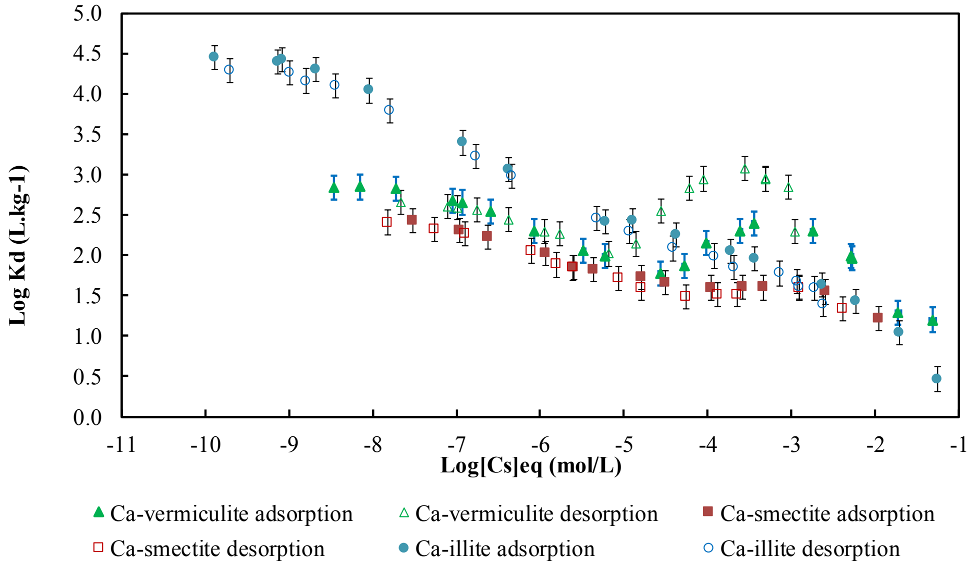
Following the Fukushima nuclear power plant accident, studies devoted to the behavior of radioactive cesium in soil environments evidenced relationship between cesium amount and clay minerals occurrence. In the Fukushima area, Cs^+ was observed preferentially associated to vermiculite-type minerals derived from weathered biotite particles. Moreover, Cs sorption on vermiculite was reported to be irreversible irrespective of cesium concentration. Recently, Cs adsorption processes studied on Ca-illite and Ca-smectite revealed reversible adsorption processes on these clay minerals. Vermiculite been classified as an intermediate phase between illite and smectite, new cesium sorption experiments are carried in order to compare the chemical reactivity of the three types of clay minerals.

Batch experiments are performed on Ca-conditioned vermiculite. Adsorption isotherms are carried out under various pH conditions (pH 3-11) and Cs concentrations (10^{-2}-10^{-8} mol.L^{-1}), in competition with calcium at a constant ionic strength of 0.03 mol.L^{-1}. Our results showed that illite displayed more affinity for cesium than smectite and vermiculite. At equivalent cesium concentration (10^{-8} mol.L^{-1}), the distribution coefficients (Kd in L.kg-1) was $10^{-4.04}$, $10^{-2.85}$ and $10^{-2.40}$ for illite, vermiculite and smectite respectively. At low cesium concentration, vermiculite seems to behave as smectite but exhibits an atypical sorption ability between 5 10^{-5} mol.L^{-1} and 2 10^{-2} mol.L^{-1} of cesium at equilibrium. Desorption experiments exhibited a reversible Cs sorption on vermiculite at concentrations below 5 10^{-6} mol.L^{-1} but a partially irreversible sorption at higher concentration.



Strong healable fibers with imogolite nanotubes

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Macroscopic assembly of nanomaterials into fibers can offer improved mechanical characteristics and the potential for multifunctionality. One-dimensional nanomaterials are particularly suited to the uniaxial geometry of fibers. In this context, clay imogolite nanotubes (INTs) represent a model nanoplatform with multipurpose applications [1]. Significantly, imogolite nanotubes form ordered liquid crystal phases in aqueous solutions [2], facilitating spinning of highly aligned fibers, and their hydroxylated outer surface allows for strong interactions with polyvinyl alcohol (PVOH), used here as a matrix.

Here, we have been able to make the first imogolite nanotube-based fibers, introducing a new and potentially widely applicable nanocomposite system [3]. Highly aligned fibers (Figure a, b), show very good tensile modulus and strength, up to 24 and 0.8 GPa respectively, significantly better than the pure polymer matrix. We quantitatively attribute it to both reinforcement and PVOH crystallisation effects induced by the presence of INTs. Moreover, most intriguingly, the fibers were found to be healable by an evaporation induced self-assembly (EISA) process (Figure c). Healed fibers recovered up to 44% and 19% of the original composite fibers tensile modulus and strength.

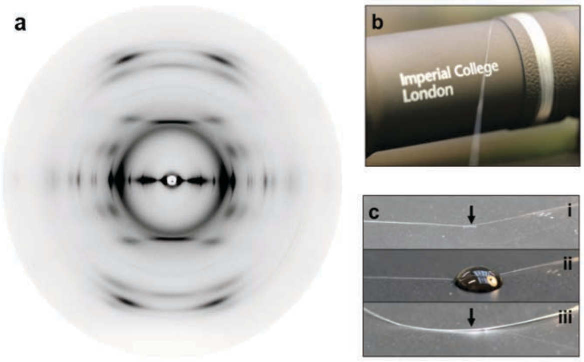

Figure. (a) Typical X-ray scattering pattern of INT/PVOH fiber; (b) Photograph of continuous wet-spun composite fiber formed on a winder. (c) Photographs of the autonomic healing process by EISA

This first example shows that it is possible to repair a strong fiber with recovery of almost half of the tensile modulus. The high aspect ratio and high hydrogen bonding capability play a crucial role in providing a scaffold for the repair of the aligned nanocomposite structure, and provides a strategy for future developments.

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Halloysite nanotubes for conservation of artworks: novel protocols for consolidation and surface cleaning

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In the last years, innovative strategies based on clay nanoparticles have been proposed for conservation of cultural heritages, including the consolidation/protection of lignocellulosic materials as well as the protective coating/cleaning of solid surfaces. Among the nanoclays, halloysite nanotubes are promising because of their hollow tubular shape, tunable interface chemistry and high specific surface. Here, we investigated the efficiency of hybrid materials based on halloysite as protective consolidants of waterlogged archeological woods as well as cleaners for solid substrates. We observed that the consolidation of archeological wood by polyethylene glycol/Halloysite aqueous mixtures confers robustness and mechanical resistance (in terms of flexural strength and rigidity) to the wooden structure. These effects are related to the homogenous penetration of the nanotubes within the channels of the archeological wood. In addition, the encapsulation of calcium hydroxide within the Halloysite lumen provides an alkaline nanoreservoir that is effective for the long-term protection of lignin. This finding was proved by both the pH and the lignin index (determined by FT-IR spectroscopy) of wood exposed to artificial aging under acidic atmosphere.[1] On the other hand, we detected that the combination of organic macromolecules, hydrocarbons and Halloysite represents an alternative strategy for the cleaning of solid surfaces. In this regards, oil in water microemulsions based on halloysite were employed for the cleaning of marble substrates. Halloysite can be considered a valuable nanomaterial in this application because it allows to a controlled cleaning reducing the risks of residues on the artfacts surface. In conclusion, this study evidenced that halloysite is a suitable clay nanoparticle in designing ecocompatible protocols for the durable preservation of lignocellulosic artworks as well as for the cleaning of artworks.

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Are clays relevant materials to have both high sorption and suitable hydraulic properties for the retention of metal pollutants and pharmaceuticals ? Application to waste landfill and waste water treatment

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Clay materials rich in smectites are usually used as geochemical barrier in waste landfill thanks to their low permeability, their expansion ability and their capacity to retain metallic or organic pollutants. These high sorption properties may also be valued as ternary filtration in waste water treatment plant. Batch experiments coupled with sorption models are often performed to evaluate their efficiency and to access the main sorption mechanisms (cation exchange, surface complexation) by varying different parameters (pH, ionic strength, pollutant concentration). However, the low solid/liquid ratio and the non-renewed solution during batch experiments are far from real hydromechanical conditions in field applications. To simulate waste landfill or waste water treatment conditions at the laboratory scale, percolation experiments were performed by using œdometers coupled with an injection system under controlled pressure. So, clay samples are firstly compacted (e.g. at 0.5 MPa to simulate the over-consolidation of an engineered clay barrier) then percolated by a selected solution (e.g. $Pb(NO_3)_2$ at pH 5 to simulate young landfill leachate). This experimental approach gives important information on the evolution of macroscopic swelling and hydraulic conductivity of clays, but also on the evolution of their sorption efficiency. For instance, after one year of percolation with Pb or Zn solution, the Ca-exchanged montmorillonite kept its sealing performance ($k = 10^{-12}$ $m.s^{-1}$) as well as a high metal retention. If smectites are well-known to adsorb cationic contaminants (e.g. metals), they appear to be less efficient to retain neutral or anionic compounds, such as some pharmaceuticals. Organoclays, hybrid materials based on clay materials and cationic surfactants, were proposed as realistic alternatives for the sorption of pharmaceuticals. If their efficiency was highlighted in batch experiment conditions, we demonstrated on the contrary that the incorporation of surfactants within the interlayer space of the layered materials increases the hydraulic conductivity of about hundred to thousand times to that of the Na-exchanged montmorillonite. This experimental approach was finally used as an analogue for a better understanding on the removal of pharmaceuticals in waste water treatment plants. The objective was here to evaluate the sorption of a pool of pharmaceuticals onto clay-sand filters using percolation experiments by varying the clay-sand ratio, the solution matrix (pure water or natural effluent) and the injection pressure. The different sorption mechanisms onto clay mineral will be discussed as a function of the charge of pharmaceuticals.

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Multi-scale modeling of clay mesopores: comparison between Molecular Dynamics and Poisson-Boltzmann

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Because of its many applications, clays have been widely studied both experimentally and theoretically. The French agency for the nuclear waste management (ANDRA) has thus been interested in these materials with exceptional properties as barrier materials in the containment of high-level radioactive waste for the deep storage project names Cigéo [1]. Due to the nanometric size of the pores inside clay systems, water and solutes transferts are greatly influenced by the surface electrostatic interactions. This implies that the solutes mobility is strongly influenced by their charge. Because of the influence of short-range interactions, Molecular Dynamics (MD) seems to be a powerful tool to study the impact of charged surfaces on the species diffusion mechanisms inside the pores. However, a decisive step in MD simulations is the choice of potentials, called force fields, that model the interactions between atoms.

Therefore, in this study we decided to compare the results on the structure and the diffusion of the species inside a montmorillonite mesopore by using different force fields provided in the literature. Two types of force fields were used, a non-polarisable one, ClayFF [2] for clays, combined with various commonly used water models and PIM [3], the polarizable force field being developed by PHENIX group. This study reveals that addition of polarizability influences the organisation of species, especially on ions, above the surface as well as the dynamics. Finally, to describe clays at higher scales we need mesoscopic codes like reactive transport codes [4], based on analytical theories like Poisson-Boltzmann (PB). Thereby, we have compared our MD results with the PB theory in order to refine the used models to best represent the reality.

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Influence of cationic valence on the adsorption of nucleotides onto montmorillonite: a Molecular Dynamics study

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According to Bernal's hypothesis, the formation of the first biopolymers would have been promotes around minerals that had created an increase in the local concentration of prebiotic organic building blocks. Therefore, adsorption of RNA and DNA nucleotides on clays, good candidates in the origin of life process, has been largely investigated both theoretically [1,2] and experimentally [3,4]. The exact conditions of the ocean during Hadean, especially on salinity and pH conditions, are still discussed. However, a recent study has shown that the pH would finally be around 7 [5]. Although the RNA nucleotide guanosine monophosphate, GMP is doubly negatively charged at this pH, experimental studies shows adsorption of GMP on negatively charged clays [3,4].

In the present study, we present Molecular Dynamics simulations of GMP nucleotide adsorbed onto a basal surface of montmorillonite, at pH around 7. The main objective is to unravel the adsorption mechanisms and the impact of the cation valence on the adsorption stability. Different types of adsorption have been observed with different stabilities. We have shown that these kinds of adsorption are not valence dependent but their stability are greatly increased when going from valence 1 to 2. The overall charge of GMP, counting ions complexed on it, has been calculated. We have observed that the more the charge is positive, the longer the nucleotide remains in the adsorbed states [6].

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Impact of the mineralogy on petroleum-contaminated soil combining mineral and organic geochemistry and microbiology approaches

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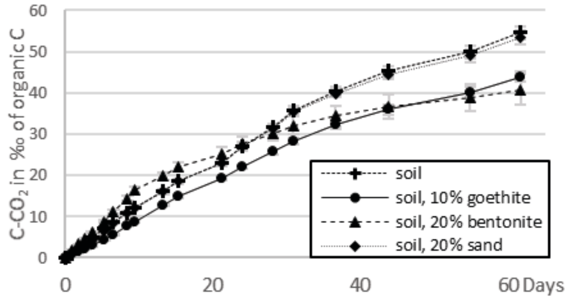
Among soil minerals, clays are particularly known to interact with organic matter and organic contaminants and impact degradation processes. They can (i) sorb the pollutant and reduce their bioavailability (ii) stabilize the contamination through catalysis of condensation reaction and (iii) influence the selection of microbial consortia.

The aim of this study is to investigate the role of clay minerals - in comparison with other minerals - in petroleum degradation of a natural forest soil. This work focuses on (i) elucidating to what extent the selection of microorganism and their activity is controlled by the presence of clay or other minerals in soil and/or by the nature of the pollution, and (ii) understanding the impact of clay mineral on petroleum contamination fate.

A forest soil, impacted by petroleum seepage for several centuries, where microbial communities are adapted to petroleum contamination, was sampled in the Haguenau forest (Alsace, France). Batch incubation was carried out with the soil, and a series of enriched soil with bentonite (20%wt), Fontainebleau sand (20%wt) and goethite (10%wt), all spiked with petroleum (5%wt) sampled on site.

Mineralogy and textural properties, total microbial community and functional population abundance, and petroleum composition were determined for the initial samples and at the end of incubation (62 days). The CO_2 production through carbon mineralization was monitored throughout the incubation.



The first results revealed that the clay minerals affect microbial activity, as shown by the evolution of CO_2 production (Figure 1). Hydrocarbon molecular analyses (GC-MS – GC-FID) showed that soil and soil/sand mixture reached higher degradation level than soil mixed with goethite and bentonite. For the latter, the degradation was very limited suggesting a possible strong sorption of hydrocarbons on bentonite surface leading to lower contaminant availability. The bacterial and fungal abundances (rDNA genes) increased during the experiment for all the conditions. The abundance of genes involved in aromatic compound degradation increased as well for all the modalities except for the soil/bentonite mixture, which tend to support the previous findings.

These first results suggest that clay minerals tend to limit the hydrocarbon degradation which could have significant consequences for the remediation of some contaminated soils. However, additional data that are currently being acquired, will implement this first conclusion.

Understanding the interactions of surfactants and clays used for the shaping of textured silicate ceramics.

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In line with recent interest in developing novel textured clay-based ceramics, the present study addresses the interactions of typical clays with some surfactants within the suspensions formulated for tape casting. Two 1:1 clay minerals were selected regarding the final microstructures and properties of use obtained after the sintering of related tapes. Namely, a kaolin and a halloysite noted K and H respectively. Since for the tape casting process, slurries are prepared with three surfactants, dispersant, binder and plasticizer, the effect of each surfactant has been characterized using zeta potential measurements. Furthermore, the influence of the incorporation stage of these surfactants has been investigated with respect to the slurries stability and rheological behaviour.

The zeta potential value of the suspensions is strongly modified, regardless of the pH value, when using H sample instead of K sample. This trend is supported by the charge located on the external surfaces of these 1:1 phyllosilicates particles. Indeed, the tubular shape of the H particles favors an external silica-like surface under acidic pH values [1], whereas the change in shape (opening of the tubes) occurring with increasing pH values tends to promote a behavior similar to that of K sample. The addition of Surfactants should be performed in a specific order to avoid the inhibition or the limitation of a homogeneous interaction of clay particles with all the complex organic additives. The zeta potential is therefore optimized, as well as the rheological behaviour as expected. The SEM observation of the slurries and of the optimized green tapes clearly shows organic branches surrounding K and H particles ensuring of steric repulsion without limiting the preferential alignment of platelets and tubes upon tape casting. It appears that when using a fibrous clay mineral, the rheological behavior was similar to that of H sample. It seems that, instead of the type of the clay mineral, (1:1 or 2:1), the shape of the clay particle plays a more significant role on the local interactions with surfactants and on the rheology of related suspensions. Nevertheless, some highlights are still under exploration regarding the changes observed when mixing clays exhibiting different particle shape.

Key words: Clays, zeta potential, rheology, textured ceramics, surfactants

Acknowledgments

The authors would like to thank A. Aimable and M. Bienia for their assistance during the zeta potential and rheology characterizations.

Layered double hydroxides and polyoxometalates: the perfect match

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The affinity of layered double hydroxides (LDHs) towards anions depends on several factors, whose charge of the anion is predominant. Usual inorganic anions have a charge of -1 (NO_3^-, Cl^-, …), -2 (SO_4^{2-}, CO_3^{2-}) and -3 (PO_4^{3-}). However, a special family is made of anions with a charge up to -10, that of polyoxometalates. They consist in polyanions based on refractory metals (V, Nb, Mo, Ta, W), either alone, like $V_{10}O_{28}^{6-}$, $H_2W_{12}O_{42}^{10-}$, $Mo_7O_{24}^{6-}$, or in combination with other elements as P or Si for example (like $PMo_{12}O_{40}^{3-}$). Understanding their interactions with LDHs is a difficult task, since their speciation in solution is complex (mixtures of different protonation degrees / composition are common) and side-reactions can occur (depolymerization, adsorption) during ion exchange. However, these systems are interesting for several applications, as catalysts preparation, ion extraction, or LDH preparation (Lefèvre, 2016).

Here, an overview of the chemistry of LDHs/polyoxometalates system is presented, with a special focus on the identification of exchanged species by in situ real-time infrared spectroscopy. This technique, in combination with DFT calculations, has allowed to follow the exchange reaction of polyoxomolybdates and polyoxotungstates in carbonated-sulfated MgAl LDH (Davantès and Lefèvre, 2013; Davantès et al., 2015), leading to the identification of the exchanged species and their affinity for the LDH. A promising application for these systems would be the selective extraction of strategic metals (W, Ta) from electronic wastes or ores. We have recently obtained some evidences on the viability of such processes to replace more pollutant ones based on hydrofluoric acid treatment or solvent extraction (Lefèvre et al., 2018)

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Enhanced stability of quantum dots InP/ZnS by intercalation in a layered double hydroxides matrix to provide sustainable solutions for lighting applications

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Miniaturization of optical devices for lighting applications, such as micro-LED, has become a trend in the last thirty years. Semiconductor nanocrystals, also called Quantum Dots (QDs), seem to be very promising for this kind of applications due to their outstanding optical properties and their nanometric size. The photoluminescence properties of QDs strongly depend on their size. Characterized by broad blue/UV absorption and a narrow band emission they are able to offer all the saturated colors of the visible range depending on their diameter.

Presently, the more efficient and studied QDs contain cadmium, a toxic heavy metal. As a result, many researches tend to develop green alternatives like the Cd-free core/shell QDs such as InP/ZnS. However, the stability, under thermal and photonic stresses, of this new generation of QDs has to be improved to meet the requirements for LEDs devices.

Herein, we present the development of a strategy to improve the stability in operating conditions of the InP/ZnS QDs without changing their optical performances and their photometric parameters (T (K), CRI, etc.). In this work we have carried out the intercalation of QDs in layered double hydroxide (LDH) host matrix (Figure 1). The synthesis as well as the structural and morphological characterizations (XRD; SEM) of the LDH-QDs based hybrid materials were described. Furthermore, the optical properties including absolute quantum yield and chromaticity coordinates were investigated upon UV/blue excitation. Finally, the durability of LDH-QDs and thus the long-term stability of their optical performances were assessed upon photonic and thermal stresses. The role played by the LDH matrix on the stability of the QDs has been studied and discussed.

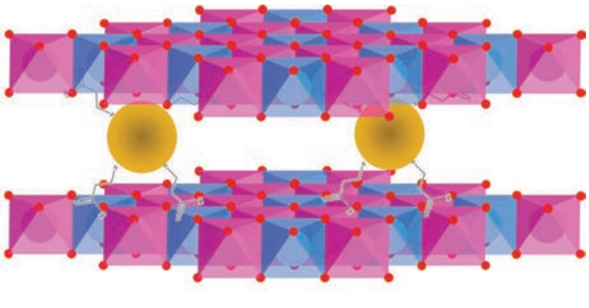

Figure 7 : Theoretical representation of intercalated QDs between layers of the LDH host matrix

Hydrogen liberation during heating of phyllosilicates

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Thermal decomposition Fe(II)-bearing phyllosilicates is driven by two reactions: dehydroxylation and dehydrogenation, which produce H_2O and H_2, respectively. However, it remains unknown how hydrogen is released from the crystal structure during dehydrogenation, how the reaction occurs under oxidizing conditions, and whether the quantity of released H_2 is quantitative related to Fe(II) content or Fe(II) position in the structure of phyllosilicates.

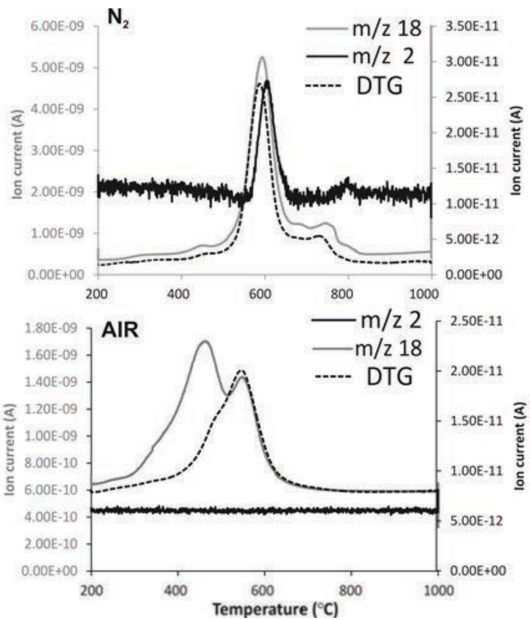

Figure 1. H_2O and H_2 evolved gas profiles obtained during ramp heating in nitrogen gas (N_2) and in synthetic air (AIR) combined with DTG curves for tested Mg-chamosite.

To trace the influence of Fe content on dehydrogenation, Mg-Fe series of chlorites and selected phyllosilicates e.g.: Fe-rich: biotite, berthierine, nontronite and serpentine; and Fe-free: illite, talc, and kaolinite were tested. The volatiles evolved during heating using thermogravimetric (TG) fast ramp heating experiments (20°C/min rate) were detected with a quadrupole mass spectrometer (MS) attached to the TG instrument. The TG-MS heating experiments were performed under nitrogen and synthetic air gas atmosphere.

H_2O evolution was observed on m/z=18 mass spectra as effect of dehydroxylation in neutral as well as in oxidizing conditions during heating of all tested samples. In the neutral gas conditions, the m/z=18 profile perfectly correlated with the first derivative of mass loss curve (DTG); under oxidation, however, certain mismatch was observed in Fe(II)-rich minerals. H_2 evolution was observed on m/z=2 mass profiles (Fig.1) only for Fe(II)-containing phyllosilicates heated in nitrogen gas. Strong correlation between Fe(II) content in the crystal structure and H_2 /H_2O peak intensities ratio on MS profiles was found for i. a.: Mg-chamosites, Fe-clinochlores, biotite, an berthierine. Under oxidizing conditions, released hydrogen combined with O_2 resulting in excess H_2O observed under MS, manifesting as an additional H_2O peak. (Fig.1).

Coupling of quantitative thermogravimetry with qualitative quadrupole mass spectroscopy is a sufficient tool to prove that the evolving hydrogen is associated only with oxidative dehydrogenation in Fe(II)-bearing phyllosilicates.

Acknowledgments: This study was funded by the National Science Centre, Poland under research project no. 2017/27/N/ST10/02544.

Structural behavior of Na-Laponite clay dispersions upon addition of charged polymers

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The structural properties of charged colloids are strongly affected by its size and charge, as well as the valency of the counterions. For synthetic Na-Laponite clay it is known that no aggregation occurs at low clay concentrations in water due to its small size, where the thickness and the diameter of a platelet is about 1, and 25 nm, respectively.

Here we will present a future perspective for an ongoing study regarding the structural behavior of Na-Laponite clay dispersions upon addition of macromolecules, such as polyelectrolytes, peptides, or proteins, which are suggested to promote aggregation depending on its size and charge. It is expected that a positive charged macromolecule will interact with the negative charged face of the clay platelet, and hence, bridge the platelets together in a face-to-face orientation, while for a negative charged macromolecule there is a possibility of bridging the clay platelets together across the rims. For this purpose, the experimental technique small angle X-ray scattering (SAXS) in combination with coarse-grained molecular dynamics simulations are utilized.

From preliminary SAXS measurements it was found that Na-Laponite mixed with the positive charged peptide Deca-Arginine or protein Histain5, Bragg peaks were clearly observed, indicating that the clay platelets aggregate face-to-face. The Bragg peaks are more pronounced for Deca-Arginine, implying that the interactions are stronger, which arises from the increased charged and size compared to Histatin5 (Figure 1). On the other hand, for Na-Laponite with addition of the negatively charged polyelectrolyte Poly(Acrylic)Acid at a moderate salt concentration, it was found that the scattering intensities at the low-*q* region levels out with an increase in polyelectrolyte concentration. This means that the scattering only arises from single platelets, and thus, there is a possibility that the Poly(Acrylic)Acid interacts with the rim of the clay platelet.

Figure 1. Kratky plots obtained for Na-Laponite, and Na-Laponite mixed with Deca-Arginine (left) and Histatin5 (right). The intensities are normalized at *q* ≈ 2 nm^{-1}.

Characterization of defect creation in kaolinite: Bridging powder X-ray diffraction with atomistic simulations

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Various environmental (i.e., mechanical, chemical) mechanisms are responsible for the creation and further alteration over time of disorder in the layer stacking of kaolinite samples. A potential means to characterize and eventually recognize the occurrence of such mechanisms is the excess energy held in the disordered crystal structure. We used a combination of measured X-ray diffraction (XRD) data and simulations to probe the layer stacking defect energy of KGa-1, KGa-2, API-9, and Keokuk kaolinite samples as an indicator of the extent of the process(s) leading to their formation. Information on stacking defects was obtained using powder XRD patterns. The agreement among a variety of laboratory and synchrotron measurements performed with different sample geometries (flat plate and spinning capillary) and sample preparation protocols (powder loaded from the front, back, or side of the sample holder) suggested that crystallites were effectively randomly oriented in space (i.e., the preferential orientation aberration was negligible). The line broadening contributions of crystallite size distribution and various types of stacking disorder were distinguished based on profiles simulated using the Debye scattering equation. As an example, the spacing and degree of overlap of individual stacked layers not only affects the *hkl* peaks but they also shift and broaden the *00l* peaks. Although roughly confirming previous estimations of disorder in layer stacking, a non-negligible relative shift of stacked layers significantly affects the estimation of stacking fault probability. We used atomistic simulations to compute the potential energy of a set of nanocrystal microstructures built according to the above-estimated stacking defect probabilities. These simulations showed that the potential energy increases in a non-linear fashion as the degree of stacking disorder increases from the ground state minimum of a perfectly stacked layer system (i.e., from the Keokuk to the KGa-2 sample, Figure 1).

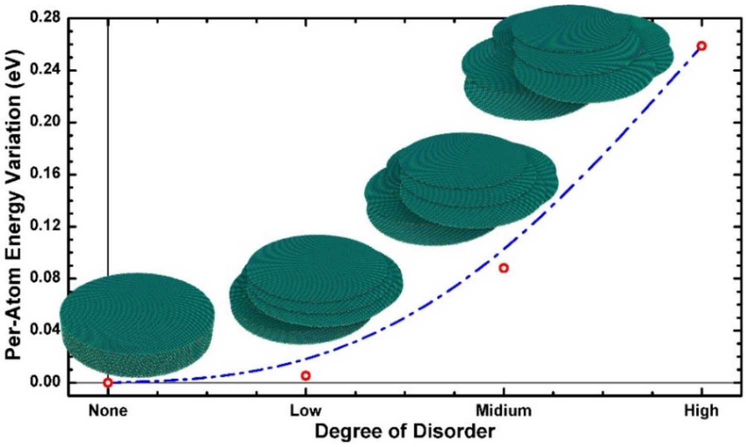

Figure 8. Variation in potential energy as a function of the degree of layer stacking disorder relative to a perfectly ordered nanocrystal.

Weathering processes in the Gault Clay formation, Paris Basin

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The Lower Cretaceous Gault marine clay formation outcrops in the area of Brienne-le-Chateau (north-eastern France) currently investigated in the context of a sub-surface repository for low-level radioactive waste. This work aimed at investigating weathering processes (depth variations, chemical reactions) and water transfers in the Gault Clay from present-day to millennial timescale. In this framework, we applied a multi-disciplinary approach to rock and water samples collected in 5 m- deep pits and deep boreholes including the critical zone developed in the Gault clay. The pits were dug along transect on the eastern side of the Aube river that crosscut two successive hillslopes probably corresponding to two alluvial layers; the boreholes were drilled on the ridgetops and in the valleys (Lerouge et al., 2018).

Field work provided evidence of Quaternary surficial formations ranging between ~5 m in valleys and on lower parts of the slopes, 5m to 10 m in filled paleo valleys localized under ridgetops, and less than 1 m on the upper part of the slopes. Slides of surficial formations and of Gault clay moved downslopes. Water comings at different depths in the surficial formations were observed during the dug of the pits. Some waters come also above slide plans at the top of Gault Clay, rather suggesting lateral water transfers. Stable isotopes (^{18}O, D) of the ground waters and pore waters in Gault clay show evaporation processes down to ~10 m depth.

Powder X-ray diffraction performed on bulk rock and clay fractions, and cation exchange capacity measurements of Gault clay and slide plans in contact with surficial formations give evidence of levels rich in swelling clay and of dissolution of pristine marine carbonates. Some secondary carbonate concretions result from precipitation of recent fluids.

Degassing of samples conditioned under He atmosphere provided evidence of a very high CO_2 production in soil (0-30 cm), and a high CO_2 degassing associated to oxygen peak in the first 2-10 m Gault Clay. The CO_2 degassing increase in weathered Gault clay relative to preserved one results from calcite dissolution due to pyrite oxidation and to organic matter degradation. The δ^{13}C of CO_2 indicates that the organic matter degradation is a major source of CO_2 down to 10-12 m, maximum depth at which we observed fossil roots. Then the CO_2 degassing decreases down to a constant value in preserved Gault Clay, where the carbonate system and the mineral assemblage control dissolved carbonates in pore waters.

Strontium (^{87}Sr/^{86}Sr) and lithium (δ^7Li) isotopic data of the exchangeable fraction allow well distinguishing surficial formations (~2-5 m) from Gault clay, and altered (~2-20 m) from unaltered Gault Clay (>~15 m).

Combined data rather indicate that weathering processes are occurring as deep as 20 m below the surface with maximum intensity of alteration in the ~2-10 m zone.

Fine Tuning for Matching (Multi)-Properties for polymer: the amazing LDH green toolbox

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Through two detailed and patented research works, layered double hydroxide (LDH) versatility is exemplified, this in an attempt to fulfill the ever-growing topical needs in different nano-technologies regarding safety (flame retardant and thermal stabilizer), functionalities (pigments, biocide), as well as eco-friendly and environmental aspects (bio-source). LDH) type material is considered today as promising and adaptable filler for polymer.

The first case will considered a bio-based polyester, Polybutylene succinate (PBS), prepared by melt extrusion process. Depending on the organic anion used in LDH fillers (selected molecules were L-tyrosine, L-tryptophan, L-ascorbic acid and 3-(4-hydroxyphenyl)propionic acid, …), it was possible to control the polymer chain extension, the rate of hydrolysis and the photo-degradation process (UV stabilizer) and to supply the antibacterial properties in some cases. Each LDH filler shows different behaviour. The highest chain extending effect was observed in the case of LDH with L-tryptophan, the worst – with L-ascorbic acid. However, L-ascorbic acid presents 100 % activity in antibacterial properties. It means, the best patented results can be obtained when PBS is mixed with different LDHs, and by this way, it becomes multifunctional bionanocomposites with new possibility of applications.

The second case will deal with the efficiency of organo-modified LDH platelets to act as corrosion inhibitor in polymer coatings, polyurethane-based, in the case of the substrate Aluminium 2024. A screening of various a-amino (aAA) acid molecules in regard of their ability to retard corrosion on AA 2024 aluminium alloy substrate was performed by using DC-polarization as well as by recording the evolution of the polarization resistance. The mechanisms of inhibition focused on the most promising hybrid materials, are tentatively explained with anion exchange and inorganic framework dissolution at the cathodic and anodic corrosion zones, respectively, with the particular occurrence of Cu-rich intermetallic zones. In terms of performance, the hit LDH/L-CYS (cysteine) assembly embedded in the polymer coating is found to retard after a prolonged time of immersion the corrosion process of AA2024 substrate and compares well with the banned LDH/chromate reference filler.

The authors would like to thank CNRS through its national program PREMATURATION for funding and SATT GC for the study of scalability concerning PBS system and BASF Coating for funding the activity on corrosion inhibition from LDH hybrid cargo.

Clay mineral assemblages and organic matter in stony soils of cold environment

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The pattern of vertical distribution of clay mineral assemblages and soil organic matter have been demonstrated based on the soil formation routes. The studied soils - Lithic Leptosols and Podzols (WRB, 2014) have been formed from the fine earth underlain by solid rocks (nepheline syenite, amphibolite, metamorphosed gabbro-diabas, metagabbro amphibolite, and dolerite) in the cold regions of Russia. The soil formation routes were represented by (a) very shallow soils that were formed on the fine earth derived from solid rocks due to its disintegration and (b) deeper soils formed from rock saprolite. These acidic and stony soils are widespread in the tundra and taiga zones in East Fennoskandia, the Polar Urals and the Altai Mountains, and in the Central Siberian Plateau. Despite differences of chemical and mineralogical composition of solid rocks these soils enriched in organic matter, and Fe and Al compounds. In the shallow soils (variant "a") pedogenesis led to transformation of soil organic matter *in situ* and (ii) formation and migration of R_2O_3 -organic complexes with the high content (up to 100%) of pyrophosphate-extractable iron in the oxalate-extractable forms. These processes are combined in one soil horizon as depth and fine earth are not enough to form a proper soil profile. The findings are in good agrrement of statement that organic acids control biochemical weathering leading to the prevalence of non-crystalline or poorly ordered materials and organo-mineral complexes in the weathering products in such cool, climatic conditions (Wilson, Jones, 1983). It seems that that amorphous components (including organo-mineral) inhibit further weathering of the rock fragments. In the mature depeer profiles (variant "b") the solid rock conversion into fine earths and clayey materials was revealed on the example of Entic Podzols on traprocks represented by chemically weathered dolerite (the Central Siberian Plateau). Development of chemical weathering in the soil environment apparent by a significant proportion of oxalate-extractable Fe, Al, and Si in the soil fine earth fraction led to formation of iron-clay-organic coatings on the surface of rock fragments and smectite aggregates. The coatings protected them against dissolution and the inhereted smectite was found even in acidic soil horizons.

Reference: Wilson M.J; Jones D. (1983) Lichen weathering of minerals: implication for pedogenesis. Pp. 2–12 in: Residual Deposits: Surface Related Weathering Processes and Material (R.C.L. Wilson, editor). Special Publications, 11. Geological Society, Blackwell, London.

Acknowledgments: This study was financed by RFBR (grant 18-05-00860a).

Structural modeling of flocculation of clay suspensions as probed by small angle scattering and TXM imagery: The q^{-3} dilemma

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The flocculation of clay suspension by inorganic salts was investigated in a recent publication [1] by small angle scattering (SAXS) and Transmission X ray Microscopy (TXM). Combining SAXS patterns and projection TXM images of unperturbed water suspensions, It was observed than small angle scattering evolves as q^{-a} on a large range of correlation lengths. Moreover, depending of the nature of the inorganic salt in water suspension, the exponent a can evolve from 2 to 4. Meanwhile, as a increases, the pseudo 001 correlation peak is reinforced. A similar evolution is also found in more and more concentrated clay suspensions.

In this presentation, we propose an analytic model to explain the evolution of SAXS patterns, showing that a cross-over from a>3 to a<3 can appears without any geometrical transition but strongly depends of the lateral stacking disorder. The main conclusion of this work is that a bottom_up approach mixing SAXS, SANS and 2D -3D imagery technics is highly needed for these types of multiscale complex systems.

[1] Michot L.J., Bihannic I., Thomas F., Lartiges B.S., Waldvogel Y., Caillet C., Thieme J., Funari S.S., and. Levitz P., Coagulation of Na-Montmorillonite by Inorganic Cations at Neutral pH. A Combined Transmission X-ray Microscopy, Small Angle and Wide Angle X-ray Scattering Study, Langmuir, 29, 3500–3510, (2013).

Adsorption of an artificial Acid Root Exudate to clays: methodology and preliminary results

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Enhanced weathering, a technology that aims to accelerate the natural inorganic carbon drawdown associated with the weathering of silicate minerals, has been proposed as a Carbon Dioxide Removal strategy. Amending cropland soils with finely crushed basalt, an abundant rock with a reasonably fast weathering mineral assemblage, is one proposed technology to enhance carbon drawdown.

As basalt weathers, fresh short-range order minerals and clays may form in the soil. The relatively large surface area and high concentration of reactive sites in the weathering products are able to readily bond to soil organic matter. While bonded, organic carbon molecules are protected against microbial mineralisation; consistent with documented trends that correlate higher concentrations of secondary minerals with higher concentrations of soil organic carbon. Therefore, through the creation of new reactive mineral surfaces, basalt-amendment could help stabilise organic matter - providing an additional carbon capture pathway while improving soil quality.

Focusing on adsorption as one of the key processes of soil organic carbon stabilisation, there have been extensive studies investigating the interaction between humic acid and clays, oxides and other short range order minerals. However, very little work has focused on how clay interacts with sugars and acids which are vital soil components released from plant roots. Experiments were designed to determine the total organic carbon adsorbed to various clay minerals (kaolinite and montmorillonite) when interacting with an artificial acid root exudate. These experiments aimed to (1) determine how much organic carbon is adsorbed when the solution and clay minerals are in equilibrium, and (2) characterise dominant processes involved in the kinetic adsorption of the molecules.

During this poster presentation, the rationale and methodology to these adsorption experiments will be presented along with some preliminary data.
The name of the presenting author should be underlined, and e-mail address should be provided. The asterisk for Author two indicates that he will be the speaker (if oral) or the poster presenter. The e-mail address is on a separate line separated by blank lines both before and after as shown. The e-mail address is for the speaker or poster presenter only. Addresses are separated by semi-colons. Do not right justify addresses. Single spacing should be used for authors' list and addresses.

Use 2.5 cm margins all around. Use the A4 standard paper size (21 x 29.7 cm). Paragraph one starts without an indent after a 6pt space from the e-mail address, and each paragraph is fully (left/right) justified. Any additional paragraphs start with a 6pt space from the previous paragraph. Normal line spacing should be used.

Up to two figures or images may be used, and these will be printed in black and white. The entire abstract must fit on no more than one page.

Effect of isomorphous substitution on the reducing capability of magnetite coupled with aqueous Fe^{2+}

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Clay minerals have variable composition of aluminum, iron, magnesium, and other cations. Among these cations, iron is redox active and commonly present in sedimentary and edaphic environments as iron (oxyhydr)oxide minerals. In anoxic environments, the interaction between magnetite and aqueous Fe^{2+} profoundly impacts contaminant reduction. The iron ions in natural magnetite are extensively substituted by other cations. These isomorphous substitutions remarkably change physiochemical properties and microstructure of magnetite, which probably affect the reducibility of magnetite coupled with Fe^{2+}. However, it is still unclear whether the substitution with thermodynamically favorable redox pairs (e.g., Co(II)/Co(III)) or with a sole valence ion (e.g., Zn(II)) plays a vital role in the reducing capability of the coupled system. This study compared the effect of Co substitution ($Fe_{3-x}Co_xO_4$) and Zn substitution ($Fe_{3-x}Zn_xO_4$) in magnetite on the reducibility of the coupled system, and investigated the reaction mechanism.

Herein, $Fe_{3-x}Co_xO_4$ ($0.00 \le x \le 1.00$) and $Fe_{3-x}Zn_xO_4$ ($0.00 \le x \le 1.00$) were synthesized by a coprecipitation method and characterized by several state-of-the-art technologies. Batch experiments of the reduction of 2-chloronitrobenzen (2-Cl-NB) and Cr(VI) were conducted in an anaerobic glovebox ($O_2(g) < 0.1$ ppm, 25 °C).

Both the reaction kinetics and electron transfer amount illustrate that Co substitution ($x \le 0.77$) generally promoted the reduction activity of the coupled system, while an overdose of Co ($x > 0.77$) retarded the process. A good linear correlation was found between the electrical conductivity of $Fe_{3-x}Co_xO_4$ and the k_{obs} values ($R^2 \ge 0.94$). During the redox reaction, the adsorbed Fe^{2+} and structural Fe(II) of $Fe_{3-x}Co_xO_4$ were gradually oxidized, while $Fe_{3-x}Co_xO_4$ maintained its spinel structure. 2-chloronitrobenzene could be completely reduced to 2-chloroanaline; Cr(III) was precipitated on the $Fe_{3-x}Co_xO_4$ surface with Fe(III) ($Cr_xFe_{1-x}(OH)_3$), or substituted for octahedral Fe in $Fe_{3-x}Co_xO_4$. The promotion effect of Co substitution was ascribed to the presence of the redox pairs Co(II)/Co(III) and Fe(II)/Fe(III) in octahedral sites, which accelerated electron transfer among Fe^{2+}, $Fe_{3-x}Co_xO_4$, and contaminants. For Zn(II) substitution, the tetrahedral Zn(II) weakened the electron transfer between tetrahedral-octahedral Fe ions in magnetite and, accordingly, the reducing capability of the coupled system.

The insights obtained in this study should lead to a more profound understanding of the self-purification of magnetite-group minerals and their impact on electron transfer and the transformation of contaminants in anoxic environments.

Adsorption of amino acids in clay minerals and their possible contribution to the origin of life

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How life emerges? The question that intriguates researchers in different fields being scientists or not. Different theories have been stipulated and different approaches presented giving birth to the Prebiotic Chemistry[1]. Studying the formation of amino acids in the early Earth and their condensation into peptides is an extremely important subject for prebiotic chemistry[2]. The clays appear in this scenario as containers capable of pre-concentrating amino acids and may also catalyze the reaction of peptide formation.

The objective of the present work is to investigate the influence of the particle size on the adsorption of a selected amino-acid, the alanine and then to study the possible peptidic condensation after thermal activation. Hectorite and laponite were chosen because of their similar chemical composition and different particle size. Indeed, Hectorite particles are at least 5 times bigger then the laponite ones. This induces a difference in their reactivity due to the difference in the OH-edges density. Isotherm adsorption were performed on both smectites. A multi-technical approach was used including X-ray diffraction, thermogravimetric Analysis, infrared and nuclear magnetic resonance spectroscopies. The results indicate that both clays are able to adsorb the amino acid, on the surface and in the interlayer space. After thermal activation, different peptides were formed. Their exact nature is under investigation by mass spectrometry.

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Hybrid pigments clay-anthocyanin: slipping between the sheets

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In despite of their use in several fields, due to their antioxidants properties, anthocyanins have limited use in the food and cosmetic industries because of their photo- and chemical stabilities (TORRES et al. 2011). Therefore, biohybrid compounds that combine these biomolecules and an inorganic counterpart such as clay minerals have been widely investigated to reverse these limitations by complexation in the host materials (KOHNO et al. 2009; OGAWA et al. 2017).

The present work described the synthesis and characterization of hybrid materials based on β-cyclodextrin (β-CD) and cetyltrimethylammonium bromide (CTAB) intercalated into saponite (SAP) and a commercially available powdered of anthocyanin dye, Crystal Red Grape (RG). The interactions between the organic dye guest and the organic-clay host were investigated by X-ray diffraction, thermogravimetric analysis, transmission electronic microscopy and solid state nuclear magnetic resonance. The results support complex formation between β-CD and CTAB, their intercalation into the clay interlayer spaces, and their interaction with RG (SAP-CTAB, SAP-β-CD e SAP-β-CD+CTAB). The hybrids pigments formed exhibit different colors, enhanced stability against visible light irradiation and basic environment conditions regarding to RG-SAP material. These dyes materials are environmentally friendly and can be promising candidates in different application fields.

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Accuracy of force fields for atomistic modelling of alcohols in nano-confined clay environments

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Intercalation of alcohols in clays such as Montmorillonite (MMT) is a long known and studied phenomenon. A useful and often necessary tool providing insight into the atomistic behavior and intercalation process is Monte-Carlo (MC) and molecular dynamics (MD) simulations. However, a fundamental problem with these types of simulations is the classical and semi-empirical nature of the force fields used to describe the atoms pairwise interactions. Different force fields often have parameters either determined from quite diverse protocols, or parameters optimized for different water models. With few exceptions,[1] it is currently difficult to find combinations of force fields suitable for both organic and inorganic multicomponent systems that have been parameterized from geochemical experimental data in a fully consistent way. Hence, many combinations of organic and inorganic force fields are not necessarily very accurate and attention is needed when choosing forcefields for modelling multicomponent systems such as geochemical systems with organics.[2]

The aim of this work was therefor to scrutinize different combinations of force fields for organics and clays. For this purpose, we tested four force fields describing the intercalated alcohols (GROMOS, Gaff, CGenFF, OPLS) in the interlayer of MMT (Clayff), water (SPC) and calcium (Åqvist) counter ions.

Overall, this exercise was conducted by simulating supersaturated systems of water and alcohol where both the alcohol and water content was successively removed to identify energy minima in the calculated immersion energies.[3] The relative accuracy of the different combinations of force fields was then determined by comparing the calculated *00l* XRD reflections obtained from mixed-layer-modelling and the corresponding experimental XRD profiles.

From the comparison between simulated and experimental XRD data it was possible to determine which force field combination was most accurate in replicating the experimental basal spacing. These results could provide a foundation for determining the validity of extrapolating onto larger organic molecules in nano-confined environments of geological materials.

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Hybrid nanoarchitectures based on Halloysite Nanotubes and polymers for drug delivery

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Hybrid nanoarchitectures based on inorganic solids and organic moieties represent an innovative and attractive perspective for a wide range of technological issues, which the scientific community needs to tackle. Among the different application fields, biomedicine and drug delivery are considered a matter of importance and interest. Hence, this work represents a contribution to the design and preparation of new hybrid nanomaterials composed by Halloysite Nanotubes (HNTs), which are promising candidates for both the loading and the release of active molecules due to their hollow cavity, and some differently charged polymers. In particular, three different nanoarchitectures have been prepared, characterized and exploited as delivery systems, by loading the nanotubes with model drugs, in order to explain how they work in relation to their structure and morphology. For instance, hybrid gel beads with a chitosan rich core, containing halloysite, and an alginate rich shell showed that the nanotubes incorporation into the chitosan matrix slightly slowed down the drug release whereas the presence of the alginate outer layer had a profound effect on the kinetics likely due to the viscosity of the shell.[1] Moreover, the selective functionalization of halloysite with stimuli-responsive macromolecules, namely two differently charged PNIPAAMs, allowed the preparation of smart hybrid nanocarriers whose thermodynamic behavior and temperature responsive features are deeply affected by the polymer adsorption site into the nanotubes lumen or onto the outer surface.[2] Finally, a biofilm made of chitosan and halloysite, the latter acting as a filler, was prepared and furtherly covered on both sides by two layers of alginate. The study of the resulting material, thus processed like a pellet, allowed to demonstrate that the release kinetics is influenced by the alginate layers and, more noticeably, by their thickness. Indeed, the amount of released drug increases after the solubilization of the coating biopolymer and the kinetics changes with the pellets size. Therefore, this work opens new perspectives into the preparation of hybrid architectures for drug delivery applications, and proposes some new strategies for obtaining tuned release by controlling the morphology and the assembly of the materials.

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Functionalization of halloysite nanotubes as drug carrier for treatment of breast cancer

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Halloysite nanotubes have attracted numerous research interest due to their tubular morphology with empty lumen, high dispersion ability in water, high thermal and mechanical stability, good biocompatibility, low toxicity, high adsorption ability, and low cost. These features allow for various biomedical applications in diagnosis and treatment of diseases. Coating the nanotubes with positive polymer shells can significantly decrease the toxicity and provide colloidal stability during blood circulation. Cationic polymer grafted halloysite nanotubes are synthesized for loading of chemotherapy drugs and/or genes in order to intracellular delivery of them and treat of breast cancer via targeted therapy. The grafting of polymers on this clay can be confirmed by various analytical methods, including the size, zeta potential, TGA, and XPS. The functionalized nanotubes generally show good cytocompatibility and decreased hemolysis rate compared with the raw halloysite. The cumulative release ratio of drugs such as doxorubicin hydrochloride from the nanoplatm is higher at pH in acidic environment than that in pH 7.4. The drug loaded nanotubes exhibit enhanced cellular uptake efficiency and can effectively inhibit the growth of tumor cells. The cell uptake of can be confirmed by fluorescence microscopy and transmission electron microscope. Flow cytometric analysis and reactive oxygen species analysis show that halloysite can increase apoptosis to breast cells. For gene therapy, modified nanotubes together with siRNA can knockdown of cellular mRNA and induced apoptosis in the MCF-7 cells. In vivo anti-cancer results demonstrated that the nanodrug treated 4T1-bearing mice showed enhanced anti-cancer efficacy than pristine drug group. Also, the nanocarrier system showed negligible toxic effects toward the major organs of mice. In vivo fluorescence imaging studies showed that the fluorescence signal of the nanodrug is stable even after 72 h post-injection. Therefore, the polymer grafted halloysite show promising application as potential nanovehicles for anticancer drug delivery in breast cancer therapy.

Surface complexation of organic groups on clay surfaces: insight from first principles simulations

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Organics-clay interactions are ubiquitous on the Earth. The microscopic knowledge of these interactions is helpful for understanding many biogeochemical processes, e.g. the origin of life, generation of petroleum, soil processes.

In this study, we investigate the binding of reactive organic groups on clays surfaces by using FPMD (first principles molecular dynamics) simulation technique. The reactive organic groups considered include carboxylate, phosphate, ammonium and quinone species. These groups are present in various biomolecuels and natural organic matters, including low molecular weight organics and the macromolecules like HA (humic acids) and FA (fulvic acids). We investigate the complexes adsorbed on clay edge surfaces (including (010) and (110) surfaces) and in interlayer region (i.e. with cation bridging).

Through the simulations, we have derived the structures and free energies for these organic groups. By integrating the surface acidity data that we calculated in previous works, we derive the pH-dependence of their surface complexation. We also try to compare the results with the available experimental measurements. We will discuss the potential applications of these results in future studies, e.g., for constructing realistic large scale organo-clay models, for understanding the role of clays in the origin of life.

Influence of principal stress direction on mechanical behavior of rocks by three-dimensional discrete element method analyses

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It is well known that loading path plays a critical role on the mechanical behavior of rocks. Practically, most projects of rock engineering involve three-dimensional loading conditions, and rocks are subjected both three different principal stresses and the rotations of the principal stress directions. Many researchers have performed true triaxial tests on various rock types to reveal the effect of different principal stresses on rock failure, deformability and failure plane angle. However, the influence of principal stress direction on the mechanical behavior of rocks are rarely reported due to the limitation of the test device.

The limitation encountered in experimental studies on rotations of principal stress direction can be overcome by employing discrete element method (DEM) which is a promising approach to linking macroscopic behavior to grain scale properties. DEM has been widely applied to study the mechanical behavior of rock under different loading conditions. And some scholars have also successfully investigated the effect of rotation of principal stress direction on the stress-strain behavior of soils using discrete element modeling.

In this paper, a numerical hollow cylinder torsional test model of rock is established by three-dimensional discrete element method. The rock sample is represented by bonding rigid particles at their contact points. Due to the lack of experimental HCA results of rock, the micro parameters used in this study is calibrated from uniaxial compression results of previously reported laboratory test. The numerical hollow cylinder specimens are tested with constant principal stress angels of 0°, 30°, 60° and 90°. The numerical results are compared with existence laboratory tests, and the development of microcracks and the evolution of major fracture are also discussed.

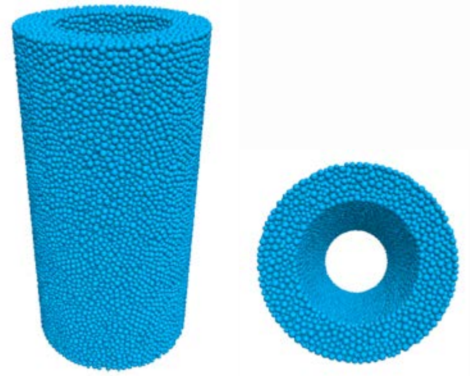

Fig.1 Three-dimensional DEM model of hollow cylinder rock specimen

Efficient Fe/Montmorillonite based Fenton-like oxidation for environment cleanup

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Montmorillonite is a layered aluminosilicate with a three-layer lamellar structure: two outer tetrahedral and an octahedral layer between them. The unique lamellar structure offers interlayer space for iron oxides, which could be active sites for Fenton-like reactions, a promising advanced oxidation technology to remove recalcitrant organic contaminates in water or soil. Development of efficient Fe/clay materials to enable Fenton-like reactions at neutral pH is crucial to avoid soil acidification upon oxidation treatment. Herein, a maghemite/montmorillonite composite was developed by a coprecipitation and calcination method. The physiochemical properties of catalysts were characterized by various measurements. The calcined composites retain magnetism, because of the inhibited growth of γ-Fe_2O_3 nanoparticles and phase transition. The catalytic activities for phenol degradation were significantly enhanced by calcinations, which strengthen the interaction between iron oxides and aluminosilicate framework, and result in more negatively charged surface. The composite displayed a high catalytic activity with more than 99 % phenol reduction after only 35 min reaction at pH 3.6. Simultaneously, this catalyst exhibited high stability, low iron leaching, and magnetically separable ability for consecutive usage, making it promising for the removal of recalcitrant organic pollutants in wastewater. Furthermore, the clay based Fenton-like reaction was applied for removal of polycyclic aromatic hydrocarbons (PAHs) in soil. After 5 days treatment at neutral pH, the removal efficiency of PAHs in soil reached 79.9%±0.8%. The influence of soil organic matters (SOM) on the PAHs oxidation was investigated. Results indicated that the soluble SOM can improve oxidation, while insoluble SOM significantly inhibited oxidation of PAHs. The clay based Fenton-like oxidation could be a promising technology for organic polluted soil remediation.

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Sepiolite as a new nanocarrier for DNA transfer into mammalian cells

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Nanofibers of sepiolite, a natural silicate belonging to the clay minerals family, might constitute a potential promising nanocarrier for the non-viral transfer of bio-molecules. Using physic-chemical approach and transmission electronic analyses, we show that sepiolite nanofibers efficiently bind different types of DNA molecules through electrostatic interactions, hydrogen bonding, cation bridges, and van der Waals forces. Moreover, Fourier-transform infrared spectroscopy identified the external silanol groups as the main sites of interaction with the DNA.

Due to its nano-size dimension sepiolite can be naturally internalized into mammalian cells. Therefore, deciphering the mechanisms of sepiolite cell internalization constitutes a question interesting biotechnology, for the use of sepiolite as nanocarrier, as well as environmental and public health concerns. Though it is low, the perfectly stable and natural intrinsic fluorescence of sepiolite nanofibers allows to follow their fate into cells. By combining fluorescence microscopy, time-lapse video microscopy, fluorescence activated cell sorting and transmission electron microscopy, we show that sepiolite can be spontaneously internalized into mammalian cells through both non-endocytic and endocytic pathways, macropinocytosis being one of the main pathways.

As a proof of concept, we show that sepiolite is able to stably transfer plasmid DNA into mammalian cells and that the efficiency can be optimized. Indeed, sonication of sepiolite prior assembly with DNA 100-fold stimulated DNA transfection efficiency. Moreover, exposure of the cells to endocytosis inhibitors, such as chloroquine, two-fold increase the efficiency of sepiolite-mediated gene transfer, in addition to the 100-fold increased resulting from sepiolite sonomechanical treatment.

These results open the way to the use of sepiolite-based bionanocomposites as a novel class of nanoplatform for gene transfer.

Toward the use of layered double hydroxides for phosphate recycling from wastewater

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Phosphorous in the form of phosphate is an essential fertilizer in agriculture and a critical raw material. Wastewater is considered an alternative phosphate source, as it contains high concentrations of phosphate. Layered double hydroxides (LDHs) have high affinity for orthophosphate adsorption and have therefore been proposed to be utilized for selectively recovery and recycling of phosphate from wastewater. LDHs are composed of positively charged layers of divalent and trivalent cations octahedrally coordinated to hydroxyl groups intercalated with charge balancing anions which can be exchanged for other anions.

The macroscopic properties of LDHs, e.g., adsorption capacity as function time, pH, concentration, and competing anions such as carbonate have been well studied. However, the mechanism for phosphate adsorption and how it depends of e.g. the choice of cation, M^{II}/M^{III} ratio, pH of the wastewater need to be fully understood prior to industrial application.

MgAl- and ZnAl-LDH were exposed to aqueous solutions with different phosphate concentration and sludge acidified to pH of 6, 5 and 3, respectively. The solid were collected and characterized by a combination of PXRD and FT-IR as well as ^{25}Mg, ^{27}Al and ^{31}P MAS NMR after an exposure time of 5-62 h. This allowed for identification of the different phosphate binding sites and quantification of the intercalated phosphate vs surface adsorbed phosphate. In addition, ^{27}Al and ^{31}P MAS NMR revealed that for LDH synthesized by the coprecipitation method amorphous aluminum hydroxide commonly present in LDH and $AlPO_4$ contribute with 13-38 % and 0-15 %, respectively of the phosphate adsorption depending on phosphate concentration, pH, M^{II}/M^{III} ratio, and exposure time. Furthermore, from PXRD it was found that carbonate contamination can be controlled by pH adjusting of the sludge due to degassing of carbonate as CO_2 below a pH of 6.4 because of the carbonate equilibrium[1].

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Illitic clay-based geopolymer: the study of the mechanochemical activation duration and coupling with thermal activation.

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The scientific community's interest in geopolymers keeps on growing under environmental and climate change pressures. Although most studies concern metakaolin or industrial by-products as alumino-silicate precursors, few are those concerning clay cuttings characterized by little or no kaolinite content. This study proposes a method to activate illitic clay in order to obtain a geopolymer with high mechanical performances. The tested illitic material contained 48% of illite/muscovite, 22% quartz, 15% feldspars and low content of calcite. The innovation consisted in coupling of thermal and mechanochemical activations favouring, respectively, the clay dehydroxylation and the destruction of the clay crystalline structure. Such increase of amorphous rate in precursor is required to make the material reactive. The structural evolutions of material after activation were followed by ThermoGravimetric Analysis (TGA/DTG), X-Ray Diffraction (XRD) and Fourier Transform InfraRed spectroscopy (FTIR). The present study focuses on variation and optimization of a single parameter, the duration of the mechanochemical activation process. The most efficient duration of the process could be determined by following the evolution of the precursor characteristics but following their geopolymerisation as well. Effectively the compressive strength (Rc) of the synthesized geopolymers was tested after 48 hours. Once the grinding optimal duration was determined, we focused this study on the optimization of the geopolymer formulation: we then obtained a geopolymer with a compressive strength up to 102MPa at 28 days. This result suggests that clayey cuttings or any natural soil without kaolinite but illite could be used as precursor materials for the realization of a geopolymer which display very high mechanical performances.

Key words: illitic clay – geopolymer – mechanochemical activation – amorphous rate - dehydroxylation

Enhanced Degradation of Rh 6G by Zero Valent Iron Loaded on Two Typical Clay Minerals with Different Structures under Microwave Irradiation

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Nanoscale zero valent iron has been a widespread concern in various fields due to its large specific surface area and high reactivity. However, nanoscale zero valent iron (nZVI) is very likely to aggregate and be oxidized, which limit its wide application in industry. Most clay minerals have a large adsorption capacity of cations due to their negative charges and high specific surface areas. In the present work, nZVI was loaded onto two typical clay minerals: kaolinite and sepiolite, to inhibit its oxidation and aggregation. The composites were applied to degrade Rhodamine 6G (Rh 6G) under microwave irradiation. The effects of pH value and microwave power on degradation were studied. The results showed that the removal amount of Rh 6G by nZVI/kaolinite was 110 mg/g in 15 minutes, while it reached 300 mg/g by nZVI/sepiolite. The difference between these two composites was mostly determined by the structures of these two clay minerals.

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High performance supercapacitor of polyaniline Nanotubes synthesized from halloysite template

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Halloysite is a natural clay mineral with nanotube structure, which can be used as hard template to prepare new nanotube-structured materials. As one of the conducting polymers, polyaniline (PANI) has been a promising pseudocapacitive electrode material for supercapacitors due to its low cost, easy preparation and superior electrochemical properties. However, poor electrochemical stability is the main obstacle for practical application of PANI electrode materials. Herein, pure phase nanotube-structured polyaniline was firstly synthesized using halloysite as hard template. Then, XRD, Raman, XPS, SEM and TEM were carried out to investigate the composition, morphology and structure characteristics of the nanotube-structured polyaniline. As electrode material for supercapacitors, the electrochemical performance of the as-prepared samples was tested in a three-electrode system, and the results indicated that the nanotube-structured polyaniline displayed higher capacitance than directly synthesized polyaniline nanoparticles. In addition, the obtained polyaniline nanotubes/carbon (PANI/C) showed enhanced cycle stability after carbon coating, and the specific capacitance can possess capacitance retention of~82% after 5000 cycles.

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Nanostructured organic-amine-decorated 13X zeolite for reversible CO_2 capture

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Excessive CO_2 emission has caused global warming, which has been tremendously promoted by fossil fuel combustion than ever in human history.[1] Meanwhile, CO_2 is a kind of important carbon resource, so the capture and storage technology of CO_2 has been widely concerned at home and abroad.[2] Adsorption method is considered to be a promising CO_2 capture and separation technology because of its low cost, simple process and low corrosive characteristics. Traditional adsorbents need high equipment requirements and high energy consumption which limits their application in industry.[3]

In our previous work, clay-based solid adsorbents have been demonstrated to be low-cost and efficient.[4,5] In this paper, natural nanostructured clay mineral 13X zeolite is found to be a superior support for CO_2 capture after activation treatment and modification with organic amines tetraethylenepentamine (TEPA) and polyethyleneimine (PEI, Mw=600), respectively. These two kinds of easily prepared organic-amine-modified 13X zeolite adsorbents are subsequently characterized to monitor their properties before and after modification with organic amines. These adsorbents are proved to have good stabilities, high CO_2 adsorption capacities (229.7 mg/g), lower CO_2 desorption temperatures (100.2℃), higher decomposition temperatures (466 ℃) at room temperature under atmospheric pressure. Taking the advantage of relative low cost and environmental properties of the mineral into account, these two kinds of solid-amine adsorbents are expected to be widely used in the sealed systems of spacecraft, submarine and satellites, as well as environment protection.

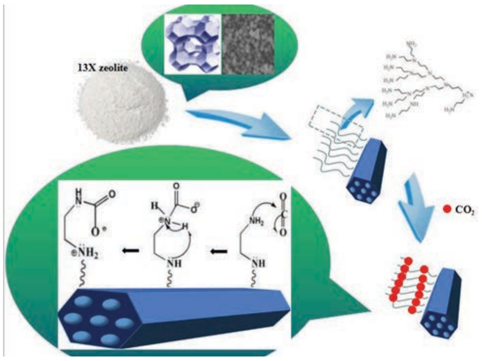

Figure 1 CO_2 adsorption mechanism of the adsorbents

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Infrared spectroscopy in studies of acid-treated clay minerals

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The aim of the present work is to review the potential of infrared (IR) spectroscopy, in both mid-IR (MIR) and near-IR (NIR) regions, to clarify the structural changes in acid-treated clay minerals. The influence of several variables, e.g. clay mineral composition, content of non-swelling layers, and the presence of alkylammonium cations in the smectite interlayers, on the dissolution rate has been demonstrated. Moreover, the effect of montmorillonite (Mt) structure degradation on the surface area and creation of acid sites has been followed via adsorption of water and pyridine molecules, respectively.

Acid dissolution proceeds via replacement of the exchangeable cations with protons which penetrate into the clay mineral layers and attack the OH groups. Consecutive dehydroxylation connected with the release of the central atoms from the octahedral sheets resulted in formation of amorphous, partly protonated silica phase. The MIR spectra of acid-untreated Mts show a complex band near 1030 cm^{-1} assigned to the stretching vibrations of the Si-O groups, the OH bending bands in the 920-840 cm^{-1} region and the Al-O-Si and Si-O-Si bending bands near 520 and 470 cm^{-1}, respectively. The NIR spectra of untreated Mts reveal a complex band near 7070 cm^{-1} involving the first overtone of the structural OH groups and H_2O molecules, broad band near 5250 cm^{-1} corresponding to the combination band of water molecules, and the bands below 4520 cm^{-1} related to the combination of structural OH stretching and bending vibrations. Spectra of acid-treated samples show a gradual decrease in the intensities of all bands related to the vibrational modes of the structural OH groups reflecting reduced octahedral atoms content. A shift of the Si-O stretching band to higher wavenumbers confirms the transformation of the layered tetrahedral sheet to a three-dimensional framework of amorphous silica. A new band near 7315 cm^{-1} observed in the NIR spectra of acid-treated samples, related to the first SiOH overtone, is an important indicator of the Mt surface acidification and/or creation of partly protonated silica phase. The extent of acid dissolution of Mts increases with increasing Mg for Al substitution in the octahedral sheets. The accessibility of the interlayers for protons significantly influences the stability of clay minerals in HCl. Mixed-layered mineral illite/smectite dissolves more slowly than Mt. The solubility of smectites in HCl has been modified if inorganic exchangeable cations are replaced by alkylammonium cations. With increasing size of organic cation dissolution rate decreases. The changes in the surface area of Mts upon dissolution affect its hydration properties as confirmed the water combination band in the NIR region. The adsorption of pyridine on acid-treated Mt allows identification of different acid sites. In addition to the bands related to the H-bonded and physisorbed pyridine, also the diagnostic band of pyridinium cation near 1540 cm^{-1} confirmed the presence of strong Brønsted acid sites in partly decomposed Mt.

The financial support of the Slovak Grant Agency VEGA (project 2/0141/17) and Slovak Research and Development Agency (projects APVV-15-0741) is acknowledged.

LOW GRADE METAMORPHIC studY to PRECISE the geodynamic history and hydrocarbon migration system of THE HIKURANGI PRISM (north island, new zealand)

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The Hikurangi subduction wedge has undergone several deformation episodes periods mainly related to subduction processes, and leading to complex stratigraphic and structural patterns: i) Initial formation of an accretionary complex on the eastern Australian margin during Triassic, Jurassic, and Early Cretaceous times; ii) a stage of tectonic quiescence during Late Cretaceous to Oligocene times; iii) and the renewal of westward subduction beneath North Island since the Early Miocene to present day. The onland exposure of Neogene trench slope basins together with their Jurassic to late Paleogene pre-subduction series permits to provide a high-resolution sampling grid including all lithostratigraphic units.

A multi–proxy approach was performed to determine organic matter (OM) maturity (organic petrography, Rock-Eval pyrolysis (REP), vitrinite (VR) and solid bitumen reflectance (BR) compared with clay mineral reaction progress (illite Kübler-Index (KI) and clay mineral paragenesis). Determining different bitumen populations and hydrocarbon migration allows a better understanding of the thermal evolution and fluid migration. The combination of clay mineral indices and organic matter reflectance and VR versus BR allows the recognition of heat flow changes during sedimentary and tectonic burial.

VR (%) and REP results show no significant maturity in the thick Neogene sedimentary cover. These measurements indicate a very low geothermal gradient during Early Miocene to Late Miocene within the Coastal Ranges. Distribution of illite/smectite interstratified phases in the Cretaceous up to the Miocene strata confirm these results.

KI determination from Late Miocene rocks from offshore wells (Titihaoa-1 and Tawatawa-1) and from onshore outcrops, indicates a clear influence of detritus using the KI from the <2 µm and <10 µm fractions. We observe that illite from Lower to Middle Miocene series are less ordered than in the Late Miocene. KI determination from Lower to Middle Miocene series reflect low-grade diagenesis while the Late Miocene series indicate an anchizonal KI grade. The deposition of detrital material can be associated with a Late Miocene erosional phase that affected the main structural highs separating the Neogene slope basins or other contemporaneous reliefs further west. At least three periods of fluids migration can be distinguished between Early Miocene to Pliocene. These are associated to bitumen migration (solid bitumen) and gas hydrate formation related to main deformational events and can be linked to the Late Cretaceous to Paleocene source rocks of the basin.

Flocculation of clay colloids: combining scattering and imagining techniques

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Flocculation is a key process in numerous environmental and industrial technologies, such as purification of waste-water and civil engineering. We study flocculation of the plate-like clay colloids by ionenes, cationic polyelectrolytes with a regular charge density, which can be tuned to match/mismatch the clay charge density [1,2]. Combination of turbidity and zeta-potential measurements allowed us to identify the optimal flocculation conditions for ionene-clay mixtures. For all systems studied flocculation started consistently at ratios of positive and negative charge significantly below 1 (as low as 0.3), indicating highly ionene-deficient aggregates [4]. This early onset of flocculation in clay–ionene mixtures is reminiscent of the behaviour of multivalent salts and contrasts with that of monovalent salts, for which a large excess amount of ions is necessary to achieve flocculation [3]. We studied the structure of clay-ionene aggregates by a combination of small angle X-ray scattering (SAXS) and scanning transmission X-ray microscopy (STXM) (Fig. 1). The combined SAXS+STXM data gives us access to scattering curves spanning four decades in length scale, necessary for a multi-scale structure of the aggregates [5]. We see a clear evidence for the formation of clay tactoids within the otherwise loose aggregates, demonstrated by the presence of a stacking peak in the SAXS spectra [6]. The relative charge density of ionene chains and clay surfaces influences the repeat distance within tactoids, tactoid abundance and possibly even the macroscopic aggregate density.

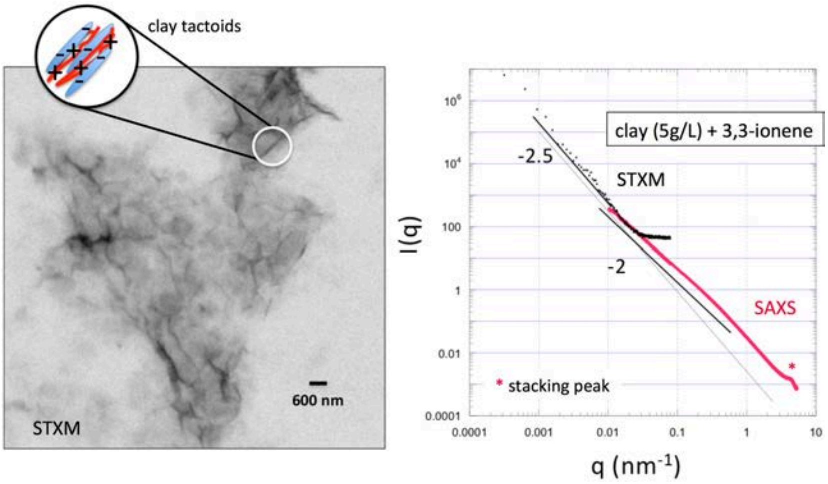

Fig. 9: Structure of clay-ionene aggregates, STXM and SAXS.

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Different alterations paths of alluvium derived from the Variscan basement in different time: Cretaceous and Messinian alterites of Sardinia (Italy)

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Mineralogical and chemical analyses on two clayey deposits, derived from weathering of alluvial material, were performed in order to compare their provenance and the weathering path experienced in two different time intervals considered hot and wet and hot and dry, respectively: the Upper Cretaceous and the Messinian.

The Cretaceous alterites (CP) are mostly composed by kaolinite, subordinate illite+/-montmorillonite, quartz, Ti-oxides, minor Fe-oxyhydroxide and boehmite, and vertically pass into bauxite. The Messinian alterites (MP) are composed by illite and kaolinite, quartz, Ti-oxides, with minor content of Fe-oxyhydroxide and gibbsite.

The Subset CP is strongly enriched in Ti and Al (2-5 x GLOSS values from Plank and Langmuir, 1998) and, to a minor extent, in Fe (1-4 x GLOSS) whereas relevant depletion (<1 x GLOSS) is observed for Si and especially Mn, Na and P. The subset MP is moderately enriched (1-2 x GLOSS) in Ti, Al, Fe, and K. Chemical index of alteration (CIA - Nesbitt and Young, 1982) of CP alterites yield a mean value of 82.3 suggesting strong weathering whereas that of MP alterites is 74.2 pointing to a less strong alteration. Chondrite-normalized REEs patterns show homogeneous and typical UCC pattern for MP samples with average La_{ch}/Yb_{ch} = 12,91 and average Eu/Eu*= 0.70. Chondrite-normalized REEs patterns of CP samples show fractionation effects likely due to intense weathering, in agreement with CIA values and A-CN-K ternary plot, including scattered La_{ch}/Yb_{ch} values (from 5 to 25). It is interesting to observe that the conservative provenance Eu/Eu* proxy has the same mean value (0,70) of the MS subset.

As MS alterites patently derives from alluvium fed by the Variscan basement (Mongelli et al., 2012), it can be assumed that this was also the provenance of CP alterites. However MP and CP alterites shared similar alteration in the first stages of the weathering path, MP, despite some high Al enrichment values, never ended in bauxite: although unexpectedly wet, the Messinian climate was not warm enough to generate ferrallitic alteration.

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Properties of the alteration clays of the Schisto-Calcaire and Inkisi Subgroups in the Democratic Republic of Congo and raw earth construction material valorisation

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The western part of the Democratic Republic of Congo contains abundant clayey resources that are mainly used in the terracotta building industry. The building bricks are handmade and heated using wood as combustible, increasing the problem of deforestation. This study aims to characterize the weathering clays of the Neoproterozoic sedimentary rocks in order to evaluate their valorization potential as ecological raw earth construction material.

The study area includes Kongo Central and Kinshasa provinces. The region is located in the West-Congolian belt. It is made by two stratigraphic units. (1) The upper 1100 meters-thick Schisto-Calcaire unit, made by calcareous rocks with sandstone, clayey sandstone, dolomitic clay limestone, and argillites. (2) The Inkisi Subgroup (600-1000m thick) includes arkoses, sandstone, psammites, micaceous sandstones with locally argillites. The weathering products provides yellow clay rocks and yellow or light brown sandy-clay soils (Delpomdor et al 2016).

Six areas containing important clay deposits have been prospected and sampled: Kinshasa, Mbanza Ngungu, Kasangulu, Nkamba, Kwilu Ngongo, and Lukala. The clay samples have been characterized by their chemical composition by X-ray fluorescence, mineralogical composition by X-ray diffraction, Atterberg limits and particle size distribution by laser diffraction. Results evidence that clay related to the weathering of the Schisto-Calcaire Subgroup is a raw clay rich in quartz (53%), kaolinite (31%) and goethite (7%), and plastic (plasticity index between 5 and 15). It is also characterized by a fine grain size distribution (10% clay, 75% silt and 15% fine sand). Clay related to the weathering of the Inkisi Subgroup has a mineralogy dominated by quartz (55%) associated with kaolinite (28%) and goethite (11%). It has a high silt content (68%) and little fine sand (20%) and plasticity index between 5 and 15. All clays present similar properties even they derive from the weathering of different geological substrates.

The next step will be the production of raw bricks which will be characterized by their mechanical and hygrometric properties.

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Mineral characterization of Ni-bearing mixered-layered clay minerals from Niquelandia deposit at Brazil

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Niquelândia, a Ni-lateritic ore deposit located in the State of Goiás (Brazil), exhibits both oxidized and silicate ores; in the oxidized ore, Ni is essentially associated with goethite while in the silicate ore, it is associated with clay minerals. Two samples from Niquelândia, identified as Niq1 and Niq2, were studied and high contents of nickel were obtained from XRF (Table 1). For sample Niq1, Ni content was close to 9%; however, for Niq2, it is nearly to 2%.

Table 1 – chemical composition (XRF) of samples Niq1 and Niq2 (wt%)

sample	NiO	Fe_2O_3	CuO	Al_2O_3	MgO	SiO_2	LOI
Niq1	8.85	6.38	0.25	13.1	22.7	34.5	13.2
Niq2	1.81	9.10	0.03	6.20	18.15	42.3	12.0

XRD patterns were obtained on air dried (AD), ethylene glycol saturated (EG) and after K saturation and heating at 350°C (K 350) samples preparations (Figure 1).

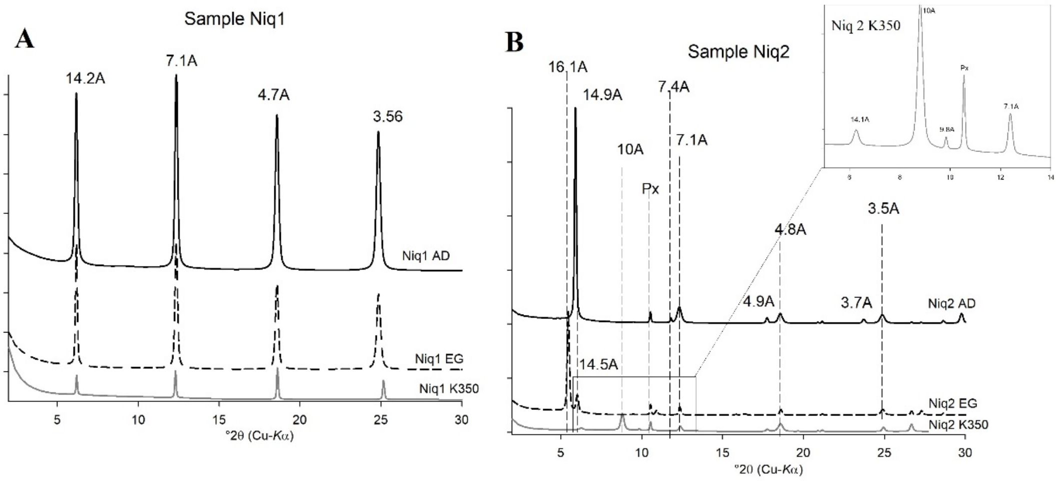

Figure 10 – XRD patterns for samples Niq1 and Niq2 after air dried, ethylene glycol and K saturation/heated at 350°C.

For sample Niq1, the d_{001AD} Ca-saturated sample is at 14.2Å and do not shift either after EG treatment or after K-saturation. Heating for sample Niq1 indicates the presence of pure chlorite and absence of other clay minerals. For sample Niq2, the d_{001AD} is at 14.9Å for Ca saturation, and following EG saturation, this peak is splitted into two peaks: one that shifts to 16.1Å and one that does not displace. Following K saturation and heating to 350°C two behaviors were observed: a large proportion of the clay minerals collapses to 10 Å while a small proportion remains at 14.2 Å. These preliminary results concluded that Niq2 is assigned to a mixture of mainly vermiculite or smectite (?) and a small proportion of chlorite. Further analyses, as SEM/EDX and FTIR will be performed to proper identify the mixered-layered Ni-bearing clay mineral.

Timing and interplay of faulting, hydrothermal alteration and weathering processes of the Rolvsnes granodiorite in southwestern Norway

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Old crystalline basement terranes are commonly pervasively dissected by dense networks of faults and fractures, so that previously formed brittle features are often reactivated. The resulting complex brittle deformation histories can only be deconvoluted by combining detailed structural analysis with mineralogical and geochronological studies (e.g., Viola et al., 2016; Scheiber & Viola, 2018). Brittle fracturing is commonly accompanied or followed by fluid circulation causing the alteration of primary minerals into an assemblage of secondary clay mineral phases. The source of these fluids may be diverse and can include meteoric water percolating from the surface along the fracture planes and fault damage zones. Secondary alteration products, however, may also be due to hydrothermal fluid circulation or weathering processes seemingly unrelated to tectonics. These can be very similar and difficult to distinguish from secondary phases forming in fault rocks during deformation. Being able to discriminate between a "structural" and "hydrothermal-weathering" origin for these phases is, however, crucial to reconstruct the evolution of basement blocks, including pinpointing *when* a crystalline basement terrane reached near-surface conditions (e.g., Fredin et al. 2017).

The 466 Ma-old Rolvsnes granodiorite, outcropping on a coastal archipelago of southwestern Norway, has been intensively investigated in recent years, since it provides evidence of both.

i) extensive and complex brittle deformation (Viola et al., 2016; Scheiber & Viola, 2018) and ii) saprolitization along fracture zones suggesting near-surface environmental conditions (Fredin et al., 2017). In order to distinguish between different alteration processes, we used a suite of detailed geochemical, mineralogical and isotopic analysis. Subtle but clear variations in the geochemical and mineralogical composition of the bedrock and associated secondary clay assemblages in the altered granodiorite allow linking measured K-Ar ratios to specific geological events ranging from Carboniferous to Early Cretaceous times.

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Use of organoclays in microemulsion-based drilling fluids

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The advance of oil and gas exploration around the world means that industries are motivated to invest in initiatives to ensure competitiveness and sustainable development. One component that can be improved in this process is the drilling fluid, which is of extreme importance in the oil and gas exploration system. The success of drilling oil well depends greatly on the composition and properties of the drilling fluid, which has, among other functions, to clean the generated cuttings, bringing them to the surface, stabilizing the walls, cooling and lubricate the drill string and drill bit. The formulation of this fluid should be ideal so that problems such as loss of circulation, inefficient cleaning of the well and, above all, the potential aggression to the environment do not occur. Oil-based drilling fluids tend to be expensive and cause damage to the environment and water-based drilling fluids generally damage rock formations, therefore microemulsion or emulsions has been presented as a relevant option because it has characteristics that are suitable for drilling wells. In this work, microemulsion-based drilling fluids were prepared using organoclays. Rheological properties and filtrated loss were evaluated, according to the API testing recommendations, in function of the surfactant used in microemulsion. The drilling fluid was formulated based on a microemulsion/emulsion composed of a 2% NaCl aqueous solution (aqueous phase - AP), vegetable oil (oil phase - OP) and a surfactant (S). Three different nonionic surfactants were used: T80, NP100 and NP150. Three ternary phase diagrams were obtained, at room temperature, in order to delimit the microemulsion and emulsion regions. Two organophilic clays (Cloisite 20A and BentPraep) were used in fluid additivation. A microemulsion-based drilling fluids was obtained with suitable viscosity, gel strength and low fluid loss (~ 5.0 mL) for organoclays studied. Rheological model Herschel-Bulkley (Huang and Garcia, 1998) adjusted the experimental dates. The organoclays used provided good formation, presenting low porosity and low permeability. Finally, the fluids formulated with these clays ensured a low volume of filtrate, an important factor to avoid the loss of the drilling fluid for the formation.

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Keywords: organoclay, surfactant, vegetable oil, microemulsion, drilling fluid.

The effect of different reaction parameters on catalytic oxidation of tartrazine induced by Oxone® activated by cobalt impregnated aluminium pillared montmorillonite

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Catalytic oxidation of water contaminants, using Oxone® as a precursor of sulfate radicals has recently received much attention. The activation of Oxone® (Potassium peroxymonosulfate, $KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) induces the generation of $SO_4^{\cdot -}$ radicals [1]. Oxone® can be activated in different ways, using heat, metal ions or UV irradiation. Among these methods, the activation of Oxone® by transition metals has attracted significant attention because of high activation efficiency, with cobalt showing the best performance. In cobalt homogeneously catalyzed decomposition of Oxone®, the problem of the toxicity of cobalt ions and the difficulty of recovering these ions occurs. The immobilization of cobalt onto various catalyst supports [1] prevents the problem of recovering cobalt ions and possible subsequent pollution.

In this work cobalt impregnated aluminium pillared montmorillonite was used as a catalyst in Oxone® activated catalytic oxidation of tartrazine dye as the water pollutant. The process of pillaring was carried out according to a common procedure comprising the following steps: pillaring, rinsing, drying and calcination [2]. The impregnation of pillared montmorillonite was performed using incipient wetness impregnation method with $Co(NO_3)_2$ followed by heat treatment at 450 °C.

The degradation of tartrazine was monitored using Thermo Scientific Evolution 220 UV–Visible Spectrophotometer in the wavelength range from 200–600 nm enabling simultaneous monitoring of decolorization, along with registering the emergence, followed by degradation, of detectable degradation products.

Reaction parameters were altered in order to examine their effect on catalyst activity. The cobalt impregnated pillared montmorillonite was found to be promising catalyst for dye decolorization and degradation of different products formed in tartrazine oxidation in the presence of Oxone®.

Acknowledgment: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, (Project No. III 45001)

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Diffusion mechanisms in clays with octahedral and tetrahedral substitutions: coupling quasi-elastic neutron scattering and molecular dynamics simulations

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Quasi-elastic neutron scattering is the technique of choice to study water diffusion inside swelling clays at low hydration states [1]. Time of flight and spin echo measurements have shown a decrease of water dynamics of a factor two to three and five to ten compared to bulk, in states containing two and one layer of water in the interlayer space respectively. Coupling the experiments with molecular dynamics simulations is valuable. Even if the agreement between both methods is not always quantitative, molecular dynamics allows discriminating between the models used to interpret the data and determining their limits of validity [2]. Moreover, it offers a detailed description of the underlying diffusion mechanisms [2,3]. On the other hand, the comparison with experiments can reveal the imperfections of the force fields used in the simulations [2,4].

In the past, the role of the counterions present in the interlayer spaces has been highlighted, especially in the case of low hydrated states where a substantial part of the water molecules participate to their hydration [3,4]. In the light of neutron spin echo experiments that we have obtained in different clays, we study the role of cations on the diffusion of water depending on the location of the clay permanent negative charge (tetrahedral of octahedral substitutions) from molecular dynamics simulations. The diffusion mechanisms are shown to be significantly different depending on charge location but also on the force field used to perform the simulation, especially in the case of clays with tetrahedral substitution. The experimental results, their interpretation and the choice of the appropriate force field will be discussed.

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Time evolution of the mineral carbonation of ceramic bricks in a simulated pilot plant using a common clay as sealing material at superficial conditions

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CO_2 is the most important anthropogenic GHG, it has increased around 40% from the preindustrial era as a consequence of the fossil fuel consumption and the change of soil use. So, technological proposals have been conducted for reducing the emissions into the atmosphere. Carbon capture and storage technologies and especially the mineral carbonation of CO_2 as an equivalent process that occurs naturally from weathering of silicate rocks into carbonates in a CO_2-rich environment has been used to reduce emission.

This research explores the possibilities of CO_2 sequestration on ceramic brick materials, in order to propose the injection of CO_2 in a quarry filled with bricks as reclamation materials. To approach this possibility a reaction chamber at pilot scale has been designed, which simulates the conditions to carry out the carbonation process in a quarry rehabilitated with materials of construction where the sealing rocks are common clay.

In previous studies materials were widely characterized as well as the employed reactor and the experimental conditions were described (Martín et al., 2018a; Martín et al., 2018b), being a novelty in this study the variable reaction time. Succinctly, bricks are composed of quartz, diopside, wollastonite and orthoclase, and minor anhydrite. The common clay (marl) contains calcite, quartz, illite, smectite and kaolinite. The reaction conditions were 0.5 bar constant pressure, 4:1 solid/water ratio and room temperature. And the reaction time was 5, 7, 9 and 12 months. After each period, a sampling was drawn and the core obtained was cut in sections of five-centimeter thickness.

With the CO_2 treatment, wollastonite, diopside, and anhydrite were practically destroyed at 12 months and calcite precipitate as new phase in bricks. Also, amorphous materials increased significantly. Significant increase in CO_2 retained at 5 months (9.5 wt%) that remains growing until 12 months (9.9 wt%). At 5 months the acid attack causes an increase in macro- and mesoporosity due to the destruction of silicates. The longer the reaction time, this porosity decreases, increasing the micro- and nano-porosity due to bigger pores close because of the precipitation of the carbonate.

On the other hand, in the common clay, an increase of the calcite content is observed. This increase rises to upper layer as the reaction time was greater. It had been observed a migration of humidity of the bricks to the clay layers that transport carbonic acid and Ca ions for a subsequent precipitation of calcite.

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G.E.S.U.S., a didactic resource for learning space groups of symmetry

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In order to introduce the student to the structural study of clay and clay minerals, as well as associated minerals, it is recommended to know their symmetry elements, and therefore, to assign the corresponding space group of symmetry. The knowledge of the structures of these minerals is very important to know the physical and chemical properties.

The teaching of space groups of symmetry entails many difficulties, particularly due to the absence of space vision and the complexity of some combinations of point symmetry elements with translations.

The proposed software (*G.E.S.U.S.*) makes it possible to teach how to recognize the operations of the symmetry elements and their combinations with the lattice translations, applying a 3D space vision to find the symmetry elements compatible with the proposed structural models. It makes it possible to identify and use symbology for the representation of symmetry elements, according to their arrangement in space, in two-dimensional representations projected on the plane of the fundamental vectors "a-b", and taking into account the coordinate according to the vector "c" when their action is carried out at values different from zero.

In addition to the identification of the crystallographic system, compatible symmetry class and space group (in Hermann-Mauguin notation) from the elements previously identified in the model.

The *G.E.S.U.S.* program is designed to perform drawing exercises of space groups of low and medium symmetry such as triclinic, monoclinic (in two setting) and orthorhombic crystallographic systems, some of which are common in clay minerals and associated (i.e. $P2_1/c$, P-1 that are the most frequents in the Cambridge structural database, CSD). Nevertheless, the software is designed to increase its possibilities by incorporating other systems of greater symmetry. Symbology, orientation and nomenclature used are based on the recommendations of the International Tables for Crystallography (Hahn, 2005).

The software consists of an executable file that does not require installation and a collection of space group of symmetry files from number 1 to 74.

G.E.S.U.S. constitutes a very useful didactic resource in the teaching of the space groups for students of a basic-medium level being very interactive and one of its most important features is that it is a self-evaluating tool.

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Molecular adsorption at layered interfaces investigated by Second Harmonic Scattering

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Second Harmonic Generation (SHG) is a nonlinear optical process, in which two photons are converted into one coherent photon at double frequency. This technique, because of its high **surface specificity**, has been widely used to **study "in situ", at the molecular scale** the solid/liquid planar interfaces[1]. The use of this process to study other geometries or **supramolecular organization** is currently a emerging field of research, for example the surface of **functionalized colloidal nanoparticles or the internal surfaces of lamellar materials**[2]. In the case of SHG coming from colloidal objects in bulk solution, the signal is called Second Harmonic Scattering (SHS).

After a brief introduction on the basic of these nonlinear optical processes, I will show their interest for the study of molecule/material interactions. **The ion exchange and the intercalation of a chromophoric organic molecule in a lamellar material (layered double hydroxide)** will be presented. In particular, I will show how the polarization resolved SHS signal can be used to achieved information concerning the **equilibrium states of the system**: ion exchange capacity, intercalation, orientation of the molecules in the interlayer, and adsorption on external faces. Monitoring of **kinetics intercalation** will also be presented and discussed[3], see the figure below.

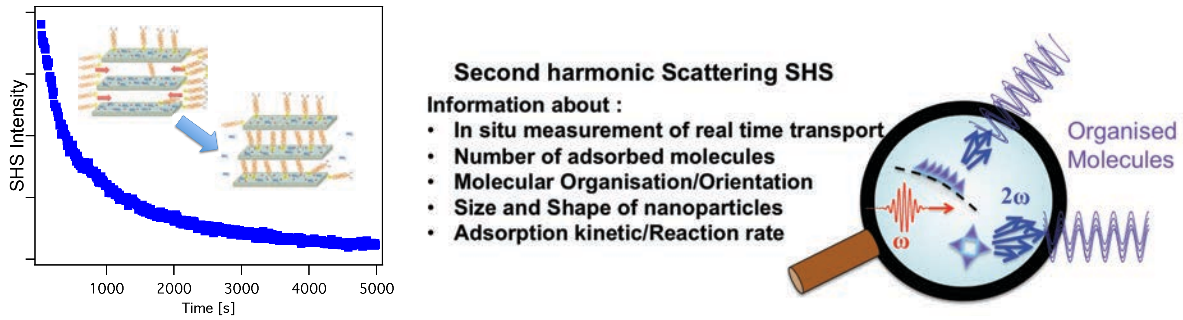

Figure : Dynamic SHS of molecular intercalation in LDH

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Acknowledgement – The authors thank the Labex CheMISyst and CAMOMILS ANR-15-CE21-0002 for funding.

A XANES, EELS and EPMA study of Fe^{3+} in natural and synthetic chlorite: Substitutions and importance of oxychlorite

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Chlorite is a phyllosilicate crystallizing in varied geological contexts, such as low to high grade metamorphic rocks, hydrothermal sites and during diagenesis. Chlorite is useful for geothermometry because its composition has been shown to vary with its crystallization temperature (e.g. Vidal et al. 2006). Unfortunately thermobarometry and thermodynamic modelling using chlorite are hampered by the varying oxidation state of iron. In chlorite, iron may be divalent, trivalent or show mixed valence, and the properties of ferric chlorite are unknown. A deep understanding of the amount of Fe^{3+}, the ferric substitutions and end-members, and the range of Fe^{3+} variation is necessary to enhance thermodynamic models for ferric chlorite.

This presentation reports on findings (Masci et al., 2019) following investigations of the crystal-chemistry of Fe-rich chlorite, and more precisely of the oxidation state of Fe, to determine substitutions involving Fe^{3+} and the associated end-members. The oxidation state of Fe in natural and synthetic chlorite is measured with Fe-K edge XANES and STEM-EELS, combined with electron microprobe analyses for major elements. Ferric chlorite is synthetized at P-T-fO_2 fixed for comparison with natural chlorite composition.

In our chlorite samples, Fe content varies from ~1 to ~35 wt.% when expressed as FeO, and from entirely divalent to entirely trivalent, only in octahedral position (excepting for Li-chlorite). Incorporation of Fe^{3+} appears linked to increasing octahedral vacancy content in structural formulas expressed with $O_{10}(OH)_8$ anionic basis. However, electron microprobe analysis of oxygen used for normalization to 18 oxygen atoms show that this anionic basis is incorrect for chlorite crystals with Fe^{3+} greater than ~1.5 p.f.u. These analyses evidence proton loss apparently linked to Fe^{3+} incorporation along the exchange vector $Fe^{2+} + H^+ = Fe^{3+}$, corresponding to proton deficient anionic basis such as $O_{12}(OH)_6$. This defines a solid solution towards a ferric, proton depleted "oxychlorite" component. For chlorite with $Fe^{3+} \leq$ ~1.5 p.f.u., Fe^{3+} substitutes along two exchange vectors: the homovalent $Al = Fe^{3+}$ substitution and the vacancy creating di-trioctahedral substitution $2Fe^{3+} = 3R^{2+} + \square$. These substitutions are observed between natural and synthetic samples as well as in zoned crystals, where mapping shows variations of the oxidation state on the scale of nanometers to micrometers.

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Panoramic overview of chemical modification of halloysite nanotubes and applications thereof

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Halloysite nanotube, an aluminosilicate of the kaolin group, is an emerging nanomaterial which possesses peculiar chemical characteristics. By means of suitable modifications, such as supramolecular functionalization or covalent modifications, it is possible to obtain novel nanomaterials with tunable properties for several applications.[1,2] In this context the covalent grafting of suitable organic moieties on the external surface or in the halloysite lumen has been exploited to improve the loading and release of several biologically active molecules. The resulting hybrid nanomaterials have been applied as drug carrier and delivery systems, as fillers for hydrogels, in tissue regeneration and in the gene delivery field.[3] Furthermore the loading and release of specific molecules have been also investigated for environmental purposes.

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Investigating the Acrisol/Ferralsol transition in Amazonia: new insights from EPR dating of kaolinites

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Dating of secondary minerals from tropical weathering surfaces shows that a single regolith can contain several generations of these minerals. They can be linked to weathering pulses resulting from specific paleoclimatic events (Retallack, 2010; Mathian et al., 2019). Thus, laterites can be envisioned as archives of the tropical climate evolution through the geological times. In Amazonia, the transition between Ferralsol and Acrisol, two of the major types of laterites covering this sedimentary basin, is poorly understood. In addition, the factors influencing their formation, their chronology and their paleoclimatic records are still unknown. In order to enhance our knowledge about this type of soil transition, two profiles, one yellow acrisol and one red ferralsol, are investigated using the electron paramagnetic resonance (EPR) dating of kaolinite. These soils, located on a poorly incised low elevation plateaus and strongly incised edges, respectively, represent the two end-members of a transect of the Curicuriari region (Amazon state, Brazil), characterized by a well-marked transition.

The presence of several generations of kaolinites within the investigated samples is confirmed by mineralogical and geochemical observations, highlighting the difference between the saprolite and the soil *stricto sensu* (ss) horizons. In both profiles, kaolinite ages from soils ss samples range from 2.5 to 1 Ma. In contrast, kaolinite samples from the acrisol saprolite are dated from 6 to 3.6 Ma and those from ferralsol saprolite are comparatively recent (< 1 Ma). Thus, the Curicuriari acrisols correspond to old soil profiles partly rejuvenated. The formation of the kaolinites from their saprolite can be linked with the evolution of Amazonian climate occurring at the end of the Tertiary. In contrast, the more recent saprolite of the ferralsol is probably still developing under the present Amazonian climate. These geochronologic trends of saprolites are mainly related to topography. This study confirms that laterites can be old weathering covers, archives of past climate evolution, but also that some regoliths located on edges of plateaus formed under the present-day tropical climate.

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New investigations of the hydrothermal signature of clay minerals in the Upper Cretaceous shaly gas/oil reservoir: Tunisian Eastern margin and the Pelagic Sea

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Cretaceous subsurface igneous activity occurred in the Eastern margin of Tunisia and the Pelagic Sea with numerous intrusions, lava flows and pyroclastic materials preserved in the sedimentary sequence. In fact, the studied area is characterized by a crustal thinning induced from the tethyan rifting; this is responsible for the subsequent evolution of the North African passive margin during the Cretaceous and the creation of the fold-thrust belt and associated foreland deformations. This thinned crust was an area of mantle upwelling that favoured the increase of isotherms, the uprise of basalt magma, and the circulation of hydrothermal fluids. This hydrothermal activity caused a transformation of igneous rocks by the presence of secondary paragenesis and generated a recrystallization of minerals in the enclosing sedimentary deposits. Petroleum investigations showed that this area constitute a prolific hydrocarbon province with numerous gas/oil fields and discoveries. In fact a sedimentary pile turonian-coniacian limestone (Bireno and Douleb Member)) and campanian-maastrichtian chalky Abiod Formation) interbedded with shaly beds constitutes the components of the oil system in this area (rock reservoir). Based on an integrated mineralogical (XRD, FTIR, SEM-EDX) and geochemical (ICP) studies of the clay minerals of the shaly upper cretaceous gas/oil reservoir have given additional information about these hydrothermal fluids. The mineralogical composition includes calcite, quartz, dolomite, pyrite, seldom sophiite and clay minerals. The fine fraction comprises: kaolinite, illite, smectite, chlorite and mixed-layer illite-smectite (I/S). The Middle Infrared spectrum shows, three strong bands in the 3648 $cm^{-1,}$ 3622 $cm^{-1}$and 3554 cm^{-1}arises from OH-stretching vibrations of the interlayer hydroxide sheet characteristic of Al chlorite (sudoite). Scanning electron microscopy coupled with Energy Dispersive X-Ray spectroscopy (SEM-EDX) analysis show the presence of Euhedral-crystallised chlorite with occurrence of inter-crystal pore. Perfect hexagonal crystals (platelets) and the vermicular chains of kaolinite are also notable. The morphology of illitic minerals steadily evolves from hairy illite to lath-shaped particles and ultimately isodiametric plates, this change of size can be attributed to increasing temperature conditions. Nodular to pseudo-hexagonal crystal morphologies of pyrite are also detected. The (PAAS)-normalized REE patterns of shaly samples of gas/oil reservoir show enrichment in Eu, Gd and Lu and an impoverishment in La, Nd, Sm, Tb, Dy, Ho and Yb. A positive Eu anomalie was observed and may be due to the contamination of these clays by hydrothermal fluids enriched on this element. It was attributed to the alteration of feldspar in the magmatic rocks and the migration of fluids through the multiple deep faults. Eventually, when these deeply sourced hydrothermal fluids intrude sedimentary deposits through fault-passages or other pathways, they provoked a local geothermal gradient, an income of chemical elements and engendered new clay mineral equilibrium. Such processes may increase the volume of the effective source rocks; improve the petrophysical properties of the reservoir and the hydrocarbon generation capacity.

Halloysite-LDH heterostructured materials: performance in removal of selected anions from aqueous solutions

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Industrial wastewaters often contain mobile anionic forms of elements which are hazardous for the environment and human health. These cannot be removed by commonly applied precipitation techniques and most of known adsorbents e.g. raw clay minerals which show high affinity to cations. Layered double hydroxides (LDH) are synthetic phases which in contrast to clay minerals *are excellent scavengers of anions. However it is reported that their use in real applications devoted to adsorption is of minor importance. This is mainly due to their swelling behavior which is not desired in dynamic column adsorption and high cost of production. Halloysite* is a natural 1:1 layered aluminosilicate clay mineral which exhibits a unique tubular morphology. Previous studies showed that in experimental conditions halloysite can remove aqueous As(V) by chemisorption [1]. Therefore, the aim of this work was to synthesize halloysite-LDH composites and to examine their sorption capacity towards As(V), Cr(VI) and S(VI) in different experimental conditions using both artificial and real wastewaters.

The halloysite sample was obtained from Dunino deposit located near Legnica (SW Poland). In turn, LDH materials of Mg-Al and Mg-Fe type were synthesized by co-precipitation method. The halloysite-LDH composites containing LDH were prepared by two different approaches: direct precipitation of LDH in halloysite suspension and physical mixing of the two phases. The materials were characterized with XRD, FTIR, DTA/TG and SEM.

The XRD and FTIR results confirmed the LDH formation in absence and presence of the halloysite as peaks and absorption bands of both mineral components were visible. The LDH peaks intensity increased along with its content in the composite. The same observations were made for the absorption bands in the FTIR spectra. *The LDH/halloysite materials in general showed lower efficiency than the raw LDH, however halloysite presence has several benefits in terms of future applications: (i) it significantly reduces the pH, especially in contrast to the calcined LDH, which enables reuse or safe disposal of purified water, (ii) it reduces swelling of the whole composite volume which opens the possibility for applications in column adsorption, (iii) it induces dual adsorption properties through additional cation adsorption and even chemisorption of selected anions e.g. As(V), and (iv) it substantially lowers the overall price of the adsorbent.*

Acknowledgement: This research was supported by the National Science Centre, Poland under the project no. 2017/27/B/ST10/00898.

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Use of X-ray diffractometry and analysis of the atomic pair distribution function to study the interactions between smectite and emerging organic pollutants

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Many emerging pollutants from pharmaceuticals, pesticides or products for domestic or industrial use are found in the environment and pose the problem of achieving good chemical or ecological status of this system. In the environment, these pollutants can interact with different phases that make up soils or sediments, such as organic matter, natural oxyhydroxides, or clay minerals. However, to date there is very little data describing the reaction mechanisms and the nature of the bonds involved in these interactions (Aristilde et al., 2013).

In this context, and in order to improve the state of knowledge on the behaviour of emerging pollutants in the environment, we propose to study the adsorption of two organic molecules, sulfamethoxazole (SMX) and metoprolol tartrate (MPT), considered as emerging pollutants onto a Ca-montmorillonite. SMX and MPT are an antibiotic and a cardioselective beta blocker, respectively, and are widely found in soils and aquatic ecosystems, with concentrations up to several micrograms per liter.

In this study, SMX and MPT have been in contact with Ca-montmorillonite for 24 hours at pH 6. Different concentrations, varying from0.1 mg/L to 1 mg/L, were studied. The resulting solids were characterized by X-ray powder diffractometry at constant temperature (25°C) and different humidities (from 10 to 90%). Initial results showed differences in the position (interlayer distance) of the 001 reflection of montmorillonite. In the presence of organic molecules and at low humidity, the interlayer distance is greater than that observed in the case of Ca-montmorillonite. This result indicates that the interlayer space has been modified, in particular by the insertion of organic molecules. For relative humidities above 50%, there are no more differences between the samples with and without organic molecules. Due to their small size, organic molecules do not induce significant swelling when the interlayer space contains many water molecules.

To complete this study, analyses of the atomic pair distribution function (PDF), were carried out on the starting materials (Ca-montmorillonite, SMX and MPT) as well as on the montmorillonite after having been in contact with the organic molecules. The comparison between the PDFs confirms the adsorption of organic molecules since characteristic peaks of C-H bonds belonging to the CH_3 groups of SMX and MPT are visible on the montmorillonite PDFs after contact with the organic molecules. However, the interatomic distances between C and H seem to be slightly modified indicating a potential reaction mechanism involving these groups.

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Effectiveness of As(V) removal from wastewaters by layered double hydroxides impregnated with Fe oxide

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In this work, the synthetic Mg/Al LDH impregnated with magnetic iron oxide (FeOx) particles was studied for As(V) removal from real wastewaters. The purpose of LDH impregnation with FeOx was to facilitate future separation of the composite adsorbent from the solution using magnetic field. In particular, the designed adsorption experiments were aimed at investigating essential properties of the studied adsorbents in the aspect of application in wastewater treatment. Among others the effect of FeOx loading on adsorption as well as the chemical stability of materials in multi-element system were evaluated.

The synthesis of Mg/Al LDH (2:1) was carried out using chemical precipitation method. In the synthesis $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ were used. The impregnation of LDH with FeOx was carried out using procedure reported earlier [1]. The FeOx loading was set to 10% and 25%. The obtained adsorbents were additionally calcined at 400°C for 3 h. The kinetics of As(V) removal were evaluated for 0.5 mmol/L. The effect of adsorbents dosage on As(V) removal at 0.005-0.05 mmol/L was also investigated. In the present study acid mine drainage water and industrial water from a synthesis gas scrubber were selected as a background wastewater for As(V) removal studies. The wastewaters were spiked with As(V) to reach 0.5 mmol/L.

In the case of LDH, the kinetic experiment showed that the As(V) was completely adsorbed after 0.5 min. While, in the case of uncalcined and calcined magnetic adsorbents, regardless of the FeOx loading the time needed to reached equilibrium was 6 min and 10 min, respectively. The adsorbents impregnated with FeOx showed higher selectivity and efficiency in As(V) removal at low concentration, in comparison to the LDH. At dosage of 1 and 2 g/L only the adsorbents impregnated with FeOx were able to remove As(V) below safe limit of 10 µg/L set by WHO. The reusability experiment showed, that for all the studied materials the removal efficiency decreased gradually after subsequent regeneration cycles and it was not affected by FeOx loading. In the experiments of wastewaters treatment, the studied adsorbents revealed high selectivity and efficiency of As(V) removal, regardless of the coexisting anions and pH.

Acknowledgement: This project was supported by the National Science Centre, Poland, under a research project awarded by Decision No. 2016/21/N/ST10/00390.

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Probing the interactions between lucigenin and phyllosilicates with different layer structures

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The incorporation of organic fluorescent dyes into inorganic matrixes could greatly improve the luminous properties of organic dyes. In this study, a series of new functional materials of organic luminescent molecules/CLSSMs were constructed. The adsorption behavior of lucigenin (BNMA) on typical CLSSMs was investigated. The relationship between the adsorption capacity and the luminescence properties of the composites were studied. The effect of adsorption sites on CLSSMs on the luminescent properties of BNMA were explored through experimental characterizations and molecular dynamics simulations. Unlike organic cationic surfactants, the adsorption of BNMA on layered structure silicate minerals was mainly caused by electrostatic attraction and ion exchanges, and the intermolecular forces have little impact on the amount of adsorption. Whereas, its adsorption on chain layered structure silicate minerals was mainly driven by surface electrostatic force. The adsorption of BNMA on MMT, kaolinite (KLN) and halloysite (HAL) conformed to the Langmuir adsorption isotherm, while its adsorption on rectorite (REC), SEP and palygorskite (PAL) corresponded to the Freundlich adsorption isotherm, and the adsorption kinetic results fitted Pseudo-second-order kinetics model well. By comparing the adsorption of BNMA on silicate minerals of different structures, it was found that the interlayer adsorption or pore adsorption was beneficial to the increase of the adsorption amount, but the surface adsorption of BNMA on the minerals was more conducive to the inhibition of fluorescent quenching. The inhibition of fluorescent quenching of BNMA by CLSSMs is firstly due to the surface-fixation of BNMA molecules, and secondly due to the dispersion of BNMA molecules by minerals. Comprehensively comparing the adsorption amount and the luminous intensity, halloysite was the most effective in inhibiting fluorescent quenching of BNMA out of the six minerals.

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On the key role of Fe-rich saponite for the abiotic synthesis of amino acids in the oceanic lithosphere

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Abiotic hydrocarbons and carboxylic acids are known to be formed on Earth, notably during the hydrothermal alteration of mantle rocks. Although the abiotic formation of amino acids has been predicted both from experimental studies and thermodynamic calculations, its occurrence has not been demonstrated in terrestrial settings. Here, using a multimodal approach that combines high-resolution imaging techniques, we obtain evidence for the occurrence of aromatic amino acids formed abiotically and subsequently preserved at depth beneath the Atlantis Massif (Mid-Atlantic Ridge). These aromatic amino acids may have been formed through Friedel–Crafts reactions catalysed by an iron-rich saponite clay during a late alteration stage of the massif serpentinites. Demonstrating the potential of fluid-rock interactions in the oceanic lithosphere to generate amino acids abiotically gives credence to the hydrothermal theory for the origin of life, and may shed light on ancient metabolisms and the functioning of the present-day deep biosphere.

Ménez B.; Pisapia C.; Andreani M.; Jamme F.; Vanbellingen Q.P.; Brunelle A.; Richard L.; Dumas P.; Réfrégiers M. (**2018**) Nature, 564, 59–63.

Physical and mechanical properties improvement of Miocene marls (Morocco) after doping with metal oxide

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The Miocene marls or calcareous clays of the southern Rif groove are one of the geological wealth of the region of Fez in Morocco. The objective of this study is to enhance the physico-mechanical characteristics of Miocene marl. Physical and chemical characterization of this marls was carried out before and after doping with Al_2O_3 following various analytical techniques such as X-ray fluorescence (XRF), X-ray diffraction (XRD), electrical, thermal (DTA-TG), and geotechnical parameters. The doping of the marls was done at different percentages (5%, 10% and 15%). The results of the mineralogical analysis of marls after this doping indicate a high proportion of kaolinite. Further characterization of the ceramics properties such as linear shrinkage, water absorption, and mechanical strength were also investigated by firing doped bricks at a temperature range of 700 °C to 900 °C. However, doping with Al_2O_3 although they have also reduced withdrawal rather, caused a decrease in porosity, and an increase of the mechanical resistance of the bricks. The use of ternary diagrams indicates that the doped marl falls inside the industrial domain, and ceramic tests performed on the product show that the doped marl can be used as bricks making owing to provided interesting properties, such as firing behavior and mechanical resistance. The marls doped acquired the property of their good electrical conductor compared to crass marl. Accordingly, the marls doped with 5% Al_2O_3 give the best improvements of physico-mechanical properties.

Keywords: marl, doping, aluminium oxide, firing, bricks, mineralogy, mechanical resistance.

Effect of cement on mechanical properties of bricks

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In this study, we have proceeded to mixing the Miocene marls from quarry of Benjalik with cement at varying proportions in order to making bricks and we used the Portland cement in the formulation for their stabilization.

Therefore, the manufacture of a strong brick with low cost seems to be an important opportunity for industrials and well contribute to the environment protection.

Indeed, the added binder leads to stabilization both of shrinkage and weight loss either in the room temperature or after firing process.

The test of water absorption was examined to knowing better the impact of porosity on strenght of bricks.

The heating process in hight temperature has increased the porosity and favored the crack growth , primarily the decomposition of the hydraulique binder transforms the material properties and causes cracking thus lead the destruction of brick. This is why, when we submerge bricks in water for 48H, the reaction of cement resumes and limit cracking.

The results of the flexural strength test, shows that the cement introduces a positive effect of marls and react mainly to low temperatures with increasing strength of mixing bricks compared to untreated bricks. Effectively, the addition of 9% of cement leads to a comparable mechanical resistance to the fired bricks.

Keyword: Miocene marls, cement, bricks, flexural strength.

Testing high-voltage electrical discharges in disintegrating fault claystone for isotopic dating and fluid tracing using hydrogen isotopes

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Authigenic illite formed in brittle fault zones contains important information on the timing of fault activity based on K-Ar dating as well as on fluid-rock interaction and fluid origin based on hydrogen isotope ratios (δD). Reliable grain size separation of the authigenic clay component helps to avoid complications that arise from artificial fragmentation of originally coarser detrital material. Therefore, clay minerals require specialized sample disintegration, clay separation and analytical methods. Zwingmann et al. (2017) used a sample from the Opalinus clay (Switzerland) to investigate the effects of several sample disintegration methods comprising disc mill, freezing-thawing and high-voltage electrical discharge on K-Ar geochronology and found consistent results among the differently processed sample separates. However, electrical fragmentation is based on high-voltage discharges passing through a dielectric solid. Discharge occurs at up to a few hundred kV with energies of up to 100 J/cm and produces localized small plasmas with high temperatures, but on a timescale of only several hundred nanoseconds.

Here, we explore the potential effects of such localized short heating pulses during electrical fragmentation on the δD values of fine-grained illite fractions and its implication for paleo-fluid studies. We analyzed grain size fractions from <0.1, <0.4 and <2 µm produced by the three different sample disintegration methods. The δD results show minor variations, ranging from -86 to -73‰ VSMOW, with lowest values consistently found in the smallest grain size fraction (<1 µm). δD data grouped by grain-sizes yield consistent results with standard deviations typically <1‰ and thus, below the standard error of the measurements (~2‰). The mean δD values of the Opalinus clay disintegrated by electrical discharge and conventional disintegration methods lack systematic deviation and the means are indistinguishable from each other within error.

Thus, our data indicate that high-voltage electrical discharge does not lead to hydrogen isotope fractionation or exchange during the sample disintegration process and that all tested techniques can be applied for δD analyses and paleo-fluid studies.

Zwingmann, H., Berger, A., Todd, A., Herwegh, M. (**2017**) Clays Clay Miner, 65(5), 342-354.

Evaluation and characterization of Melo Bentonite clay for cosmetic applications

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Clays are used in cosmetology with different applications, which are conditioned to the chemical and mineralogical composition and physical-chemical characteristics of these materials. Therefore, the aim of this work was to evaluate the potential application of Melo Bentonite (BEM), clay from Uruguay through different tests.

Initially, it was performed the characterization of BEM by X-ray Diffraction (XRD), X-ray fluorescence spectroscopy (XRF), thermal analysis (TGA/DTG), particle size distribution and surface area. The microbial content of natural Melo Bentonite clay was also verified.

Two calamine suspensions were formulated with bentonite clay, one containing BEM and the other containing bentonite clay (BE), both at concentration of 5% w/w in glycerin. Bentonite clay was used as standard. The suspensions were characterized through tests of sedimentation rate, viscosity and pH determination.

The physical-chemical characterization of BEM indicated compatible characteristics with those of clay; it was observed only smectite and quartz reflections as crystalline phases and in terms of chemical composition the major presence of silicon, aluminum and magnesium was verified. The microbiological evaluation showed that microbial content of Melo Bentonite presents acceptable limits, according to the Brazilian legislation for cosmetic products.

BE was tested by a suspending agent. The sedimentation amount obtained for the suspention that was prepared with BEM was (0.73 mL/minute) and with BE (0.63 mL/minute). BEM is a better agent suspensor than BE. The viscosity presented by the sample containing BEM was lower than that containing BE; both of them showed non-Newtonian behavior and pseudoplastic flow. The pH of the sample containing BEM was close to neutral (7.72 ± 0.005), while the pH of the sample containing BE was 8.17 ± 0.026.

The results showed a possible application of BEM in cosmetic products.

Mineral assemblages and temperature associated with copper enrichment in the Seival area (Neoproterozoic Camaquã Basin of Southern Brazil)

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The Neoproterozoic sequence of volcanic rocks in the Camaquã Basin included in the Lavras do Sul Shoshonitic Association hosts disseminated Cu deposits. The volcanic sequence in the Seival Mine area includes andesitic lava flows, lapilli tuff, volcanic agglomerate and andesitic dikes with pervasive alteration.

The hydrothermal alteration is interpreted to be a product of late–magmatic fluids or the mixing of magmatic with meteoric fluids or basinal brines. The late–magmatic hydrothermal system started after volatile oversaturation and degassing in a magmatic system, which was partially segregated into vesicles.

The chlorite compositions used in the geothermometer were obtained by electron microprobe.

The crystallization of titanite and Fe–clinochlore to Mg–chamosite followed the albitization process. The temperature range associated with the chloritization process was estimated using chlorite geothermometer developed by Inoue et al. (2009) and Bourdelle & Cathelineau (2015). The chlorite temperatures varied from 251 ± 56 to 183 ± 39 °C. The precipitation of Mg–saponite and smectite–rich chlorite/smectite mixed–layers in some andesitic lava flows and the precipitation of quartz, calcite, barite and hematite in fractures suggest fluid circulation with temperatures lower than the chloritization process.

The alteration minerals are represented by chlorite and albite associated with pyrite–chalcopyrite, while chlorite/smectite mixed–layers and barite or hematite are associated with bornite–chalcocite–covellite.

Thermodynamic calculations (MELTS software modeling and PHREEQC interactive) confirm the potential coprecipitation of pyrite–chalcopyrite with chlorite and albite. The occurrence of bornite–chalcocite–covellite and barite seems to be favored by low–temperature chlorite/smectite with neutral to mildly acidic water influx.

Consequently, albitization and the process of chloritization at high temperatures (> ca. 251 ± 56 °C) can be used as an exploration guide for primary pyrite–chalcopyrite enrichment, and chlorite/smectite at low temperatures (ca. 250 to 50 °C) can be related to bornite–chalcocite–covellite or the process of Cu enrichment.

Formation of clay minerals in the earliest phases of geological activity on Mars, with implications for origin of life

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Mars, a planet without plate tectonics and with low weathering rates through most of its history, contains a much older and better-preserved geologic record than the Earth. Mars may have been cold, arid, oxidizing and generally inhospitable at the surface for much of its history, however hydrothermal conditions in the near surface or subsurface might have been considerably more clement. Infrared remote sensing has revealed the presence of hundreds of deposits of hydrothermal materials on Mars, dating to the first billion years of the planet's history (Figure 1). Among the exhumed phases are serpentines, Fe and Mg-rich smectite clays, chlorites, carbonates, and amorphous silica that seemingly indicate widespread subsurface hydrothermal alteration.

Most of the martian crust is ultramafic or mafic, and likely contains interlayered volcanics and impactites. Given the lower temperature gradient on Mars compared to Earth, it is likely that Lost City-type (low-temperature, alkaline) serpentinization reactions occurred over a large range of depths on ancient Mars, producing bioavailable H_2. Exhumed subsurface carbonates, and the presence of vein carbonates in martian meteorites exhumed from the subsurface suggest that these reactions happened in the presence of CO_2 and may have produced abiogenic hydrocarbons. It is probable that fluids within alkaline crustal hydrothermal systems would have mixed with descending acidic, sulphur- (H_2S, SO_2) and CO_2-rich fluids from surface and near-surface environments.

The quest to understand life's origins could be described as Follow the energy sources: sulphur, iron and H_2. That mantra would lead us to Mars, an iron and sulphur-rich planetary crust with abundant evidence for ancient hydrothermal processes, clay mineral formation and H_2 production that could have fuelled an early chemosynthetic biosphere.

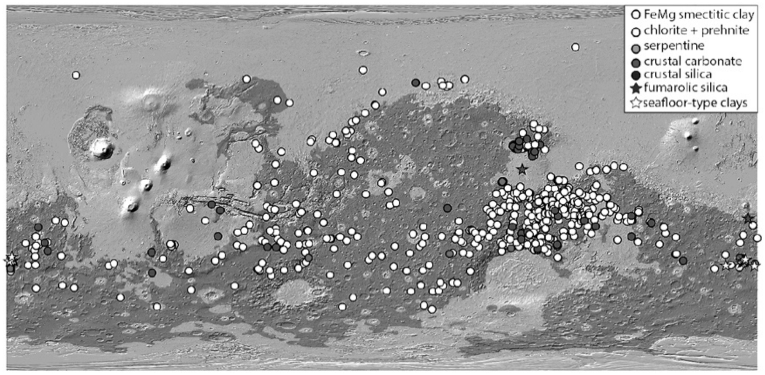

Figure 1: The distribution of hydrothermal minerals, including many clay minerals on Mars. This is a global cylindrical projection showing the most ancient (Noachian) terrains in darker tones. The points correspond to hydrothermal minerals detected spectroscopically with infrared remote sensing.

Water vapor diffusive transport in a smectite clay: Cationic control of normal versus anomalous diffusion

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The transport of chemical species in porous media is ubiquitous in subsurface processes, including contaminant transport, soil drying, and soil remediation. We study vapor transport in a multiscale porosity material, a smectite clay, in which water molecules travel in mesopores and macropores between the clay grains but can also intercalate inside the nanoporous grains, making them swell. The intercalation dynamics is known to be controlled by the type of cation that is present in the nanopores; in this case exchanging the cations from Na^+ to Li^+ accelerates the dynamics. By inferring spatial profiles of mesoporous humidity from a space-resolved measurement of grain swelling, and analyzing them with a fractional diffusion equation, we show that exchanging the cations changes mesoporous transport from Fickian to markedly subdiffusive. This results both from modifying the exchange dynamics between the mesoporous and nanoporous phases, and from the feedback of transport on the medium's permeability due to grain swelling. An important practical implication is a large difference in the time needed for vapor to permeate a given length of the clay depending on the type of intercalated cation [1].

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In-situ intercalation of pharmaceutics in smectite clays

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Clay nanoparticles are promising host materials for drug delivery research. We are studying smectite clays, which belong to the family of phyllosilicates, exhibiting a negative net charge of layers, which is compensated by the positively charged interlayer cation. The interlayer-spacing and charge balance of this family of clays are ideal characteristics for defining capture, storage, transport and release mechanisms for guest molecules. We are monitoring the trapping of drug molecules in smectite clays by observing the expansion of the interlayer spacing. The swelling of clays due to entrapment of small molecules driven by electrostatic interaction is strongly dependent on the type and charge of the interlayer cation. We are studying Fluorohectorites with different cations: Ni^{+2}, Li^{+} and Na^{+}. Our studies have shown that Fluorohectorite clays can host gas, water molecules and pharmaceutics [1,2,3]. We have studied the intercalation dynamics of several drug molecules into the synthetic smectite clay lithium fluorohectorite using a continuous flow cell for in-situ synchrotron X-ray diffraction. Here we show that the interaction between Fluorohectorite clays and four commercial drug molecules presents dynamics on the order of sub-minute and depends on the type of drug, pH and temperature of the system.

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Clay nanoparticle organization at the air-liquid interface

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We present a study on the structural organization of clay colloidal particles at the air-liquid interface where we monitor the film self-assembly and stability. Clays and modified clays are studied on a Langmuir Trough using Grazing Incidence techniques (GID and GIXOS). The film thickness and in-plane organization are monitored to determine the efficiency of the mechanisms for adsorption control on different interfaces. The results are important for particle coating studies and for the development of new methods of assembling clay colloidal particles on liquid surfaces/interfaces. This effect is currently much studied in relation to Pickering emulsions where particle coatings on droplets effectively prevent droplet coalescence and produce very stable surfactant-free emulsions. The adsorption of colloidal particles at the surface of liquid droplets [1] has applications in several areas like pharmaceutics, oil and gas sector, not only for encapsulation properties using surfactant-free emulsions, but also for the features of manipulation of the colloidal particles such as clays through external forces, like electric field [2]. Here we show that we can study the ordering of clay nanoparticles in a confined two-dimensional surface like a Langmuir Trough and recreate the process of Janus clay-platelets preparation using synthetic Fluorohectorite clays [3].

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Crystalline and osmotic swelling of clay minerals. Recent advances

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The way in which water interacts with swelling clay minerals is a fascinating subject that has been investigated for almost a century. In fundamental terms, the processes that occur are rather complex, as they involve a subtle interplay between electrostatics, hydration forces and osmotic effects. Since the seminal paper by Norrish in 1954[1], two types of behavior are classically considered depending on the ratio between water amount and solid clay content, i.e. crystalline swelling and osmotic swelling. Studying phenomena in these two swelling regimes requires the use of various experimental techniques and modeling approaches. In this talk, we will try to give an overview of recent results obtained in both water activity ranges. In experimental terms, we will try to show how the use of large-scale facilities (synchrotron and neutron reactors) provides unique opportunities for such studies and how progresses in clay minerals synthesis represent a major asset for such investigations. We will in parallel try to illustrate how simulation techniques and theoretical approaches widen our understanding of the various phenomena involved in clay water interactions provided that a constant collation between simulation results and experimental data is maintained.

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Adsorption of Emerging Micro-Pollutants on Clay Minerals

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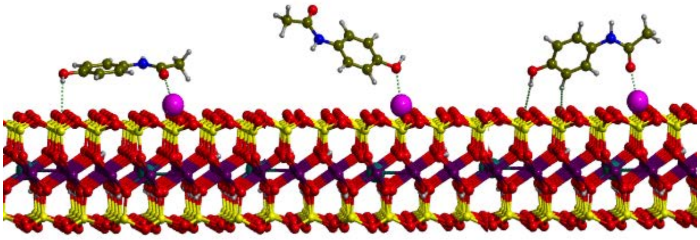
The increasing use of contaminants stemming from industrialization, agriculture or daily life activities is responsible for their dissemination in the environment and in particular into soils. Because of their remanence in our environment it is our great concern to understand the faith of emerging micro-pollutants such as antibiotics, hormonal steroids, etc… into soils.



Clay minerals have been identified as a key mineral species for the retention of molecules in soil. Adsorption isotherms as well as X-ray diffraction experiments have been carried out in combination with theoretical simulations to determine and model the role of clays in molecular retention.

A relatively weak affinity of medicinal drugs such as paracetamol or carbamazepine for phyllosilicates is observed, concomitantly with no interlayer opening. This is commented in terms of molecular interactions between molecules and clay surfaces collected from classical molecular dynamics as well as high-level DFT calculations. In particular, theoretical results allowed identifying and describing favorable adsorption modes in terms of the stabilizing interactions through interlayer cation-bridging, Van der Waals interactions and/or H-bonding.

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Adsorption of RNA/DNA nucleobases and nucleotides on clay surfaces. On the role of mineral composition

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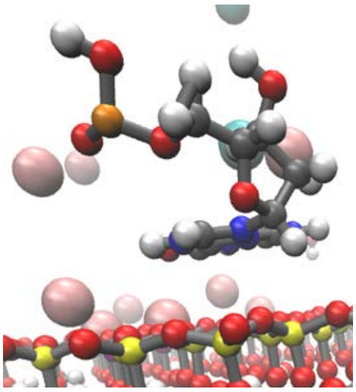
In the context of RNA oligomerization, clays have been proposed as good candidates providing geochemical niches allowing for biomolecules concentration and catalysis. It is thus important to understand the adsorption mechanism of RNA nucleotides and/or nucleobases on clay surfaces and describe molecular interactions that may be responsible for their affinity with various minerals. To this aim, atomistic simulations have been carried out to investigate the adsorption of nucleobases on the dry basal surface as well as the hydrated montmorillonite interlayer [1]. Among most energetically favorable adsorption modes, interactions through interlayer cation-bridging, Van der Waals interactions and/or H-bonding were highlighted.



Recent experimental works investigated the preponderant role of salts cations that might have been present at high concentration in the primordial ocean [2]. It was observed that nucleotides adsorption increases in the presence of divalent cation and in particular transition metals. Moreover, clay composition has also been found to play an important role in nucleotide adsorption, with an increased adsorption for nontronite as compared to montmorillonite. In this context molecular simulations have been performed to investigate both clay composition and salts cations effects. Classical molecular dynamics simulations allowed to show a different structure of water/cations complexes at the basal surface of the mineral, depending on its composition and implying different adsorption states. In addition, high level DFT calculations have been performed on dry models allowing for an accurate description of cation bridging adsorption at clay basal surfaces.

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Controlling the Architecture of Grafted Polymer-Clay Composites for Enhanced Sorbent Performance

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Many studies have reported the development of polymer-clay composite sorbents based on the adsorption of polymers to clay (APC). Only a hand full of studies have reported the design of polymer-clay sorbents based on covalently grafting and polymerizing from the clay (GPC). In the current study, we developed new brush like sorbents based on covalently grafted poly vinylpyridine (PVP) to montmorillonite. The sorbents were prepared in five stages 1. Acid activating of the clay 2. Covalently grafting 3-aminopropyltriethoxysilane (ATPES) to the clay 3. Surface initiation with 2-bromoisobutyryl bromide and 4. Surface initiated atom transfer radical polymerization (SI-ATRP) of PVP 5. substitution of the pyridine with bromo-ethanol. The architecture of the composites, distance between the brushes and length of brushes, were controlled by ATPES concentration (stage 2) and polymerization time (stage 4). The composites were characterized by zeta potential, XRD, FTIR, TGA and XPS measurements. In comparison with traditional adsorbed PVP composites, the GPC presented superior characteristics; higher polymer loading without polymer release and higher zeta potential. These superior characteristics explained the significantly higher removal of organic and inorganic anionic pollutant, by this composite in comparison with the removal by APC. Furthermore, among the different designed GPCs, the composite with less dense brushes demonstrated the highest removal of anionic organic and inorganic pollutants, diclofenac and selenate, respectively. The adsorption of these anionic molecules was attributed to the interaction with the highly charged polycation. On the other hand, the high removal, by this composite, of cationic organic and inorganic molecules, metoprolol and potassium, respectively, was attributed to direct interactions with the clay surface despite the overall positive zeta potential. Such negative sites on the clay were available since the ATPES grafting was spaced. Finally, developing composites, in which the organic modifier is covalently bound to the clay, presents a new class of sorbents with improved properties. Such sorbets bear a high polymer loading, higher polymer stability and a more organized polymer structure.

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Decontamination of Sarin in Water by Designed Oxime-Clay Composites

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Organophosphates are well-known toxic compounds including the nerve agent Sarin, which prevents acetylcholine binding to acetylcholinesterase leading to neural damage. Common medical treatment includes applying oximes, containing quaternary pyridine ring such as 2-pyridinealdoxime (PAM), as they catalytically hydrolyze Sarin to non-toxic compounds. However, developing materials for treating these hazardous molecules from water is much less explored. On the other hand, the adsorption of organo-pollutants from water by clay composites has been widely developed, tested and employed. But adsorption, of such toxic compounds, is not satisfying without their degradation to non-toxic compounds. In the current study PAM-clay composites were designed as a delivery system for the release of the oxime to water for enhanced sarin degradation. The hydrolysis of the organophosphate nerve agent sarin, is prone to rapid catalytic hydrolysis by oximes. In this study, an oxime-clay composite, based on the adsorption of 2-pyridinealdoxime (2-PAM) to montmorillonite (MMT), was designed as a delivery system of oxime for sarin degradation in water. 2-PAM adsorption reached a plateau at ~0.5 mmol/g; however, the degree of 2-PAM desorption from composites was not constant and increased with an increase in its initial added concentration. The composites were characterized by SEM, XRD, FTIR-ATR and TGA measurements. We suggest 2-PAM adsorbs in three modes; in a planar orientation 1. intercalated or 2. directly adsorbed on the external surface, and 3. “weakly adsorbed”, as a multilayer on the external surface. The removal of sarin (40 µg/mL) in the presence of MMT-PAM composites enhanced dramatically compared to its spontaneous hydrolysis in distilled-, tap- or buffered water e.g., from a half-life time of 2.5 h in tap-water to 0.3 h in a composite suspension (6.4 g clay/L). Sarin removal was attributed, not to adsorption, but rather to catalytic hydrolysis by released oxime, forming non-toxic compounds. The kinetic coefficients were extracted from pseudo first-order equation. The rate of sarin degradation was further enhanced by applying composites designed to release higher concentrations of 2-PAM.

Influence of media synthesis and thermal post-treatments on the properties of the Layered Double Hydroxides

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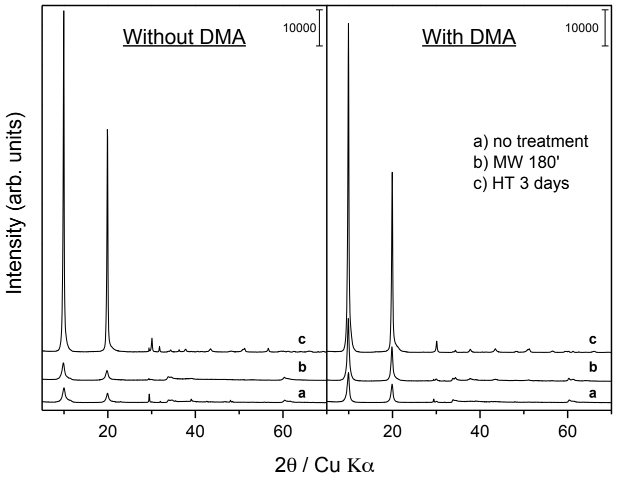
Layered Double Hydroxides (LDHs) have proven to be good materials as inorganic nanofillers in nanocomposites, due to their compositional versatility and their structural properties. LDHs or hydrotalcite-like compounds are solids with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]$ $A^{n-}_{x/n} \cdot mH_2O$, formed by octahedra sheets in a lamellar structure with anions in the interlamellar space (Wang & O´Hare, 2012). The properties of the final nanocomposite will depend on the dispersion degree, aspect/ratio and compatibility between the filler and the polymer matrix. So, a larger dispersion can be achieved with small particle size, hopefully modifying the thermal, electrical and optical properties (Pereira et al., 2009).



LDHs with a Zn^{2+}/Al^{3+} molar ratio 2/1 were synthetized by coprecipitation from precursor salts of the corresponding cations. The basic media was obtained using NaOH and dimethylamine (DMA) as precipitating agents. Our aim is to study how the nature of the precipitation media and the post-synthesis hydrothermal treatment affect the properties of the solid obtained. The solids were heated under microwave (MW) treatment for 180 min or by conventional heating (HT) for 3 days. All solids were characterized by XRD, FT-IR, TG-DTA, particle size distribution and surface properties. Results obtained from XRD indicate that polycrystalline compounds with a hydrotalcite-like structure were obtained. The crystal size increased with the hydrothermal treatment, specially using a conventional heating. The use of a weak base in the precipitation media allowed to obtain solids with larger crystal sizes and lower particle sizes.

Acknowledgements: This work was funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (ERDF) through the project MAT2013-47811-C2-R. A. Misol thanks Junta de Castilla y León and the European Social Fund for a PhD contract.

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Evaluation of clay-based geochemical barriers for cadmium migration

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Sorption onto solid phases is one of the most powerful mechanisms to retain pollutants. In this study we analysed the retention of cadmium in costumed barriers. Cadmium is considered by the World Health Organization one of the ten chemical of major public concern, with very low permissible exposure limits.

Clay materials are often used as principal materials in geochemical barrier to contaminant migration because they show high sorption capability, they are environmentally suitable and reasonably cheap.

However, the material used in geochemical barrier can be tailored considering both the environmental conditions (pH, salinity, etc..) and the specific properties of the contaminant, to optimize its retention. In particular, the addition of natural additives, as metal or oxide nanoparticles may improve significantly contaminant retention.

To select the type and the quantity of additive to be added to the clay, the first step is to study in detail contaminant sorption in the separate mineral phases and to develop predictive model to describe the behaviour of the mixed system in the widest as possible range of chemical conditions.

Cadmium retention in a sodium smectite was experimentally studied under a wide range of pH, ionic strength and Cd concentration and the whole set of data was modelled considering both cationic exchange and surface complexation; then, the effect of the additions of CuO, CeO_2 or Fe-oxide nanoparticles was quantified.

Results will be discussed considering different possible environmental scenarios and evaluating the best mixtures to be used for cadmium retention in each case.

Introduction of hierarchical structure for enhanced photocatalytic activity of Cu nanoparticles hybridized with saponite nanosheets

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Hybridization of metal nanoparticles (NPs) with nanosheets has recently been gaining significance in low-dimensional nanocomposites [1]. We have previously established a synthetic method of Cu NPs on layered clay minerals [2–4] including diameter-controlled Cu NPs on saponite (Sapo) nanosheets. In this nanocomposite, the nanosheets were assembled microscopically. We herein report photocatalytic activity of the Cu NPs enhanced by flocculation of the Sapo nanosheet assembly. Photoinduced electron transfer (PET) was chosen as the model reaction, and methylviologen (MV^{2+}) was used as the electron acceptor. Upon UV irradiation, the bands of $MV^{+\bullet}$ appeared around 400 and 620 nm. Hence, it was found that the PET from the Cu NPs to MV^{2+} took place, while the suspension showed flocculation by addition of MV^{2+} (Fig. 1 (Left)). In contrast, the PET did not take place efficiently when the suspension was dispersed stably in spite of the same [MV^{2+}]/[Cu NP]. The produced amount of $MV^{+\bullet}$ was quantified by absorbance area of the 400-nm band. Analyzing STEM images, the density of the Cu NPs was found to be higher in the flocculate than the dispersion, because the Sapo nanosheets were assembled fiercely. Considering that MV^{2+} was distributed homogeneously on the Sapo nanosheets, both MV^{2+} and the Cu NPs were assumed to be accumulated in the nanosheet assembly, enabling the efficient PET in the flocculate. Indeed, the amount of $MV^{+\bullet}$ was strongly correlated with the density of the Cu NPs in the assembly (Fig. 1 (Right)). Therefore, it was concluded that hierarchical structure of three-dimensional assembly was important for the photocatalytic activity of the Cu NPs, even though the Cu NPs and MV^{2+} were adsorbed on the two-dimensional Sapo nanosheets.

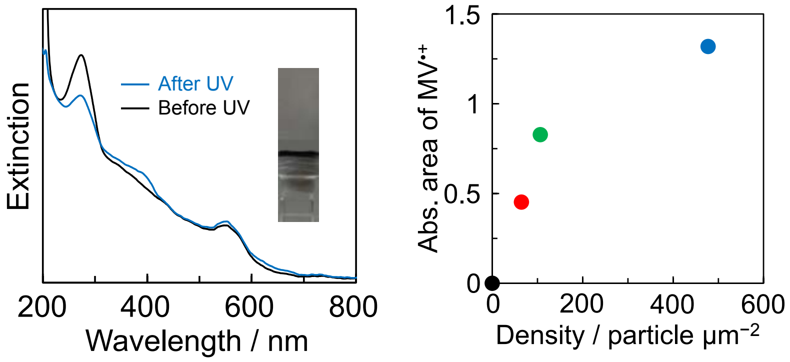

Figure 1. (Left) An UV-vis spectrum, a STEM image and a photograph of the suspension;

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Impact of initial structural heterogeneities on the long term hydro-mechanical behaviour of a bentonite pellet/powder mixture. Experimental and modelling results.

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Most European concepts for deep geological disposal of high and intermediate level-long lived radioactive waste involve bentonite-based materials as buffers, backfills and seals of disposal galleries and access shafts/ramps to ensure isolation and containment of the waste from the biosphere. Swelling pressures of buffers, backfills and seals are requirements for these components to achieve their safety. It is well documented that the swelling pressure depends principally on the dry density of material. Accordingly, a relatively small change in density can induce significant changes in swelling pressure. That is why most of laboratory and large scale tests have focused on achieving the required average dry density. However, very few experiments have focused on the dry density heterogeneities at initial state and in the course of hydration and their influence on swelling pressure. For long-term safety assessment of the repository, it is essential to predict the evolution and the final state of the initially heterogeneous seal and to evaluate the effects of remaining density gradients and swelling pressure differences on its long term performance. To this end, an appropriate constitutive Hydro-Mechanical (HM) model that accounts for spatial and temporal distributions of the relevant properties of the bentonite pellet/powder is fundamental.

In this paper, the hydro-mechanical behavior of a pellet/powder MX80 bentonite mixtures were investigated by means of Microfocus X-ray Computed Tomography (μ-CT) observations and laboratory small scale infiltration tests. This material, consisting of a mixture of low-density bentonite powder and highly compacted bentonite pellets, is obviously highly heterogeneous in its initial state. The degree and distribution of heterogeneities will vary during hydration and the average dry density might be not sufficient to characterize its final state and containment performance. Radial and axial swelling pressures were monitored while wetting. Two configurations were considered: for the first, a pellet/powder mixture was prepared following a specific protocol to minimize initial structural heterogeneity; the second one was specially designed to study a strong heterogeneous mixture distribution. In addition, a HM model which takes into account the initial heterogeneous distribution and transient microstructural features characterizing the high density bentonite pellets (damage upon wetting) is developed. The formulation is applied to the modelling of the small scale infiltration tests. The model allows the anisotropic swelling behaviour of the mixture to be satisfactorily reproduced when accounting for the spatial variation of the material initial porosity. Detailed analysis of the modelling results demonstrates the existence of dry density gradients at long term and their influence on swelling pressure anisotropy.

Structural resolution of clay-like nanotubes

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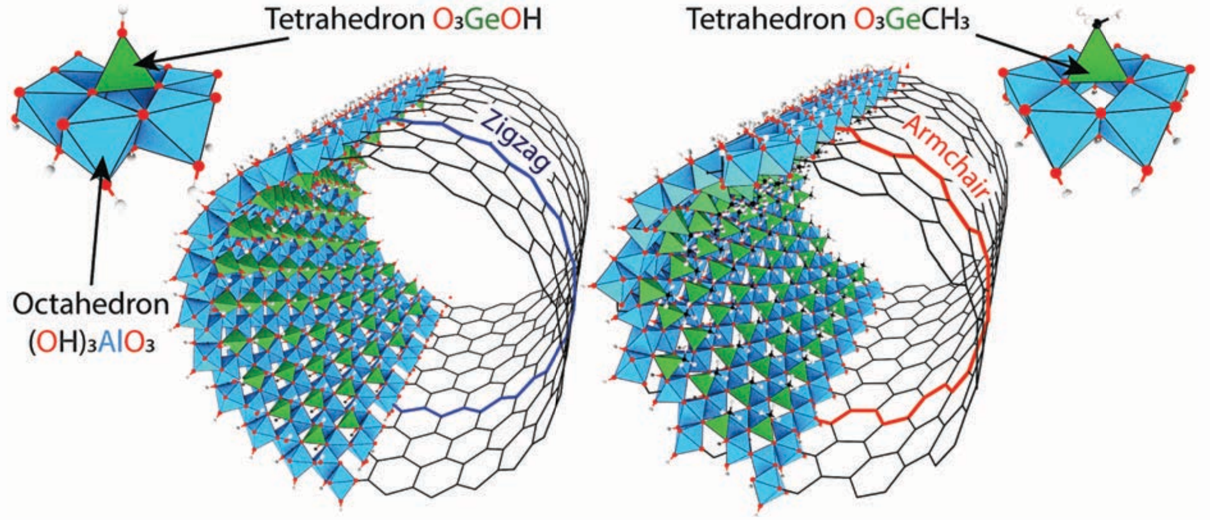
Clay imogolite nanotubes (Si-INT) with composition $(OH)_3Al_2O_3SiOH$, their alumino-germanate analogs Ge-INT and functionalized m-Si-INT or m-Ge-INT, where the inner cavity is covered by methyl groups, are easily synthesized by sol-gel methods, with possible applications in various fields [1]. But quantitative determination of their atomic structure is missing.

Their X-ray diffractograms inherently exhibit rather broad features due to their nanometric lateral size, giving access to a very limited number of structural parameters. Here we introduce a new methodology, based on the use of helical symmetries and on semi-empirical energy minimization, to reduce the number of fitted variables needed to determine the atomic structure [2]. Further adjustment of the X-ray data, supported by Density Functional Theory simulations, gives access to the structure of m-Si(Ge)-INT [2] and of Ge-INT (results not yet published). In particular, an unexpected 'armchair' rolling mode is revealed for m-Si(Ge)-INT while it is 'zig-zag' for hydroxylated nanotubes, as illustrated in the figure. These structural insights open up for improved understanding of structure-property relationships of clay-like imogolite nanotubes.



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Unique properties of alumino-germanate imogolite nanotubes as water nanocontainers

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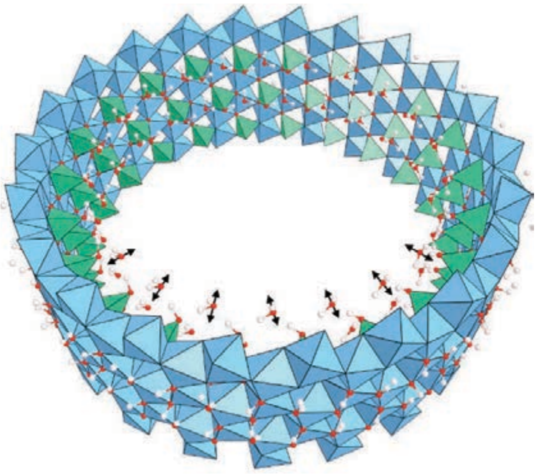
Imogolite-like nanotubes are ideal platforms for studying the novel properties of molecules confined at the nanoscale. Compared to the well-known carbon nanotubes (CNT), clay-like imogolite nanotubes (INT) own well defined diameter. Moreover, the molecular affinity of their inner cavity is tunable [1]. It should be underlined that such properties confer to these tubular structures a wide range of potential applications, from filtration to depollution of water.

Here, we show that alumino-germanate imogolite nanotubes are nanocontainers of interest in the growing field of nanofluidics. Alumino-silicate and alumino-germanate INTs of nominal composition $SiAl_2O_3(OH)_4$ and $GeAl_2O_3(OH)_4$ (Si-INT and Ge-INT) are hydrophilic nanochannels. The structure and dynamics of water in Si-INT have been recently investigated [2, 3]. Surprisingly, the properties of water are modified when molecules are confined inside Ge-INT of slightly larger diameter [4]. Inelastic neutron scattering experiments coupled to ab-initio molecular dynamics simulations reveal a unique structure of the water layer adsorbed inside Ge-INT. It differs from that of water in Si-INT and, to the best of our knowledge, from that of any kind of two-dimensional water. We show that the dynamics of INT and water are interrelated, which has not been evidenced in Si-INT. A well-defined translation vibrational mode of water molecules with respect to the nanotube wall (illustrated with black arrows in the figure) is also observed. Finally, the evolution of mean square displacements of water molecules as a function of temperature is found to differ markedly in Ge-INT and in CNT [5], in which water slips without friction, which is attributed to the peculiar bonding of water molecules with germanol groups.



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Synthesis and characterization of zinc-bearing silicates phases: a new way to assess health risks from polluted sites

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Due to Human presence, the soil anthropization is high and exponential pressure on soils. Contaminants Are widely distributed in the environment due to industrial, mining or agricultural activities. One of the major issues concern health risks related to direct contact from byproducts of mining activities. The main health problem is mainly due to the fact that during ingestion, the contaminants may be dissolved in the digestive fluid and reach the target organs to exert its toxicity. The conventional approach of bioaccessibility consists in simulating the composition of the entire gastrointestinal tract via the UBM (Unified Barges Method) bioaccessibility protocol. However, because polluted soil system is complex, it is therefore difficult to define which solid phase contributes to the health risk. Thus, it seems necessary to simplify this system to better understand the associated health risks of each bearing phases.

For this purpose, it has been proposed to synthesize some representative Zn bearing phases to assess their reactivity in supergene context. In this abstract, we focus on (i) sauconite, a 2:1 layer structure (ideal formula $Zn_3(Si,Al)_4O_{10}(OH)_2$) and (ii) hemimorphite, a sorosilicate mineral (ideal formula $Zn_4(Si_2O_7)(OH)_2\cdot H_2O$). Each synthetic phase was characterized by XRF, XRD, FTIR, Raman and SEM-EDS. Then, the synthetic phases (similar grain size) were subjected to the bioaccessibility BARGE protocol (i.e., gastric/gastro-intestinal fluid mimic, 37°C) to assess the metal(loid)s geochemical behaviour. Some exposition scenarios have also been performed to calculate from which the percentage of each phases non-carcinogenic effect can occurs. The discussion will focus on the metal's behaviour as well as the reactivity and stability of each phase in terms of health risks, and eventually the sustainable management of polluted sites and soils.

Detection of nucleotides absorbed onto clay by UV Resonant Raman spectroscopy: preliminaries to the search for biological traces on Mars

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The payload of Mars 2020 space mission includes Raman spectrometers. In particular, the SHERLOC instrument is dedicated to the detection of luminescence and Raman signal of condensed carbon and aromatic organics that could be biosignatures, with a deep UV laser source. [1] Among minerals present in Mars soil, phyllosilicates exhibit a strong affinity for organic molecules. The mechanisms of absorption of DNA nucleotides onto clay minerals are well documented. [2] Unfortunately, there is a lack of an overview in Raman studies with visible and UV laser wavelengths of organic compounds absorbed onto this family of minerals.

We have used an ultraviolet resonant Raman (UVRR) setup to track down the signatures of DNA nucleotide desoxyguanosine-5'-monophosphate (dGMP) absorbed onto a series of clay minerals. With a 244 nm laser excitation, we avoid luminescence of natural phyllosilicates and enhance Raman signal of the organic compound. The minerals studied (pyrophyllite, chlorite, nontronite and lizardite) have a variety of stacking sequences of structural groups of atoms. Furthermore, they have a variable composition in Al, Mg and Fe. Therefore, the absorption of nucleotides, the capacity to keep and protect them from solar UV irradiation may differ.

The deep UV energy of the laser focused onto the samples may actually induce severe photo-damage to the organic compound. [3] With a laser spot-size of ca. 1 µm diameter, the irradiance is from 8 up to 260 J depending of the time of exposition. We used the Raman signature to characterize this effect after an irradiation of several minutes up to a stable spectroscopic signal detected. In this study we present promising results on the strategy for the detection and preservation of adsorbed dGMP, even at very low concentration.

The presence of oxidants such as hydrogen peroxide and perchlorate, which have been detected on Mars, [4] are currently being considered in future experiments because of their potential implication in the degradation of nucleotides under UV irradiation.

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Clay Minerals composition of the Late Neoproterozoic Zenifim Formation (southern Israel)

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A vast Late Neoproterozoic clastic wedge, locally interbedded with volcanics, was deposited on the northern outskirts of the Arabian-Nubian Shield (ANS) within a wide basin that extended into areas currently at the foothills of the Taurus and Zagros belts. The southern limit of this basin is manifested in the subsurface of southern Israel (Negev area) by a few km thick arkose sequence known as Zenifim Formation. The detritus stored in this formation was mostly eroded from the adjacent ANS at the cessation of Neoproterozoic orogeny. Along a ~200 km long transect in the subsurface of Israel, the arkosic facies of the Zenifim Formation changes from a proximal alluvial fan in the south, to a sea marginal facies in the north reflecting the transgression of the proto-Tethys onto the decaying Neoproterozoic orogen. We studied the clay mineralogy and geochemistry of core samples from different parts of the Zenifim Formation in order to constrain its depositional environment and late diagenetic/metamorphic processes that have affected it.

In the southern Negev the mineralogical composition of the clay fraction near the top of the section, at ~1200 m depth, is dominated by randomly-ordered mixed layer illite-smectite (I/S) with minor illite and kaolinite, passing to illite-dominated mineralogy, accompanied by regularly-ordered I/S at depth of 1550 m (the base of the formation was not drilled). In the northern Negev the entire Zenifim section, extending from 2300 to 3350 m depth, is dominated by illite, with minor regularly-ordered I/S, chlorite and kaolinite. Within the volcanic units encountered in this area the mineralogical composition of the clay fraction is dominated by chlorite. Overall, the clay mineralogical assemblages in the Zenifim Formation are compatible with diagenetic changes expected by increasing temperatures under the current burial depth and geothermal gradient of ca. 21°/km. No indications were found for significantly deeper burial depths or higher geothermal gradient in the past. The I/S-dominated clay assemblage of the relatively shallow samples from the southern Negev section may thus represent the primary clay assemblage, derived from weathering of the ANS magmatic rocks during the late Neoproterozoic.

Electrolytically supported processes of capture and release of CO_2

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CO_2 capture and valorisation are, according to present knowledge, possible solutions, involving economic and industrial challenges, for reducing atmospheric CO_2 emissions. Although chemisorption using amine-based solvents (MEA) is the farthest advanced in terms of industrial development (performances: 0.4 tCO_2/t_{MEA}; energy cost: 1-3GJ/tCO_2), various obstacles to its use must be overcome. Notably health and environmental risks associated with the use and handling of amines must be duly specified and verified for industrial-scale facilities. Given this two-fold challenge, both economic and environmental, the development of alternative eco-compatible and efficient processes is crucial for cost-effective post-combustion CO_2 capture/release.

This research aims at developing a powerful technological breakthrough in the CO_2 capture (Fig. 1A), using Layered Double Hydroxides (LDHs) that have a strong affinity for CO_3^{2-}. The electrochemical control of the oxidation state of the multiple valence cations, constituting the lamellar sheets, is the core process, which also includes CO_2 dissolution reaction to CO_3^{2-} from the gas effluent, as well as, after capture and release of CO_3^{2-}, the CO_2 degassing from released CO_3^{2}.

Synthesis and formulation of chemically co-precipitated Co-based LDH was optimized to perform electrochemical cycling according to:

$$Co^{(II)}_6Fe^{(III)}_2(CO_3)(OH)_{16} + (x/2)CO_3^{2-} \leftrightarrow Co^{(II)}_{(6-x)}Co^{(III)}_{(x)}Fe^{(III)}_2\,(CO_3)_{(1+x/2)}(OH)_{16} + xe^-$$

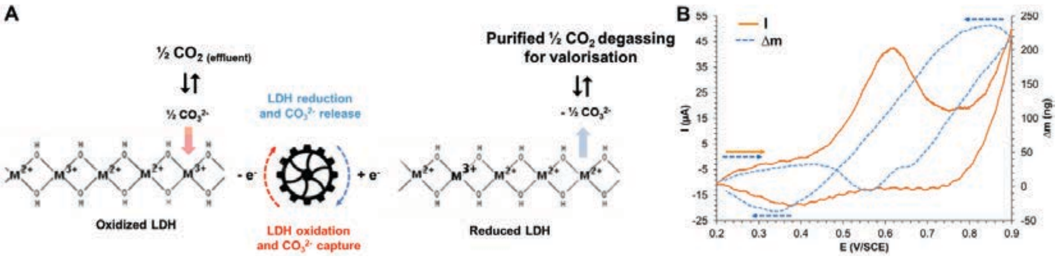

Fig. 1: A. Electrolytically supported processes of capture and release of CO_3^{2-} using LDHs. B: Coupling of CV and QCM, using thin LDHs films, coated on platinum-based quartz electrodes.

The coupling of Cyclic Voltammetry (CV) and Quartz Crystal Microbalance (QCM), using thin LDHs films, coated on platinum-based quartz electrodes (Fig 1B) enabled to (i) investigate the concomitant redox reactions and mass variations, (ii) demonstrate CO_3^{2-} intercalation/ deintercalation and (iii) determine the involved mechanisms. Using LDHs slurries, chronocoulometry, and chemical and physical analyses enabled to determine the kinetics constants associated to the concomitant electrochemical and chemical phenomena. The electrical electrolysis cell consumption of the CO_2 capture/release was evaluated via the applied current and the operating cell-voltage.

Atrazine-Montmorillonite/Beidellite intercalates: a Density Functional Theory study

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Atrazine, a s-triazine, has been one of the most employed herbicide. Owing to its negative impact in health and environment[1], is necessary to remove it from the ambience. Clay minerals, like mont-morillonite or beidellite, are fitting aspirant to immobilize organic contaminant, e.g. from waste water. These clays are highly hydrophilic, as a result show very limited adsorption capacities for hydrophobic organic compounds.

Beidellite (Bd) and Montmorillonite (Mt) are aluminosilicates with isomorphic substitutions, predominantly in tetrahedral sheets, and octahedral sheets, respectively. This different charge distribution in beidellite improves a stability of prepared organoclays[2].

Density Functional Theory (DFT) in solid state, PBE functional[3] with D3 method for dispersion correction[4], was used for study of interactions in atrazine-Bd and atrazine-Mt structure.

This study aims to characterizes the interaction between the $[Na(H_2O)^4]^+$ and tetramethylphosphonium cations (TMP) with atrazine (A) in the interlayer space in Bd and Mt, and calculate the vibrational spectra by means of *ab initio* molecular dynamics method (AIMD) to show possible hidden bands in the experimental FTIR spectra.

Six models are proposed : 1. A-Bd ; 2. TMP-Bd ; 3. ATMP-Bd ; 4. A-Mt ; 5. TMP-Mt ; 6. ATMP-Mt.

The results revealed that in the optimized models, atrazine has a flatty arrangement in Bd and Mt interlayer space. The interactions that form the intercalates are mostly weak hydrogen bonds. The presence of TMP cation in the interlayer space improves the interactions of atrazine.

Acknowledgements : Author are grateful for the financial support by the Slovack Research and Development Agency APVV-15-0741, APVV-15 0479 and VEGY 02/0021/19.

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Synthesizing antibacterial minerals

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The rapid rise in antibiotic resistant bacteria is seriously hindering our ability to treat and control the spread of life-threatening infectious diseases. As a result, our approach to medicine and agriculture will require significant changes if we are to successfully maintain current levels of healthcare. Naturally occurring antibacterial clays have been shown to be effective in eradicating antibiotic resistant bacteria and have therefore been proposed as a new paradigm to fight the potentially devastating effects of the post antibiotic era. However, natural samples, by their nature, exhibit variable antibacterial effectiveness and minerals with reproducible antibacterial activity are needed. We have developed synthetic versions of naturally occurring bactericidal minerals while controlling the chemical purity and antibacterial potency. Nano-iron-sulfides and smectite clay minerals were synthesized using solvothermal and hydrothermal methods. The clay iron-sulfide mixtures were tested for antibacterial activity against *E. coli* and *S. epidermidis,* and were found to be highly effective. Understanding the geochemical and mineralogical processes that regulate the antibacterial activity of synthetic mineral systems, and learning how to optimize them, will help to usher in the medical application of new mineral-based antimicrobials.

Comparative effect of bovine bone ash and cassava starch on the microstructure of porous ceramics using kaolinite clays from Cameroon

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Porous ceramics are widely applied in fields such as membrane support, ceramic filters, catalyst supports, and piezo-electric materials [1,2]. The aim of this study is to investigate the microstructure and properties changes of porous ceramics elaborated using bovine bone ash or cassava starch. Samples were prepared by mixing two natural kaolinitic clays from West-Cameroon with bovine bone previously calcinated at 700°C for 2h and cassava starch. Additives were introduced up to 15 mass%. Unidirectional pressing was used to shape cylindrical ceramics samples (compacting stress = 12 MPa). The as-obtained samples were oven-dried at 40°C for 48h and 100°C for 24h, and then sintered at 1000°C and 1150°C for 2h. The properties of sintering porous ceramics were characterized using SEM analysis, porosity and pore size measurements, three points bending tests, BET specific surface area and XRD analyses. Results showed that the addition of bone ash improved the mechanical resistance conversely to the addition of cassava starch (figure 1). SEM images revealed heterogeneous microstructures for all the specimens. A hierarchical pore arrangement was noted for samples containing cassava starch. Indeed, ceramics structures were more consolidated with the addition of bone ash, thanks to a lower porosity compare to starch-based samples (figure 2). Despite the firing temperature, specific surface area was quite similar when using cassava starch (up to 9 m^2/g) or bone ash (up to 8 m^2/g). Pores size are low than 0.3 µm, and thus these porous ceramics can be use as ceramic filters for cleaning drinking water.

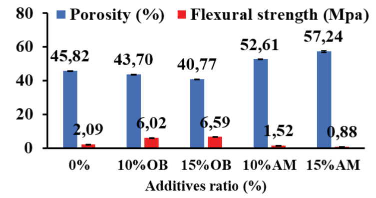

Figure 1. Porosity and flexural strength obtained at 1150°C

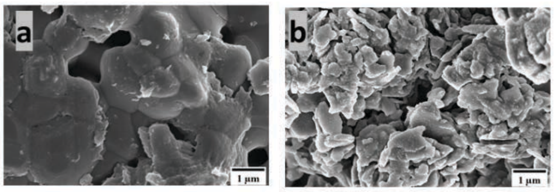

Figure 2. Porous ceramics with a)bovine bone ash, b) cassava starch at 1150°C

Keywords: microstructure, kaolinitic clay, Porous ceramics, mechanical properties, consolidation

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Sequestration of quaternary ammonium compounds by soil smectites – implications for antibiotic resistance development

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Quaternary ammonium compounds (QACs) are surface-active, biocidal, High Production Volume Chemicals with broad application in agriculture.

Predicted environmental concentrations (PEC) for QACs that are applied to soils with manure are in the order of 3.5 mg kg^{-1} (Mulder et al., 2018). The positively charged QACs are in all likelihood sorbed to clay minerals but data on QAC concentrations and sorption behaviour in soils are still missing. On the other hand, the occurrence of QAC resistance genes in soils has been well documented (Byrne-Bailey et al., 2011; Jechalke et al., 2014).
We propose that QACs might be sequestered into interlayer regions of 2:1 layer silicates in clay-rich soils, reducing their acute toxicity, while increasing their persistence.
In order to test our hypothesis, we determined the minimal inhibitory concentrations (MIC) of QACs for various bacteria in the presence and absence of clay minerals. In the presence of smectite the MICs for all tested bacteria and both QAC-compounds were significantly reduced, while kaolinite had no effect on the inhibitory concentration of the QACs. Sorption isotherms confirmed that in the microbial trials, the free QAC concentrations were reduced by smectite thus buffering their acute toxicity.
The release of QACs from sequestered form potentially maintains concentration levels in soil solution that are sufficient to select for antibiotic resistance in the environment.

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Thermodynamics of CO_2 rich fluids in cement nanopores from atomistic simulations

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Cement is a ubiquitous material utilized in various industries, including sub-surface geo-energy operations. The enormous potential of these operations, for instance in the mitigation of anthropogenic carbon footprint, has attracted multiple studies in the recent years (e.g., Matter et al., 2011; Gíslason et al., 2018). However, under these extreme conditions, cement is simultaneously facing tremendous challenges in terms of environmental impact and durability. To minimize these risks and to optimize sub-surface operations, a proper understanding of the fluid thermodynamics and transport pathways in wellbore cement is important.

Here we employ atomistic computer simulations to model CO_2/H_2O fluid interactions with cement's main hydration phase: calcium silicate hydrate (C-S-H). Tobermorite is taken as a basic mineral structure to develop atomistic models of C-S-H phase with varying C/S ratio from 0.83 to 1.75. The molecular level investigations contribute to an improved understanding and quantification of fluid thermodynamics and migration through wellbore leakage pathways. The effects of pore size distribution are taken into account by varying the pore sizes from 1 to 5 nm. At the first step, the intercalation potential of CO_2/H_2O fluid mixtures is investigated using grand canonical Monte Carlo (GCMC) simulations for the C-S-H porous systems in equilibrium with binary CO_2/H_2O bulk mixtures at 323 K/90 bar and 348 K/130 bar, mimicking typical *T*/*P* conditions of CO_2 sequestration. Increasing the C/S ratio of the confining cement pores decreases the adsorption of CO_2 as water competitively adsorbs on the calcium cations, blocking access of CO_2. The equilibrium fluid compositions and structures obtained from the GCMC simulations are then used as an input for molecular dynamics (MD) simulations with both classical ClayFF (Cygan et al., 2004) and reactive ReaxFF (van Duin et al., 2001) interatomic potentials . The structural properties of nano-confined CO_2/H_2O fluids (i.e., density profiles, radial distribution functions, preferential molecular orientations), their transport and reactivity are quantitatively evaluated and compared for the two approaches.

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Importance of (meta)kaolins crystallochemistry toward their alkali treatment reactivity

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INIFUGE project, supported by Andra under the "Investments for the Future Program" , is focused on the development of a brand-new geopolymer binder with fire retardant properties. Geopolymers are materials based on the alkali activation of aluminosilicate minerals, generally metakaolins, obtained by dehydroxylation of kaolinites. However, metakaolins exhibit different reactivities during geopolymers formulation, leading to the wide scope of application of geopolymers. The metakaolin reactivity in alkaline media depends on their preparation mode (flash calciner, rotary kiln, cell oven), their composition (especially the amount of accessory minerals like quartz) and the nature or the crystallochemistry of the initial kaolinite used for their preparation. Moreover, to better understand the reactivity of metakaolins in alkaline media, it is important to know how the raw kaolinites react in their contact. To complete this goal, one original solution is to combine mineralogical and chemical techniques to understand and control the metakaolin reactivity and its thermal activation for various applications. Then two references kaolinites with different crystallochemistry (KGa-1 and KGa-2) and their derived metakaolins prepared at different dehydroxylation temperatures (480, 500, 550, 600, 650, 700°C), were submitted to 2 *M* of KOH, NaOH and KOH + NaOH solutions. The experiments were performed at 80°C for different step time varying from 0 to 24 h for the kaolinites and 0 to 1 h for the metakaolins. The proportion of Al and Si released by aluminosilicates in solution was measured by MP-AES and the solid residues were investigated using XRD, FTIR, SEM and TEM. The results display (i) the effect of the crystallochemistry of kaolinites, (ii) the cation effect (Na^+ or K^+) onto dissolution process, (iii) different kinetics of dissolution, (iv) the precipitation of zeolites and (v) the effect of the dehydroxylation temperature. *In fine*, the sum of data obtained clearly evidences that the crystallochemistry of kaolinite controls the reactivity of metakaolin for the using range of temperature.

Use of synthetic kaolinite to understand the kaolin reactivity in alkaline media

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This study is a part of INIFUGE project, focused on the development of a brand-new geopolymer binder with fire retardant properties. Andra, under the "Investments for the Future Program", financially supports this project. In order to understand the reactivity of natural kaolinites in alkaline media, and *in fine* the resulting metakaolinite, which is one of the main raw material for geopolymer, it is important to be free from certain parameters such as purity or crystallo-chemical variations within the sample. To counteract this interference, it is proposed to prepare synthesized kaolinites by varying the crystallochemistry and to study their reactivity in a basic medium. The hydrothermal syntheses were carried out for 5 to 8 days at 220°C with a modified protocol using silica fume and gibbsite-like compound as alumina source in acidic conditions. The synthetic kaolinites were then characterized by XRD, FTIR, SEM and TEM. The results exhibit flaky particles of kaolinite with various crystallinity range. An alkaline treatment (2*M* KOH or NaOH solutions) has been applied to each sample. Finally, the results were compared with natural kaolinite behaviour and evidence the role of the crystallochemistry toward alkali treatment.

Towards zero carbon emission power via CO_2 increased shale energy recovery

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The major challenge faced by our 21st century global society is to provide high value energy resources in support of environmentally sustainable economic development. Here we provide numerical simulations for carbon capture utilization and storage (CCUS) within emerging unconventional shale reservoirs (e.g. Nadeau, 2016; Tovar et al., 2014) for increased energy recovery (IER). The results (Berawala et al., 2018) demonstrate that CCUS in North American shale plays have current storage capacities of approximately 5% of global carbon emissions (36 Gt CO_2) on an annualized basis. This capacity is expected to grow with increasing production volumes from these newly acquired energy resources on a global scale. The opportunity now exists to create carbon neutral power grids, particularly when integrated with wind/solar, and battery storage with the expanding electric transportation vehicle fleet. The increase in recoverable energy reserves is c. 2 to 5 times the currently estimated producible reserves. This volume is sufficient to provide carbon neutral power for the foreseeable future, c. 10^2 years.

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Phosphate sorption of soils with different clay content

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Phosphate fertilizers are widely applied in plant growing. Phosphate anions bind to the different soil components, including clay, in different interfacial processes and chemical reactions. The sorbed phosphate species are usually considered as weakly, tightly sorbed and precipitated ones. The ratio of these species was studied by radioactive tracer method using ^{32}P isotope as phosphate ion. Five soil types with different clay content were investigated. The effect of soil type, clay content, phosphate quantity, incubation time and plant growing was studied.

The ratio of weakly sorbed phosphate can be studied by heterogeneous isotope exchange; the quantity of water soluble/weakly sorbed phosphate as well as the transport rate of phosphate in a steady state between the soil and soil solution was determined. We constructed and tested a correct thermodynamic and mathematical model for the evaluation of the heterogeneous isotope exchange of the radioactive P-32 isotope. In long term experiments, the rate of the transformation of weakly to tightly sorbed phosphate was determined and compared in case of soil types with different clay content.

Acknowledgments:
This study was financed by by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008.
The work was supported by the Hungarian National Research, Development, and Innovation Office (NKFIH K 120265).

Electric alignment of liquid crystalline binary colloids of niobate and clay nanosheets

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Nanosheets obtained by exfoliation of inorganic layered crystal in water form colloidal liquid crystals. Colloidally dispersed liquid crystalline nanosheets are aligned under external forces such as electric and magnetic fields. We have investigated niobate nanosheet colloids as a model system of nanosheet LCs, and clarified that liquid crystalline niobate nanosheets are aligned with an electric field or laser radiation pressure to generate hierarchically organized macroscopic nanosheet assemblies (Nakato et al., 2014; Tominaga et al., 2018). On the other hand, binary nanosheet colloids involving two different nanosheets show complicated phase behavior compared with single-component colloids. Binary colloids of niobate and clay nanosheets show phase separation at a microscopic scale (Miyamoto and Nakato, 2003). Application of external forces to these colloids will generate unusual colloidal structures that are not attained by the single-component colloids. We report herein the electric alignment of nanosheets in binary nanosheet colloids of niobate and clay.

Binary nanosheet colloids were prepared by mixing colloidal nanosheets obtained by exfoliation of layered niobate $K_4Nb_6O_{17}$ and synthetic hectorite (Laponite). The sample was injected into a thin-layer ITO cell, and applied by an AC electric voltage of 10 V (peak-to-peak), 50 kHz.

Before applying the electric field, we observed a niobate-clay binary nanosheet colloid by an optical microscope. The clay nanosheets distributed homogeneously in the sample through a fluorescent observation which selectively detected the clay nanosheets, while the niobate nanosheets were located among the clay nanosheets as µm-sized domains based on a bright-field observation which selectively detected niobate nanosheets. After applying the electric field, the niobate nanosheets changed their orientation to the direction parallel to the electric field. However, the clay nanosheets were distributed similarly to those in the absence of the electric field. The results indicate that only the niobate nanosheets respond to the electric field in the binary colloid of niobate and clay nanosheets. The aligned niobate nanosheets are segregated and located between the clay nanosheet domains.

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The role of Kuroshio Current in the sedimentation of Izu-Bonin-Mariana rear arc (IODP Expedition 350): evidence from clay minerals (<1 Ma)

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Expedition 350 of the IODP (International Ocean Discovery Program) conducted a drilling hole (site U1437) in the rear arc region of Izu-Bonin-Mariana (IBM) arc. Recent work in adjacent areas have demonstrated the importance of the use of clay minerals, together with other factors, for the identification of submarine sediments provenance. Geochemical studies show that external components to the arc were a good part of the volume of fine sedimentation, being rich in Nb, Th and light rare earth elements (LREE). The purpose of this study was to identify possible source area(s) for volcaniclastic sediments external to the IBM arc with age up to 1 Ma through clay mineralogy. X-ray diffraction (XRD) analyzes were performed by the powder method of bulk and of oriented mounts for the <2 µm particles collected from unconsolidated volcaniclastic sediments. Quantifications of powder analyzes used the Rietveld's method, while proportions between clay minerals from oriented analyzes were quantified by the method of Biscaye. The results obtained by the Rietveld method were succesfully compared to lithogeochemical data previously obtained by the Expedition 350 scientists, in order to validate the quantifications by XRD. The clay minerals represent about 20% of the total volume of the samples. By the method of Biscaye, illite is the most abundant clay mineral, while kaolinite and chlorite are reported in smaller proportions. The results suggest Taiwan, along with particles eroded from China loess deposits, as the most probable source areas for the studied volcanoclastic sediments, mainly by the abundance of illite. The mineralogical variation of clay minerals in the volcaniclastic sediments of the rear arc and adjacent continental areas indicates the action of transport agents in the arc, like the Kuroshio current, which participates in the pattern of sediment circulation in the Pacific Northwest since Pliocene and has a larger meander that crosses the region of the drilling hole.

Key-Words: IODP, illite, Kuroshio Current

TG-DTA and synchrotron-radiation X-ray diffraction investigations of nanopyroaurite-type material obtained from bauxite washing residues

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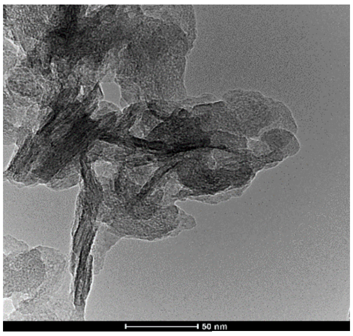
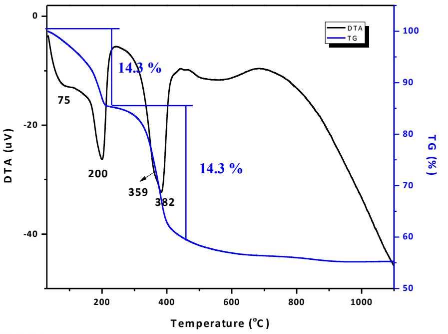
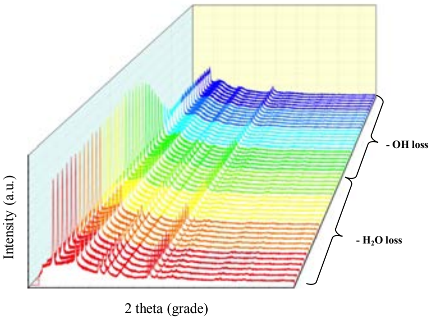
The aim of this research was to develop a simple process to synthesis pyroaurite-type layered double hydroxide employing bauxite mining residues from Amazon Region (northern Brazil), which actually has no commercial importance. The final product was characterized by High-resolution transmission electron microscopy (HR-TEM), Thermogravimetry (TG) and Differential thermal analysis (DTA), as well as *in situ* X-ray diffraction with synchrotron radiation (SR-XRD). The nanoparticles having average size of 20-50 nm were obtained by co-precipitation and hydrothermal synthesis at 75 °C for 1 day. The thermal behavior measured by using TG-DTA analysis revealed five main endothermic events at around 70 ºC (small), 200 ºC (large), 360 ºC (small) and 380 ºC (large) upon heating. The SR-XRD patterns collected during heating from 30 to 300 ºC elucidated that the peaks at around 70 ºC and 200 ºC corresponded to the loss of adsorbed water and dehydration, respectively. The events at approximately 360 and 380 ºC could be related to the continuous loss of the OH units (dihydroxylation). The results have shown that bauxite mining residues could be a low cost starting material for nanopyroaurite synthesis with thermal stability up 300 ºC.







Sorption properties of natural hydrotalcite

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Layered double hydroxides and products of their heat treatment are applied in such fields as catalysis, production of pharmaceuticals, photochemistry, electrochemistry, etc. Application of LDHs as sorbents for wastewater treatment is of particular interest, they were proved to be rather effective for sorption of different anionic pollutants.

Synthetic LDHs are described quite well while the potential of natural hydrotalcites is underestimated. There are at least 6 hydrotalcite deposits in Russia. In the present work, sorption properties of natural hydrotalcite from the Praskovye-Evgenievskaya mine (Chelyabinsk region, Russia) were studied and compared with the properties of synthetic MgAl-LDH.

Identification of the structure and phase composition of the samples was performed by the XRD (fig.1). The morphology and thermic transformations were also characterized.

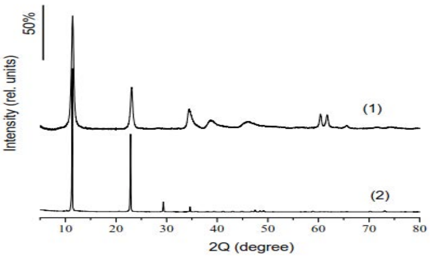

Fig.1. XRD pattern of LDHs:
Mg-Al-LDH-syn (1); Mg-Al-LDH-nat (2)

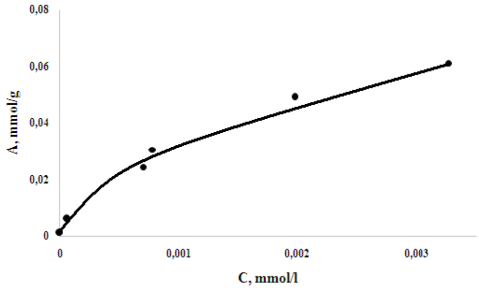

Fig.2. Sorption isotherm of Congo red by natural hydrotalcite at 25^{o}C

The sorption capacity of hydrotalcites was studied using Congo red dye as an example (fig.2). This dye is a widespread model for characterization of LDHs [1-3]. Kinetic and equilibrium experiments have been carried out. The effect on the rate and completeness of sorption of such factors as contact time, temperature and concentration was studied in detail.

This work was supported by the Russian Foundation for Basic Research, grant № 18-29-12103.

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Mixed-valent iron precipitates formed via interfacial electron transfer at clay minerals control chlorinated contaminant reduction

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The redox activity of iron-bearing minerals is interlinked with the environmental cycling of elements, nutrients, metals, and contaminants. Earlier work has demonstrated that Fe in clay minerals is less susceptible to reductive dissolution compared to Fe oxides and (oxy)hydroxides, rendering clay minerals a potentially renewable source of reduction equivalents in subsurface environments. Indeed, Fe in clay minerals can be reduced by microbial activity as well as chemical reductants and the resulting structurally bound Fe(II) can reductively transform a variety of organic and inorganic contaminants, including nitroaromatic compounds, chlorinated solvents, radionuclides, and metals. More recently, we, and others, demonstrated that clay mineral Fe can also be reduced via interfacial electron transfer from aqueous Fe(II). Interestingly, the aqueous Fe(II) that is oxidized during electron transfer forms a new Fe precipitate and a range of mineralogies have been proposed for these precipitates. We propose that the identity, and consequently the redox reactivity, of the precipitate(s) is determined by the solution chemistry at the time of formation.

Here, we explored the effect of clay mineral Fe content and aqueous Fe(II) concentration on the identity and reactivity of the Fe precipitate(s) forming due to interfacial electron transfer between aqueous and clay mineral Fe. We used a combination of XRD and Mössbauer spectroscopy to identify the mineralogy and characterize the Fe speciation in the precipitates; and we used hexachloroethane (HCA) as our reactive probe to investigate the precipitates' effect on the fate of recalcitrant contaminants.

We found that the reduction of HCA depended on both the clay mineral Fe content and the initial aqueous Fe(II) concentration used. At the same initial aqueous Fe(II) concentrations, approximately twice as much HCA was degraded in the presence of clay mineral with low Fe content (SWy-2) compared to when high Fe content clay mineral (NAu-1) was present. For the same clay minerals, lower initial Fe(II) concentrations resulted in decreased HCA reduction extents. Although Mössbauer analysis shows that the precipitates formed in the presence of the two clay minerals contain similar amounts of Fe(II), the ratio of Fe(II) bound in the precipitate relative to the clay mineral Fe is far greater for SWy-2 compared to NAu-1. We suggest that this ratio might be a practically useful parameter, rather than the aqueous Fe(II) concentration, for assessing the reactivity of the resulting clay mineral-Fe precipitate system. Additionally, our combined Mössbauer and XRD data suggest that the Fe precipitates' identity gradually changed from Fe oxyhydroxide-like at low aqueous Fe(II) concentration to resembling an Fe(II)-rich silicate mineralogy at the highest Fe(II) concentration. We are currently finalizing our analyses of both the mineralogy and the formation pathway of the precipitates.

Surface complexation of metal cations at the (010), and (110) edges of montmorillonite: MD computer simulation with updated ClayFF potential

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Realistic molecular scale simulations of clays are often challenging because of the great diversity of their chemical composition and significant degree of their structural and compositional disorder. ClayFF was originally developed in response to a strong need for a robust and flexible force field for classical atomistic simulations of such materials and their fluid interfaces (Cygan et al., 2004). However, in most computer simulations to date, clay particles are represented by their basal (001) surfaces only (e.g., Cygan et al., 2009).

Here we present a molecular dynamics simulation study of the adsorption and surface complexation of several metal cations (Na^+, Ca^{2+}, Ba^{2+}, and Sr^{2+}) at the (010) and (110) edge surfaces of montmorillonite, and compare the results with the adsorption at the basal (001) surface, using the new parametrization of the ClayFF model capable to accurately represent the structure of hydrated clay particle edges (Pouvreau et al., 2017; 2019). Cation exchange phenomena between the interlayer and interfacial regions in the (010) and (110) systems are quantitatively analyzed and the interlayer *vs* interfacial free energy calculations showed that cations are more stable in the interlayer region. The most probable adsorption sites are determined for each surface and site-specific adsorption free energies are calculated for each of them.

The MD simulation results are not only consistent with recent *ab-initio* calculations (e.g. Zhang et al., 2017) and accurately reproduce experimental trends regarding the adsorption properties of the edge *vs* basal surfaces of clays, but also highlight the effects of isomorphic substitutions and cation size on the strength of adsorption at different specific sites.

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Clay Minerals and Mineralization of Permian Illite in a Geothermal Drillhole – Northern Upper Rhein Graben, Germany

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A geothermal field near Groß-Gerau (northern part of Upper Rhein Graben) was explored by a local energy supplier due to a high geothermal gradient in the vicinity (up to 5.6 °C/100m) that had been observed in former hydrocarbon boreholes targeting at Tertiary sediments. The target formation for the geothermal exploration was much deeper, namely the Donnersberg Formation (Permian). In 2016, a borehole of nearly 3700 m vertical depth was drilled. The cuttings of this formation consist of partly hydrothermally altered sediments and volcanic rocks. Samples of rhyolitic ash tuffs from the depth of 3500 – 3700m were selected for this study. XRD, XRF, TEM, FT-IR, and microscope investigations of thin sections were performed to characterize the mineralogical composition and formation of clay minerals as well as to estimate the levels of thermal maturity based on the rate of illitization of smectite.

Clay minerals (CM) composed of muscovite (1M and 2M1 polytypes), illite, illite-smectite interstratifications (IS-ml), chlorite, and non-clay minerals such as quartz and feldspars were detected. The 2M1-polytype might be the only original CM in the parent rock while the others occur as consequence of mineralization of Permian illite under hydrothermal conditions. The development of CM with illite and IS-ml particles observed by XRD and TEM indicates three mechanisms of illitization corresponding to three populations of secondary 2:1 sheet silicates (illite type).

In a first step, the volcanic tuffs were largely altered to Na-smectite. This phase transformed layer-to-layer to IS-R1 and IS-R3. Subsequently, the formation of CM shows the following scheme: rhyolite tuff → Na-smectite/or IS-R0 (d_{001} = 12–12.4 Å) → IS-R1 (d_{001} = 10.26 Å-10.1 Å) → IS-R3/or illite (d_{001} = 10.02 Å–9.9 Å). In TEM-investigation the crystals are found as platy, flake forms as well as lathlike and pseudo-hexagonal particles of illite 1M and 2M. In a second step, the appearance of euhedral crystals from 1Md and 1M illite polytypes is considered as result of dissolution-crystallization (DC) mechanisms. These crystals were newly formed by direct in situ precipitation from fluids in a very high thermal event and not by replacement of the precursor smectite. In thin-section and TEM-images fibrous and lathlike illite and IS-ml (1Md and 1M polytypes) show that the parent 2M1 platy muscovite and plagioclases crystals probably dissolved in places by hydrolytic reaction as result of a third step of alteration.

IS-ml from all samples are characterized by mixtures of IS-R1 (25-35% smectitic layers), IS-R3 (<10% smectitic layer), and illite. The modelling of diffractograms of oriented specimens shows a dominance of IS-R3 and illite (>80 wt.%) with IS-R1 as minor phases (<20 wt.%) and traces of chlorite (<5 wt.%). The high amount of IS-R3 indicates peak hydrothermal temperatures of smectite illitization between 200 and 230°C which are comparable to calculated temperatures from geothermal gradients of some shallower boreholes in the URG. In conclusion, the three populations of secondary illites detected can attributed to three thermal events that can presumably be correlated to Permian volcanism, Oligocene thermal paroxysm, and hydrothermal fluid migration.

Mineralogical Alteration of Fe-smectite in High Alkaline Solutions

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Bentonites play a significant role in different multibarrier safety concepts for long-term storage of high-level radioactive waste isolating and stabilizing canisters in the final repository. The demand for a long-term safety for such engineered barriers requests a better knowledge of possible mineralogical alteration processes in bentonite. Two Fe-smectites, Co Dinh clay from weathering products of serpentinized ultramafic rock in Vietnam and Rokle clay from weathered volcanic tuffs in Czech Republic, were percolated with either NaOH 1N or KOH 1N at a temperature of 60°C or overhead shaking at 20 rotations per minute, respectively, on a duration of 30 days and a solid-to-liquid ratio of 1 to 4 Mineralogical phase and chemical structure of 02 untreated materials and the 08 run products were characterized by X-ray diffraction (XRD), Fourier transmission infrared spectroscopy (FT-IR), transmission electron microscopy linked with energy dispersive X-ray (TEM-EDX), and scanning electron microscopy linked with energy dispersive X-ray (SEM-EDX).

The XRD indicated that the divalent cation in tetrahedral sheet of Fe-smectite was changed to monovalent cation after experiment runs. Calcite was detected apparently as a newly phases in XRD and FTIR. Co Dinh clay shows significantly less morphological changes than Rokle clay as observed in SEM. The TEM-EDX and SEM-EDX have shown that the Si enrichment and Si mitigation provoked in tetrahedral sheet of Rokle and Co Dinh clay, respectively. The alteration behaviour of two clays could explain by specific potential of dissolution of each clay as shown by Nguyen-Thanh et al. (2014). High amount of Fe in octahedral sheet will increase the sheet stress on the particles and therefore the higher rate of alteration can occur. This parameter is strongly related to the chemical structure which is a result of the original geological environment of the clay. Otherwise, the combination of smectitization and newly formed calcite could be more problematic than the illitization regarding the collapsed stacks welded together caused broaden voids in structure of Fe-smectite as previously reported by Pusch et al. (2007).

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Linking the properties of layered double hydroxides to their atomic level structure

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Layered double hydroxides (LDH), anionic clays, find application within, e.g., environmental remediation, catalysis and as energy materials due to their flexible chemistry and ion-exchange properties. Their general chemical composition is $[M(II)_{1-x}M(III)_x(OH)_2A_y$ $nH_2O]$, where the M(II) and M(III) cations include Mg(II), Ca(II), Zn(II), Ni(II), Al(III), and Fe(III). The interlayer anion, A, is needed for charge balance. The LDH properties and hence function is controlled by the choice of metal ions and anion. Especially, the distribution of metal ions in the cation layer has a large impact on the properties, but this information is difficult to obtain by diffraction techniques due the often poor crystallinity of LDH. Structural characterization of LDH from the atomic level to the bulk composition has been obtained by combining multiple experimental techniques (PXRD, solid state NMR, vibrational spectroscopy, electron microscopy and ICP), which has advanced our understanding of the atomic level structure of LDH.[1-4] It will be illustrated how detailed insight into the distribution of catalytic active Ni(II) in MgNiAl-LDH and 2D derived materials has been obtained. Furthermore, our characterization protocol allowed for preparation of the first pure $ZnAl_4$-LDH, a LDH obtained by insertion of Zn(II) into bayerite, following extensive synthesis optimization. Finally, the results from phosphate adsorption properties of LDH has been investigated towards the potential use of LDH for phosphate recycling from waste water.

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Virtual teaching on mineralogy, identification techniques and their crystallographic basis at the University of Granada

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Some representative tools for virtual learning, implemented and widely used by the students, at the University of Granada will be presented. Some of them form purely virtual courses, to be followed without face-to-face assistance. Others are offered as a complement to regular classroom courses. The preferred computer tool depends on each kind of learning. For theoretical master classes a Power Point presentation (the same used in the face-to-face classes) including audio explanations linked to the various figures and/or short notes, is perfectly able to reproduce the *in situ* lesson. In this way, the lesson can be completely reproduced at any time and at the personally proper rhythm of each student. The same tool may be adequate for some practical classes; however, when they imply the use of some gadget or handling, a plain video of the operation, with oral explanation, is usually preferred. These videos are publically available at the Youtube platform. They are frequently visited by a wide audience from outside the student community of the Granada University. The Power Points which use figures with copyright need to be restricted to enrolled students.

The material covers 1) Crystallographic concepts, as lattices, symmetry operators, point groups, crystalline systems, space groups and generation of structures from their atomic coordinates and space group. 2) Stereographic projection of crystalline solids 3) The use of the Wulf Net 4) Identification of space group and atomic coordinates of structures 5) Mineralogy basic concepts as metallic, covalent and ionic structures, silicate structures, solid solutions, polymorphism, polytypism, crystal nucleation and growth, twins, etc. 6) Physical properties of minerals and their tensor treatment. 7) Transmission Electron Microscopy (TEM) and related techniques 8) A lesson, at divulging level, about the main techniques used in mineralogy.

Preferred format: Oral

Session number and name: E1. Teaching clay science

Formation of low-crystalline magnesium silicate at Kamuikotan metamorphic belts, Hokkaido, Japan

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Magnesium silicate formation at ambient temperature has been receiving a lot of attention in various engineering fields including CO_2 geological storage. When CO_2-rich brine in a CO_2 reservoir dissolves mineral in the reservoir rocks and caprocks, as well as cement constituting wellbore, magnesium silicates may be precipitated as secondary minerals from the brine besides carbonate minerals (Carroll et al., 2011). Although some experimental studies (e.g., Nied et al., 2016) suggested that a magnesium silicate mineral precipitated at ambient temperature is low-crystalline, the magnesium silicate formation in nature has not been studied well. Therefore, its formation conditions and geochemical properties have not been clarified yet. In this study, we collected precipitates from the surface where fluid flows out from serpentinite rocks around Kamuikotan metamorphic belts, Hokkaido, Japan to investigate whether a low-crystalline magnesium silicate is formed at ambient temperature in nature.

Although a clear X-ray diffraction pattern was not observed from the bulk precipitate samples, electron microscopic observation (Field emission scanning electron microscope and transmission electron microscope; TEM) clearly identified mineral phases including aragonite, a calcium carbonate mineral. Electron diffraction with TEM showed diffuse halo rings from some particles in the samples, showing the formation of low-crystalline phase. TEM-energy dispersive X-ray spectrometry indicated that the low-crystalline phase was composed of Mg, Si, and O. The chemistry of the fluid collected from surface is alkaline ($9.50 \leq pH \leq 10.67$) and saturated with respect to a magnesium silicate hydrate (Lothernbach et al., 2018). Although the fluid is also supersaturated with aragonite, aragonite was only observed in one sampling point at which the water was also supersaturated with monohydrocalcite. Since monohydrocalcite is thought to be a precursor for aragonite, monohydrocalcite can transform into aragonite in the site.

This study demonstrated the formation of a low-crystalline magnesium silicate interacting with alkaline fluid and coexisting with carbonate mineral in nature. This presumably supports to understand mineral-water interaction in the Mg-Si-H_2O systems for CO_2 storage and the other engineering fields such as enhanced oil recovery, geothermal power generation, concrete degradation, mineral clogging in radioactive waste disposal, and contaminated soil remediation.

Photoluminescent Cu nanoparticles induced by energy transfer on saponite nanosheets

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Observation of plasmonic photoluminescence (PL) of metal nanoparticles (NPs) has historically been investigated in films [1], but has scarcely been reported in dispersion, probably because distance between adjacent NPs is too far, one of which can not enhance the plasmonic PL of the other. We herein propose usage of Cu NPs synthesized directly on saponite nanosheets [2]. In this nanocomposite (Cu−Sapo), it may be possible to excite the immobilized Cu NPs efficiently by energy transfer from a cationic dye, focusing on photofunctionalization on the nanosheets or in the interlayer space [3]. In the present study, the plasmonic PL of Cu−Sapo was investigated by using acridine orange (AO) as the energy donor. We call this nanocomposite (AO,Cu)−Sapo, hereafter.

The PL spectral intensity of (AO,Cu)−Sapo was decreased compared to that without the Cu NPs when AO was excited, indicating PL quenching of AO by the Cu NPs. In addition, a broad band was observed around 570 nm assignable to the plasmonic PL of the Cu NPs, which was further confirmed by temperature dependency on the PL spectra, as shown in Fig. 1(a). The spectral intensity got higher as increasing temperature, characteristic of the plasmonic PL of the Cu NPs [4]. Thus, it was found that the Cu NPs showed the plasmonic PL by the excitation of AO. The energy transfer was investigated by the PL spectra measured at different [Cu NP], as shown in Fig. 1(b). The 530-nm band assigned to AO monomer was decreased at high [Cu NP], and the 510- and 545-nm bands were observed clearly. The former was assingned to AO dimer and the latter was red-shifted at higher [Cu NP] due to the plasmonic PL band. Therefore, it was concluded that the energy transfer from AO monomer to the Cu NPs took place, followed by the plasmonic PL.

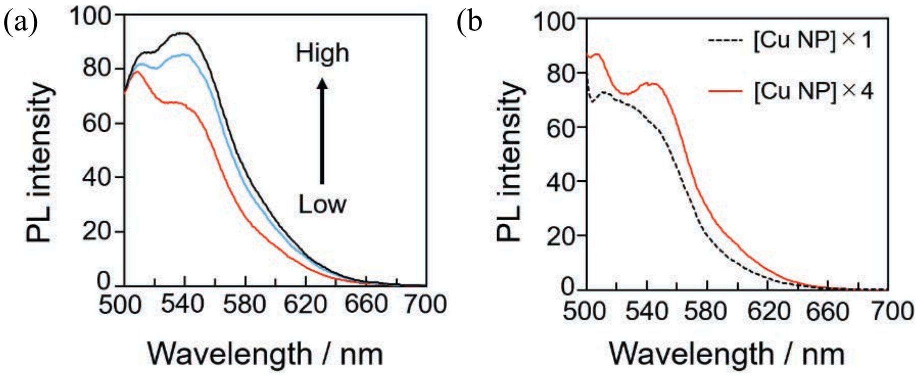

Figure 1. PL spectra (a) at different temperatures and (b) at different [Cu NP],

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Computer simulation of mechanical properties of kaolinite nanotubes with different orientations

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Previous experimental results have shown several different orientations of kaolinite nanotubes (scrolls, rolls, curlings). In order to predict the contribution of these different nanotubes in composites to the total mechanical performance, molecular simulation method was adapted to investigate the mechanical difference among these nanotubes. The nanotube models with six orientations and radius range from 2 nm to 14 nm were constructed. The following calculations showed that the formation energies of these tubes could be divided into two different kinds; the Young's modulus of nanotubes gradually decreased with the increase of radius then reached to a balance. Moreover, the absolute values of Young's modulus were clearly different for various orientations. The difference revealed here should be considered when evaluating the failed strength of composites including kaolinite nanotubes in practical applications.

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Thermal constraints on clay growth in fault gouge and their relationship with fault zone evolution: Case study of gouges from granitic rock in central Japan

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Faulting in brittle regimes often results in the development of fine-grained, clay-rich fault gouge. Wide-ranging studies of a fault gouge including structural, mineralogical, geochemical and chronological analyses can assist in reconstructing the history of fault activity. In this study, X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM) observations and K–Ar dating were performed on fault gouge samples from the Kojaku Granite of central Japan to elucidate the process of mineralization of clay minerals in fault gouges and their relationship with fault zone evolution. The area studied is suitable for understanding thermal constraints on clay mineralization because meso- to microscopic structures of the fault zones are well studied, and the wall rock is homogeneous and its thermal history well defined. The three increasingly fine fractions (<0.1, <0.4, and <1 µm) were separated for each sample. The XRD results indicated that the clay minerals in the gouge samples were dioctahedral smectite, kaolinite, and 1*Md* illite. Major K-bearing minerals in the gouges were K-feldspar and 1*Md* illite. K-feldspar decreases in abundance as the size fraction decreases, and most of K-bearing minerals in <0.1 µm fraction are 1*Md* illite. According to the TEM observations, lath-shaped particles identified as 1*Md* illite were visible in the <0.1 µm fraction. K–Ar dating showed younger ages in finer fractions. The K–Ar age for the <0.1 µm fraction indicated that the low-temperature alteration leading to the production of 1*Md* illite was dated to ~40 Ma. Based on the cooling history of the host rock granite constrained by fission-track, U–Pb, and K–Ar dating methods, the 1*Md* illite formed at temperatures of 60–120ºC. This temperature range was at the lower limit of the range reported in previous studies for faults. The results of XRD and K–Ar analyses, as well as structural analysis, suggest that the fault zone has not experienced tectonic activities associated with significant high-temperature thermal event since the 1*Md* illite production at *ca.* 40 Ma. In addition, the K–Ar ages have not been reset by fracturing due to recent near-surface fault activity.

Iron oxides formed in an experimental forest fire related to the presence of hematite and maghemite in Weichselian sediments in Denmark

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In a number of areas formed during the late Weichsel period, we find iron oxides as hematite and maghemite along with goethite and ferrihydrite in the upper 20 cm topsoil. The soils have an iron content as high as 8-40% which cannot be related to conventional soil formation. Most likely, this has to do with precipitation of iron oxides formed in wells where groundwater-containing Fe^{II} , released to the water by oxidation of pyrite in Tertiary sediments, meet the atmosphere. In that scenario, ferrihydrite and possibly goethite is precipitated. This, however, does not account for the content of hematite and maghemite in the mixed topsoil material, which is an unresolved puzzle. Hematite and particularly maghemite would normally not be expected to occur under the temperate humid Danish climate, but be interpreted as the result of high temperature as found in tropical areas or after forest fires. However, a body of evidence argues against these sites having been exposed to fire. In an attempt to get closer to an explanation of this iron mineralogy, an experimental forest fire was produced. The results showed a clear mineralogical zonation down to 10 cm depth. This was not observed at the natural sites, which contained a uniform mixture of goethite/ferrihydrite, hematite and maghemite down to 20 cm depth. The experimental forest fire furthermore left charcoal and ashes at the topsoil, produced high pH and decreased organic matter content, all of which is in contrast to the natural sites. Physical and chemical date as well as XRD, Mössbauer spectroscopic data and TEM micrographs from the sites will be presented. The conclusion from this work is that the mineralogy of these sites is not consistent with exposure to fire, but may rather result from long term transformation within a reducing environment, possibly involving microorganisms.

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Hybridization of titania with clay minerals as photocatalysts

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Titanium dioxide (TiO_2) is a well-known wide band-gap semiconductor with a variety of application as white pigment, catalyst, and so on. In addition to the on-going application, the advanced materials' application of TiO_2 has been reported taking advantages of such characteristic features of TiO_2 as the natural abundance, chemical stability, and non-toxicity. Designing the composition (including heteroelements' doping) and the morphology (nano-particles, film etc.) has actively been done for the modification of their intrinsic electronic/optical properties. The hybridization with various materials including fabrics and membranes has been done for practical applications. As a way of the development of such TiO_2 based advanced materials, the hybridization of TiO_2 with various nanomaterials has been done toward the sophisticated hierarchical structural design.[1,2]

The complexation of TiO_2 species with clays and clay minerals has been investigated for possible applications as catalyst. Taking advantages of the natural abundance and eco-friendly nature of clay minerals, various hybrids have been synthesized from clays and clay minerals.[2] The state, the size and the shape of the TiO_2 particles (or domains) as well as the hierarchical structure of the hybrids are thought to be key factors to control the functions of the resulting hybrids. TiO_2 species have been complexed with clays and clay minerals as isolated molecular species and oxide nanoparticles. Several molecular or polymeric precursors have been employed with varied synthetic conditions to control the materials characteristics. In this paper, the preparation, the characterization and the photocatalyst functions of the hybrids composed of TiO_2 with synthetic smectites will be discussed.[3-6] The hybrids were used as photocatalysts in aqueous suspension as well as film. The film was successfully applied to construct photocatalytic flow reactor.[4] The reaction selectivity is controlled where clay minerals played a role.[7]

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New opportunities for drug delivery carrier of natural allophane nanoparticles on human lung cancer A549 cells

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Clay minerals are mainly used around traditional cosmetics and industrial products, but currently their target application is continuously expanding into pharmaceutical industry and tissue engineering. To broaden the knowledge of *in vitro* cytotoxicity of allophane nanoparticles against human cancer cells, the cytotoxicity of both natural and synthetic allophane nanoparticles for cultured human alveolar basal epithelial (A549) cells was examined. For both natural and synthetic allophones, the A549 cell viability was maintained at > 70% for concentration up to 3160 μg/mL, implying higher biocompatibility of allophane nanoparticles as compared with that of hectorite nanoparticles. The cell adhesion kinetics coupled with cytotoxic characteristics against A549 cells was analyzed using quartz crystal microbalance (QCM) technique to distinguish the dynamic cell adhesion signatures.

In addition, the complexation of allophane nanoparticles with cisplatin, *cis*-dichlorodiammineplatinum (II) (CDDP) to deliver platinum prodrug into cancer cells was investigated. Using A549 cells, profound studies including cellular uptake (endocytosis) analysis of allophane nanoparticle, cell cycle arrest abilities and apoptosis induction profiles were discussed in detail. As well as the features against A549 cells to emerge a promising strategy to enhance their anti-cancer activity and to mitigate side-effects were discussed.

Role of mineralogy, chemistry and surface properties of different zeolitic materials synthesized from perlite by-product on retention of selected elements from soil pore water.

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Specific porous structure of zeolites is responsible for unique physico-chemical properties such as high cation exchange capacity, cation selectivity and molecular sieving, ability to adsorb gases and vapors, low density and large void volume. Due to these properties, zeolites are considered as an effective adsorption materials with high pollutant removal efficiency. The fine powdered perlite (FPP), a by-product of processing of raw perlite from the Lehôtka pod Brehmi deposit (Slovak Republic), was used in the present study for zeolite synthesis. FPP has very limited application (only as a partial replacement for cement in concrete). The conversion of FPP into zeolites is proposed to recover this by-product and to obtain value-added material (i.e. zeolites). Synthesis conditions (temperature, time, NaOH concentration) had strong effect on the quantity, crystallinity, crystal size, morphology and type of synthesized zeolites. As volcanic glass alteration proceeded, crystallization of zeolites having a lower Si/Al ratio was favored. Phillipsite, zeolite P and X rich materials were synthesized from FPP. The highest-grade zeolitic material contained 77 wt% of zeolites, 16 wt% of unaltered volcanic glass and 7 wt% of accessory minerals. The synthesized zeolitic materials displayed hierarchical porous structure, associated with different pore sizes of zeolite channels, zeolite crystallites and aggregates. Some of the zeolitic materials reached $S_{BET} = 324\ m^2/g$, $V_{micro} = 0.170\ cm^3/g$ and CEC = 371 meq/100g. The sorption efficiency of synthesized zeolitic materials was tested using a set of time-dependent batch adsorption experiments. In order to simulate potential real-scale scenario, soil pore water (SPW) obtained from highly metal-contaminated alluvial soil from Příbram District (Czech Republic), polluted by historical mining and smelting activities (mainly by Zn and Pb), was used as a testing solution. The impact of different contact time (10 min – 24 h), pH (2 – 12) and sorbent properties (distinct quantity and type of zeolite, CEC, S_{BET} and V_{micro}), on the concentrations of Pb, Zn, Cd, Mn, Mg, Ca, Na, Sr, Ba, Si in the SPW was investigated.

The authors are grateful to the VEGA (1/0196/19) and APVV (APVV-0339-12) for funding this research.

Adsorption and photostability of tetracycline onto different clays

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Photodegradation is one of the major ways of the degradation of drugs [1]. Tetracycline (TC) is a well-known antibiotic and is extensive use in the therapy of human and animal infections, but its light stability is still poorly studied [2]. The objective of this work was to investigate the photostability of the tetracycline incorporated onto smectite and fibrous clays such in a mixture of the montmorillonite and saponite (Veegum©) purchased from Vanderbilt Company (USA) and palygorskite pharmasorb colloidal© purchased from Basf (Germany). Adsorption experiments was performed in 50 mL of TC aqueous solution (2 g L^{-1}) mixed with 100 mg of each clay sample under stirring for 1 h in controlled pH. Light stability tests were performed by exposing of the samples to UV light for 200 h. The adsorption behavior of the antibiotic molecule onto different clays was investigated. Drug/clay systems were characterized by carbon elemental analyses, N_2 adsorption/desorption isotherms, X-ray diffraction and thermogravimetric analyses. The loading of TC onto clays decreased specific surface area of samples also total volume pores and suggested that the pores were blocked due incorporation of the organic molecule into raw clays [3]. XRD results showed the intercalation of the tetracycline in the interlayer spacing of the layered clays [4]. In fibrous clay, the drug was possibly located in the exterior surface, the grooves and the entrances of the channels of this structure [3]. Among the analyzed systems, the tetracycline incorporated in mixture of the montmorillonite and saponite clay minerals presented higher stability under UV light.

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Clay minerals and ionic liquids or humic acids composites for applications in wastewater treatment

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In the last two decades, most studies have concentrated on using organoclays to remove organic and inorganic contaminants from wastewater and soil. Organoclays are prepared by intercalating specific organic molecules in the interlayer space of a clay mineral through an ion exchange reaction. The surfactants, known as quaternary alkylammonium salts, are the most commonly used organic compounds for the preparation of organoclays. However, cationic surfactants, such as, hexadecyltrimethylammonium bromide and octadecyltrimethylammonium bromide can be environmentally hazardous.

Ionic liquids are organic salts (mainly phosphonium and imidazolium salts) in liquid or solid form at room temperature and with melting points below 100°C. Ionic liquids are a new alternative to the cationic surfactants, because they are less toxic and with better thermal stability than the alkyl ammonium cations. Whereas, humic acids are high-molecular weight polycationites which results from long-term physical, microbial and chemical transformations of organic debris.

The research aim was to prepare environmentally friendly clay sorbents for applications in wastewater treatment. Imidazolium based ionic liquids with different alkyl chain lengths and extracted humic acids from peat were separately used for modification of clay minerals. The properties of the clay composite materials were studied using x-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and thermogravimetric technique. The sorption of contaminants, such as, dyes and pharmaceutical substances from aqueous solutions onto the modified clays was studied using batch sorption experiments.

Results indicated that ionic liquids and humic acids can be used as environmentally friendly and less toxic compounds for clay modification thus obtaining an effective sorbent for the removal of organic pollutants from wastewater. Furthermore, currently humic substances from different sources are produced in quantities of tons and can be considered as a low cost natural material.

This work was supported by Latvia Council of Science Council of Latvia for providing a grant "Properties and structure of peat humic substances and possibilities of their modification" lzp-2018/1-0009.

Preparation and characterization of natural anthocyanin and montmorillonite composites

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Anthocyanins (in Greek *anthos* - flower and *kyanos* - blue) are the largest group of water-soluble natural pigments visible to the human eye. Anthocyanins belong to widespread class of phenolic compounds named flavonoids that are responsible for orange, pink, red, violet and blue colors in flowers, fruits and leaves of vascular plants. Anthocyanins have physiological properties - antioxidant activity, which plays a vital role in the protection against many diseases, such as cardiovascular illnesses, cancer, diabetes and other degenerative disorders. However, practical applications of anthocyanins are limited by their instability under several conditions such as pH changes or light irradiation. The research aim was to intercalate anthocyanins from the *Vaccinium* species berries into montmorillonite to enhance the stabilization of anthocyanins and evaluate potential application in biomedical, food and biocosmetic industries. The properties of the montmorillonite-anthocyanin composites were studied using x-ray diffraction, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric and other techniques. Obtained results indicated that intercalation of anthocyanins into the galleries of the clay minerals enhances their stability and can be used, for example, as environmentally friendly colorants in the food industry and biocosmetics or as enterosorbents in biomedicine.

The work of L.Klavins was supported by scholarship provided by “Mikrotikls” LTD, administered by the Foundation of University of Latvia.

Colloidal properties of imogolite nanotubes

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Significant developments have been proposed over the last decade on the synthesis of imogolite-like nanotubes such as germanium-based nanotubes $(OH)_3Al_2O_3GeOH$ (Ge-INT) [1] or hydrophobic methylated $(OH)_3Al_2O_3Si_xGe_{1-x}CH_3$ nanotubes [2]. These recent achievements have paved the way for novel INT nanostructures with fine control of their morphologies and properties, which could find applications in a wide range of domains, including stimuli-responsive porous materials, photocatalysis, molecular separation or storage [3]. For most of the intended applications, a prerequisite remains the control of nanotubes arrangement. We have recently evidenced that the positive surface charge of imogolite can be used to control nanotubes bundling by anion condensation [4].

Here, we propose an experimental fresh look on the colloidal properties of INTs, by exploring the effect of ionic strength (IS) in samples of synthetic double-walled (DW) Ge-INTs. Surface charge properties are assessed thanks to electrophoretic measurements, revealing that their outer surfaces are positively charged up to high pH values. Different suspensions have been prepared at fixed IS by osmotic stress to scan the volume fraction/IS phase diagram. Optical observations and Wide Angle X-ray Scattering (WAXS) experiments allow us to unravel different domains for nanotube organization. At low ionic strength (IS $\leq 10^{-2}$ mol.L^{-1}), Ge-DWINTs are fully dispersed in aqueous suspensions while they form an arrested (gel) phase above a given concentration threshold. By contrast, higher salt concentrations induce aggregation phenomena with the progressive formation of small bundles in suspension. These results are completed by using Small-Angle X-ray Scattering (SAXS) experiments to assess correlations over large distances. The swelling laws derived from the interparticle distances obtained by SAXS display a transition from isotropic swelling at low volume fractions to 1D swelling at higher volume fractions. The combination of these data with optical observations allow us to propose the first phase diagram for the colloidal assembling of metal oxide imogolite nanotubes.

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Synthetic imogolite nanotubes: a flexible building block with multipurpose applications

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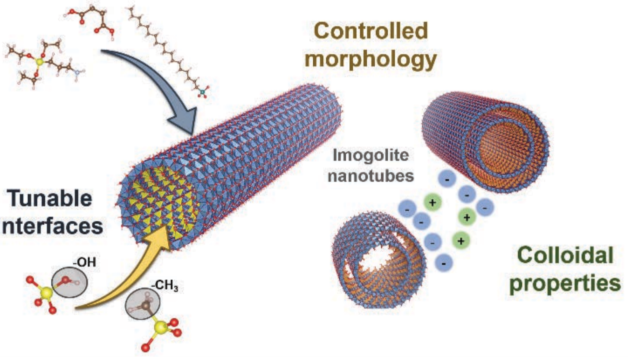
Hollow cylinders with a diameter in the nanometer range are carving out prime positions in nanosciences. Thanks to their physico-chemical properties, they could be key elements for next-generation nanofluidics devices, for selective molecular sieving, energy conversion or as catalytic nanoreactors. Some challenges such as fine diameter and interface control are solved for imogolite nanotubes (INTs). Belonging to clay minerals, imogolite exists in its natural state but widely dispersed in environment, thus limiting its applications. The major breakthrough for using INTs was certainly their synthesis by sol-gel methods under mild conditions [1].

We will first focus here on the recent developments of INT synthesis, particularly in terms of morphological control [2] and surface functionalization [3]. We will show that it is now possible designing innovative INTs with modular interfaces in a predictive way, which has recently led to some progress in the field of imogolite-based functional materials (nanocomposites, stimuli-responsive materials, (photo)catalysis, molecular separation and storage…) [4-5]. It is interesting to note also that most of the applications explored up to now do not fully exploit all properties (controlled morphology, tunable interfaces and colloidal properties) of these peculiar nanostructures. The latest advances in the synthesis of INTs open up new perspectives in particular by combining the well-defined morphology of INTs with their ease to self-organize to produce novel nanocomposites or artificial ion channel devices [6].



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Influence of dry grinding on the structure of dioctahedral and trioctahedral smectites and organo-modified smectites

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Structural modification of various smectites upon dry grinding was evaluated with the aim to study the influence of: a/ smectite type on the extent of structural changes, b/ type of organic cation exchanged to the smectites.

Four different smectites, trioctahedral hectorites - synthetic Laponite RD (Lap) and natural SHCa and dioctahedral montmorillonites (Mt) – Kunipia (K), Jelšový potok (JP). In addition, organo-exchanged montmorillonite was prepared using four organic cations: tetraoctyl- and tetrabutyl-ammonium (TBA, TOA) and -phosphonium (TBP, TOP).

Scanning electron microscopy (SEM) analysis indicated significant changes in morphology of particles from more compact “platy-like” observed for initial clay minerals to smaller grains of various shapes. Thermal analysis coupled to mass detector was employed to compare the rate of structural alteration of montmorillonites and hectorite. While DTG profiles of montmorillonites ground for 6 min did not show any clear effect due to the mass loss of hydroxyl groups above 500°C, the presence of DTG peak and the corresponding maximum detected in the profiles of mass 18 ions, corresponding to the H_2O evolution, was confirmed for hectorites. Shift of the absorption bands and decrease in the bands intensities in the IR spectra confirmed the extensive amorphisation of studied samples after treatment for 6 min. The absorption bands assigned to structural OH groups were not detected in the spectra of JP. On contrary, the IR spectra of trioctahedral Lap clearly showed the presence of the both, νOH and δOH vibrations of structural OH groups. This may indicate that the structure of hectorites is less affected by grinding than structure of Mt.

Organo-montmorillonites subjected to mechanical treatment showed higher stability of the structure compared to initial sample. While the IR spectra of un-modified smectites undergone pronounced alteration in the bands positions and intensities reflecting the extensive structural changes, the presence of organic cations preserved structure of smectites diminishing thus changes in the spectra profiles. The bigger organic cations used for modifications, the higher resistance to mechanical treatment was observed.

The authors acknowledge financial support from the Slovak Grant Agency VEGA (project No. 2/0132/13), Slovak Research and Development Agency (project Nos. APVV-15-0741 and APVV-15-0347).

Laponite® derived porous heterostructures for hydrogen production

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The environmental problems and the need to improve air quality enforce the development of the efficient systems to produce clean and high energy content sources. Particularly hydrogen energy attracts much attention. The hydrogen is mostly extracted from natural gas, coal and liquid hydrocarbons but production using the catalytic steam reforming of biomass-derived liquids such as bioethanol is being intensively investigated. In this study our attention was mainly focused on the application of rarely used clay minerals to develop the new eco-friendly materials active in H_2 production. We have shown that formation of hybrid structures merging the properties of crystalline clay mineral and amorphous mesoporous silica in porous clay heterostructured composite (PCH) and its further functionalization with Fe species can serve as a very promising approach in design of unique nanoscale structures for H_2 production. Laponite®, the synthetic clay mineral with silicon as central atom in tetrahedral sheets, and magnesium as dominant central atom in octahedral sheets, with a small 25 nm plate-like particles provided suitable nano scaffolding on which the amorphous-crystalline composite was created. Basing on the ion-exchange ability of the layered magnesium hydrosilicate and the use of surfactant templated method the amorphous silica was formed between the galleries of Laponite®. It resulted in expanding of the interlayer distance of clay and developing the surface area with channel like structure. The metal-organic $C_6H_5FeO_7$ and inorganic $Fe(NO_3)_3$ Fe-sources were used for functionalization of all supports to obtain after calcination or autoclaving the materials with Si/Fe ratio equal 10. In this study we compared the development of active Fe species on the extended surface of three types of supports: clay derived and purely siliceous (MMS-41 or SBA-15 type). The effects of FeO_x formation and their nature on the support surface via tuning the preparation methods and the role of clay in H_2 production were investigated by XDR, SEM, FTIR, H_2TPR, methods and advanced XPS, ^{57}Fe Mössbauer technics. All catalysts after functionalization exhibited high specific surface area ~400m^2/g. Detailed analysis indicated the nanocrystalline structure of the surface Fe species crystallizing into Fe_3O_4 or α-Fe_2O_3 after calcination. The use of autoclaving ensured better dispersion of FeOx nanostructures on the surface of clay derived supports, while induced the formation of more crystalline structure of oxides on the surface of siliceous MMS-41 or SBA-15 supports. The slight dissolution of Mg^{2+} cations from the octahedral sheets of clay mineral as a result of PCH network impregnation at low pH or pressure treatment induced slightly basic character of the composite surface, what affected the steam reforming of ethanol. In contrast to purely siliceous supports functionalization of PCH structure resulted in generation of three types of centres active in H_2 generation. Besides redox centres (FeO_x oxides) and oligomeric Fe species generated some acidity, highly beneficial was development of basic centres resistant mainly toward coke formation, which raised the yield of H_2 production to 65% in 550°C while on siliceous support it didn't reached 40%.

Flow agents for calcium-free binder systems

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The properties of mortars and concretes in the fresh state with the addition of calcined clays are decisively influenced by the physical properties of the meta-clays. The substantially higher water demand significantly influences the workability and requires effective superplasticizers in order to be able to process concretes and alternative binder systems such as geopolymers in practice. The biggest problem with binder systems with calcined clays is the high water demand due to the high specific surface of the meta-clay (BET 15-20 m^2/g). While fly ash with a specific surface of approx. 1 m^2/g can be used to produce processable binders with a lower water content, meta-clays require large quantities of mixing water in order to achieve a processable consistency. Since, in contrast to cements, only small amounts of water are bound in hydrate phases, too much mixing water leads to pores and bubbles in the hardened binder, which leads to a drop in strength and durability. One way to reduce the water requirement is to use liquefying admixtures. For cementitious systems, high performance plasticizers such as polycarboxylate ethers (PCE) are state of the art. The suitability of PCE for meta-clay-based alkaline activated systems has not yet been comprehensively investigated.

In this study, rheological investigations were performed on geopolymer binder systems consisting of metakaoline activated with potassium water glass. The aim was to find suitable additives that increase the flowability of the binder system while maintaining the w/b value of 0.5. The dispersing performance of superplasticizers from the cement industry (PCE and polycondensates) were investigated. In addition, novel anionic and cationic superplasticizers based on starch were synthesized and their flow properties characterized in the geopolymer binder system. In addition to the flow effect, it was investigated whether the addition of superplasticizers influences the reaction mechanism of the binders. For this purpose, calorimetric investigations were carried out and the hardening process was determined by ultrasonic velocity measurements. In order to characterize the mechanism of the flow effect, adsorption experiments were carried out using the phenol-sulphuric acid method for the starch-based flow agents. Furthermore, fresh and solid mortar investigations were carried out. In addition to the determination of the influence on the air content and the spread size of the mortar, the influence on the porosity as well as compressive and flexural strength was recorded.

While the commercially available superplasticizers for cementitious systems in the geopolymer binder system cause almost no flow effect, the starch-based superplasticizers showed a remarkable liquefaction of the binders. Especially the cationic superplasticizers showed the highest dispersion performance. In addition to improved workability, the mechanical properties such as compressive strength and flexural strength were also improved by the starch-based additives.

Effect of various nano-clays on structural and mechanical properties of fly ash-based geopolymers

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In the present study, the effect of three different nano-clays; untreated halloysite, calcinated halloysite and metakaolin/halloysites blend were investigated on the mechanical and structural properties of fly ash based geopolymer mortars. Nano-clays were incorporated into the geopolymer mortars at different dosages of 2 wt%, 5 wt% and 10 wt%. The physicochemical properties of the raw materials and geopolymer mortars were investigated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) as well as compression and flexural testing machines. The results showed that a water/solid ratio of 0.37 gives the best compressive and flexural strength and addition of 2 wt% of halloysites was the optimum amount to increase the flexural strength of the geopolymer mortar whilst a 2 wt% of metakaolin/halloysite (75/25) blend was the optimum amount to increase the compressive strength of geopolymer mortars. FTIR analysis indicated that the addition of nanoclays results in a more complete geopolymerization reaction in the geopolymer mortar while XRD observations showed that calcinating halloysites at 750 °C causes the halloysites to transform to an amorphous state. Microstructural results illustrated that adding nano-clays reduces the porosity on the fly ash surface by having geopolymerization occur around the nano-clays instead of the fly ash particles.

Using halloysite nanotubes in fabrication of sustainable cementitious composites for construction and building applications

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Concrete is one of the most widely used building materials in the world. Not only it is strong and durable, the raw materials in making concretes are relatively cheap and can be molded into various shapes. Cement is the main ingredient in making concrete and the main contributors of carbon dioxide. In this research, pure and composite cement paste samples were prepared according to ASTM C305-14 standards. Lightweight composites such as halloysite nanotubes (HNT), metakaolin (MK) and calcined halloysite (HNT-MK) were used as a partial substitution for cement to reduce the consumption of Ordinary Portland cement (OPC) and at the same time producing lightweight concrete without neglecting its durability and strength. Kaolinitic clays are abundantly & ubiquitously available to produce MK. Production cost for MK is cheaper and more sustainable thorough energy saving. Greenhouse-gas emissions produced is 55% lesser than OPC, this is mainly because cement requires 2000°C while MK requires 800°C to be used in cement paste. Compressive and flexural strength tests were carried out for three different curing ages and FE-SEM was performed to observe the interaction between nanofillers and cement matrix. Samples that were subjected to vibration had better dispersion of these nanofillers and at the same time reducing cavities within the cement paste. From the result, partial replacement of OPC with MK can increase flexural strength and the influence of MK with OPC was more apparent than the use of HNT or HNT-MK in terms of mechanical strength.

Profile Refinement for XRD Analysis of Illite-Smectite Interstratification in Clays from Athabasca Oil Sands

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The presence of illite-smectite (I-Sm) interstratification in oil sands clays is often overlooked due to its minor abundance. It cannot be easily observed by routine XRD analysis using random powder mount preparation. In this work, two estuarine ores (E3 and E7), two marine ores (M13 and M18) ores, and solids from bitumen froth (F1) were analyzed. XRD patterns were collected on oriented mount specimens prepared from Ca-saturated <2 µm clay suspensions separated from these samples, then air dried (AD) at controlled 54% relative humidity and treated under ethylene glycol (EG) solvation. The illite 001 reflections observed in XRD patterns of AD specimens all showed a very broad and asymmetric shape with a low-angle-side shoulder, and became sharper and more symmetric after EG solvation, which is characteristic of I-Sm interstratification. Profile fitting for the whole angular range of the measured XRD patterns was performed using TOPAS 6.0 program. Diffraction lines with split-Pearson-VII (SPVII) line shape were used to fit the experimental profiles of each illite and kaolinite 00*L* reflections observed in the XRD patterns. Rietveld refinement with standard crystallographic models was used to fit the diffraction peaks from minor amounts of associated minerals such as quartz and chlorite, which were present in the separated clay samples. This profile refinement approach models precisely, to within counting statistics of measured diffraction intensities, the experimental profiles of all observed illite and kaolinite 00*L* reflections, for XRD patterns from both AD and EG preparations. It also overcomes peak-overlapping issues between kaolinite and chlorite, and of illite with quartz, allowing integrated-intensity (*I*) areas of individual 00*L* reflections from illite and kaolinite to be accurately determined. In turn, using the integrated-intensity areas from SPVII diffraction lines refined for (001) and (003) illite reflections from AD and EG preparations, the degree of expandability owing to the presence of swelling (smectite) layer in the I-Sm component may then be directly quantified using the intensity ratio method [1–2]. Degree of expandability of the interstratified I-Sm component was found to be relatively higher in marine ores compared to estuarine ores while that of the clay solids from bitumen froth was in between these two sets of values. This correlates well with batch-extraction unit bitumen recovery measured previously [3]. Our aim is to apply this methodology to a larger number of samples, including oil sands ore and related process streams, in order to precisely evaluate the effect of the presence of I-Sm interstratification on bitumen recovery, product quality and tailing management.

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Kinetics of cesium sorption on Ca-illite: experiments and modelling

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Understanding chemical adsorption and desorption phenomena is essential to predict radionuclide mobility in the environment. Previous studies evidenced that cesium adsorption/desorption processes on illite depend on time and on cesium concentration. Moreover, Cs adsorption on illite is often reported qualified as irreversible. By consequence, kinetics and potential adsorption process irreversibility will impact on Cs migration through soil and constrain its predictability. In order to improve reactive transport model applied to Cs, a kinetic study has therefore been conducted on Ca-illite using batch experiments. Ca-illite was exposed to four initial cesium concentrations at eight different contact times (from 5h to 528h). Desorption experiments have also been conducted to study the reversibility of cesium sorption on illite in these experimental conditions. Results evidenced that Cs adsorption on illite may be described with four different sorption sites, each of them with their own properties (exchange capacity and affinity). This way, a low exchange capacity and high affinity site was invoked to explain the Cs sorption at low concentration (10^{-6} M). A reversible adsorption process was shown even at low concentration in our experimental conditions. Different kinetics rates were found for adsorption and desorption. At the lower initial cesium concentration, desorption expresses a lower rate than adsorption. Sorption behavior, described with a multi-sites ion exchanger model, led to elaborate different kinetics models, taking into account adsorption and desorption. Two three-sites kinetics models were developed as follows:

$$\frac{dC_s}{dt} = (k_1^+ CE_1 + k_2^+ CE_2 + k_3^+ CE_3)C_{aq}(t) - (k_1^- + k_2^- + k_3^-)C_s(t)$$

Where C_s is the adsorbed cesium concentration, C_{aq} is the cesium concentration in solution, k_i^+ is the adsorption kinetics constant and k_i^- is the desorption kinetics constant for site *i*. The two models differ in the site's definition which is based on the sorption contribution for the first, and on the exchange capacity for the second. Both models indicate different kinetics parameters attributed to each site but refer to comparable trends. A four-sites model has also been tested with kinetics parameters differing for each site and following the order of site contribution and site affinity but following the opposite order of site size.

Mineralogical controls on Earth's climate

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Redox active iron and manganese (hydr)oxides are some of the most reactive minerals in the clay sized fraction of soils and sediments. Through coupled sorption and oxidation reactions they can exert a first order control on the abundance and distribution of trace elements in the terrestrial and marine environment, and in particular, they can control the concentration and speciation of several important macro and micro nutrients. These nutrients are essential for life and their bioavailability regulates photosynthetic activity, which in turn regulates the drawdown of atmospheric carbon dioxide and ultimately climate. The processes governing the bioavailability of nutrients in the environment are complex but in many cases soils and sediments provide an important sink for these bioessential elements, locking up nutrients with iron and manganese (hydr)oxides. Investigating the processes by which trace elements become locked into these minerals, and whether trace elements are retained or released by these minerals as they age and change with time, is critical to understanding the role of soils and sediments in the carbon cycle and climate. This talk will use case studies from our work to introduce the importance of trace elements in the Earth system, the importance and peculiarities of iron and manganese (hydr)oxides, the processes by which trace elements are scavenged by these intriguing phases, and what happens to trace elements as these phases change during diagenesis. We will see that the global scale cycling of trace elements is governed by molecular scale interactions between trace elements and minerals.

Production of ketones derived from fatty acids using a layered double hydroxide catalyst derived from waste-material: An efficiency and parameters comparison study

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A promising alternative to address the use of petroleum oil as a raw material for the generation of a diverse portfolio of chemical commodities is the use of biomass. Different strategies have been studied to transform oils and sugar extracted from biomass to bio-derived synthons as ketones and alcohols. In the present work, lauric acid, a 12-chain fatty acid and the main constituent of coconut oil, a well-known and largely consumed oil, can be efficiently deoxygenated following the route of ketonic decarboxylation in the presence of a solid base layered hydroxide/mixed metal oxide catalyst to form ketones. However, many catalyst materials are not prepared from sustainable routes. Here, we use a circular economy approach to take waste material and transform it into added-value products – solid base catalysts. For the purpose of this study, different base catalysts were screened, comparing results in between each catalyst. The ketonic decarboxylation efficiency from a low-value waste product from acid mine drainage known as ochre and a LDH synthesized from the latter were compared with the efficiency obtained using magnesium oxide.

Mineralogical composition of a clayey landslide, Wolfsegg am Hausruck, Upper Austria.

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« Hydroslide » is a joint project between France and Austria (funded by the Austrian Science Fund FWF, Project number: I 2619-N29) and monitors hydrological processes in clayey landslides at three different investigation sites. One site is close to the village Wolfsegg am Hausruck located in the western part of the Upper Austrian Molasse Basin. This study covers the qualitative and quantitative determination of clay minerals, grainsize distribution and geotechnical properties aiming for a better understanding and mitigation of landslide processes. The research area in Austria is situated in the gentle sloping Hausruck mountains comprising a hilly topography of up to maximum 800 m elevation. The district is historically well known for landslides resulting from the local geologic situation along with former coal mining activities. Recent damages to residential areas in the village Wolfsegg have initiated this investigation.

Five boreholes with up to 30 meters depth were drilled and cored. The boreholes were logged with natural gamma-, electromagnetic- and nuclear magnetic resonance tools. In total, 31 samples from the cores were probed and analyzed. The wells are characterized by comparable lithological composition comprising three stratigraphic units from top to bottom: Hausruck-Formation (Pannonian), fluvial, sandy, fine to coarse grained gravels; Ampflwang-Formation (Pannonian), limnic to fluvial coal bearing clays and sands; Ottnang-Formation (Lower Ottnangian) shallow marine clay silts. The landslide disturbs the first two formations and exhibits an approximate thickness of 15 meters.

These three stratigraphic units can be clearly distinguished by their carbonate, feldspar and phyllosilicate bulk rock mineralogy. The clay mineralogical composition is also significantly different. The clayey sediments in the coal bearing Ampflwang-Formation show a predominance of kaolinite, vermiculite and expandable mixed-layers. The Ottnang-Formation is dominated by smectite and partly vermiculite without traces of kaolinite. The highest amount of cation exchange capacity (CEC) and natural water content was detected within the coal bearing formation. The clay mineralogy is notably influenced by weathering alterations evidenced by the presence of expandable mixed-layer clay minerals and vermiculite. Due to the mineralogical composition and the high CEC, an abundant occurrence of slip surfaces within the coal bearing Ampflwang-Formation (at 4 -15 m depth below surface) is inferred. Following heavy precipitation incidents, the coal bearing Ampflwang-Formation acts like a lubricant triggering repeated land slide events.

The hydration behavior of mineral clays monitored by NAP-XPS

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Swelling and hydration of clay minerals has been a long studied subject due to its impact in a wide variety of environmental and geochemical technologies such as stabilization of carbon in soils, deep geological storage and long-term nuclear waste disposal in geological formation [1]. Clay hydration is induced by the presence of counterions in their interlayer structure, which influence this phenomenon depending on their charge and size. Despite its ubiquity in the aforementioned physicochemical processes, still little is known about the fundamental behavior of confined water and ion dynamics at the mineral-water interface, on a molecular scale.

Synchrotron radiation near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) appears as a cutting-edge tool to characterize hydration of clays, as it allows to monitor in real time the chemical environment of the interlayer cations in the early stage of the process in presence of water pressure up of few mbars and reach the water vapor pressure at 10°C [2]. In contrast with other techniques, NAP-XPS has the advantage of offering a synoptic view from both the gas phase (reactants and products) and the solid-phase (the surface and adsorbed species). Within this new approach, I present here, a study on the hydration of synthetic smectite clays with different counterions (Cs+, Sr2+, Na+) is monitoring in real time the influence of different partial pressures of water on the main core-level peaks binding energies.

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Sepiolite from Spanish deposits in Toledo and its derived organoclay materials

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It is well known that sepiolite is frequently present in the Tertiary continental Tagus Basin in Spain, in thick beds together with another type of clay minerals, especially of the smectite type. Sepiolite has a powerful interest to produce commercial products for many diverse applications mainly based on its surface and rheological properties (Murray et al., 2011). A new deposit of this special clay has been discovered in the Toledo province (Spain), offering a raw material with a high sepiolite content (> 95% w/w) showing a wide range of potential applications as advanced nanomaterials. As occurs with other high quality sepiolite samples, this mineral can be considered as a natural nanoplatform able to assemble many diverse molecular, polymeric and nanoparticulated species, giving rise to diverse nanostructured materials provided of suitable functionality for uses from photocatalysis to non-viral gene transfection (Ruiz-Hitzky et al., 2011; Aranda & Ruiz-Hitzky, 2018). As a representative example of sepiolite-based nanomaterials, organoclays derived from this microfibrous clay mineral are prepared by treatment with quaternary ammonium salts, or with other more sophisticated products such as silicones and related compounds. This communication will describe a deep characterization of these sepiolite samples from the Toledo deposits, as well as the study of their controlled modification by using different types of reagents, and their physico-chemical characterization mainly based on spectroscopic tools (FTIR, NMR), being also introduced a discussion on their organophilic behavior determined by means of contact angle measurements and water adsorption isotherms. Finally, the rheological properties of these systems in water as well as in organic media were studied, before and after their functionalization, introducing a discussion in comparison with other related products.

Acknowledgements: financial support from MINECO (Spain): RTC-2016-5065-5 and MAT2015-71117-R.

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The role of interlayer cations on the stability and on the crystal-chemistry of nontronite

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Previous studies revealed that Na-nontronites ($[Si_{4-x}\,{}^{[4]}Fe(III)_x]\ {}^{[6]}Fe(III)_2\,O_{10}(OH)_2\,Na_x$) with variable tetrahedral $^{[4]}Fe(III)$ content (x) could be synthesized under alkaline pH conditions (from 11 to 14) (Decarreau et al., 2008; Baron et al., 2016). Notably, the extent of tetrahedral substitutions (x) was very large, ranging from 0.43 to as high as 1.54 per half-unit cell. The pH of the crystallization fluid was shown to control the layer charge of the Na-nontronite. Recently, these Na-nontronites were found to be labile metastable phases kinetically favored with respect of aegirine ($Si_2Fe(III)NaO_6$ pyroxene) and hematite (Baron et al., 2019). Aegirine clearly appears to be the stable Fe(III)-silicate in the ($Na_2O – Fe_2O_3 – SiO_2$) experimental system under surface and subsurface conditions (Decarreau et al., 2004; Baron et al., 2019). The aim of this work was to study the role of the nature of the alkaline cation (K^+ and Ca^{2+} compared to Na^+) on the crystallization of nontronite.

For this purpose, two types of experiments were conducted: (i) nontronite ($[Si_{4-x}\,{}^{[4]}Fe(III)_x]\ {}^{[6]}Fe(III)_2\,O_{10}(OH)_2\,R^+_x$) were synthesized at pH 11 and 13.2 using KOH solutions for 6 and 31 days at 150°C, and (ii) ($[Si_{4-x}\,{}^{[4]}Fe(III)_x]\ {}^{[6]}Fe(III)_2\,O_{10}(OH)_2\,Na_x$) were first synthesized at pH 13.2 for 2 days at 150°C, then saturated with K^+ or Ca^{2+}, and then hydrothermally treated in water, KOH and NaOH pH adjusted solutions at 150°C for 29 days.

For the first type of experiments, XRD and FTIR data of the synthesized products revealed the formation of K-nontronite for all the ageing times. Contrary to the Na-nontronite, the highest layer charge was around 1 par half unit cell even for the highest pH, and the K-Fe(III)-mica formed appeared stable under the experimental conditions used. For the second type of experiments, FTIR data showed that the layer charge changed with ageing time suggesting dissolution-reprecipitation processes. For K experiments, part of the synthetic products was K-nontronite that remained stable during the time of experiments whereas some aegerine probably issued from remaining Na-nontronite could also be observed. For Ca experiments, a part of the synthetic products was identified as Ca-nontronite and appeared only for the experiments with water (pH around 10).

These preliminary results reveal that the nature of interlayer cations play a major role on the nature, crystal-chemistry, and on the stability of the clay minerals crystallizing in a given chemical system.

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Thermal behavior of several clay mixtures

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In a context of circular economy, the valorization of by-products resulting from an exploitation activity is a growing concern for the industrial. The National Agency for the Management of Radioactive Waste (Andra) is carried out work for the construction of a geological disposal center for radioactive waste. If its construction is allowed, its progressive operation should generate the excavation of several million tons of rock. This rock is mainly composed of clay minerals, carbonates and tectosilicates. Among the opportunities for the valorization of this clay, the development of new fire resistant and durable construction materials which can be used in the storage site. This work, supported by Andra under the "Investments for the Future Program, aims to understand thermal behavior of several clay mixtures.

To achieve this objective the different raw materials such as various clays and its mix calcined at different temperatures were used. Moreover, the different type of mixtures based on kaolin and additive (calcite, dolomite…) were prepared. Structural characterization by XRD, NMR, and FTIR spectroscopies before and after calcination of the raw materials were carried out.

The characterization of the different mixtures evidences structural differences depending on the type of the used raw material, additive and the calcination temperature. The results show the relationship between thermal behaviors of clays and their chemical and mineralogical composition.

Modification of the internal cavity of methyl-imogolite

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Imogolite is a natural aluminosilicate nanotube discovered in 1962 by Yoshinaga and Aomine in volcanic Japanese soils [1]. This nanotube has a monodisperse diameter below 3 nm and a polydisperse length (from a few tens of nanometers to several microns) [2]. In recent years, it has been realized that many structural and chemical modifications of imogolite-like structures can be achieved [3]. Kang et al. managed to functionalize this nanotube by grafting or substituting the internal silanol groups by organic moieties [4]. These modifications change the hydrophobicity of the cavity and the adsorption capacity of these new nanotubes.

Figure 11 – NR in dodecane (a) and NR trapped in pure imo-CH_3 (b), in modified

In 2010, Bottero et al. succeeded in modifying the tube internal surface by substituting the usual silicon precursor with a methyltriethoxysilane [5]. This allows for the formation of a methyl-imogolite (imo-CH_3) with a hydrophobic internal surface covered with methyl groups. This nanotube, transparent and dispersed in water even at high concentration, exhibits a 1D hydrophobic polar nanochannel which can capture small hydrophobic molecules in water [6,7].

In this presentation, we will show the 1st functionalization of the internal surface of imo-CH_3. The substitution of some of methyl groups is evidence by the modification of the optical properties of Nile Red (NR) dye trapped in the different nanotubes synthesized (figure 1).

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Methyl-imogolite: a new hybrid nanotube for water remediation

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Imogolite is a natural aluminosilicate nanotube discovered in 1962 by Yoshinaga and Aomine in volcanic Japanese soils [1]. This nanotube has a monodisperse diameter ranging from 2 and 2.8 nm (depending on its formation and composition) and a polydisperse length (from a few tens of nanometers to several microns) [2]. In recent years, it has been realized that many structural and chemical modifications of imogolite-like structures can be achieved [3]. In 2010, Bottero et al. succeeded in modifying the tube internal surface by substituting the usual silicon precursor, tetraethoxysilane, with a methyltriethoxysilane [4]. This allows for the formation of a methyl-imogolite (imo-CH_3) with a hydrophilic external surface and a hydrophobic internal surface covered with methyl groups. This nanotube, transparent and dispersed in water even at high concentration, exhibits a 1D hydrophobic polar nanochannel [5].

In 2015, Amara et al. showed that such Janus nanotubes can capture small hydrophobic molecules in water [6]. Later, we showed that these hybrid nanotubes can stabilize oil-in-water Pickering emulsion and extract a dye from an organic phase [7]. These properties were attributed to the ability of methyl-imogolites cavities to accommodate oil or oil/dye mixtures (figure 1).

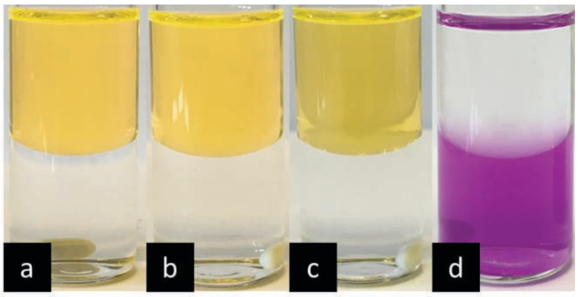

Figure 12 – Dodecane/Nile Red solutions in contact with water (a/c) and with a

In this presentation, we will show imo-CH_3 can trap in their cavity various organic molecules (soluble or insoluble in water, polar or nonpolar). Moreover, these nanotubes can be used as optical sensor for instance when pyrene molecules are confined in their cavity.

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H_2 production from radiolysis of water confined in imogolite nanotubes. Impact of water content and surface chemistry.

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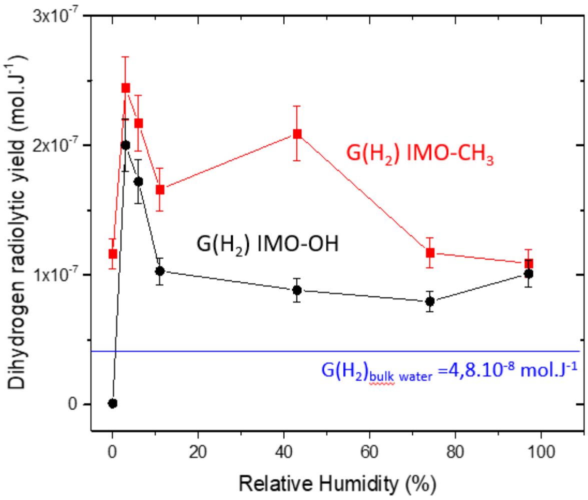
Imogolites are hydrated aluminum silicate nanotubes[1]. Silicon tetrahedra make up the internal surface while the external face consists of aluminum octahedra. Both surfaces are covered with hydroxyl groups and are therefore hydrophilic (IMO-OH). The inner surface can be functionalized with methyl groups (IMO-CH_3), which gives a hydrophobic behavior on the inside while the outside surface is still hydrophilic.

An infrared spectroscopic study of confined water in imogolites[2] has provided information on the H-bonding of water inside and outside of the tube. As expected the water filling differs between the two types of imogolites. In IMO-OH, water adsorption starts at low relative humidity (RH) (<10%) by forming patches on the inner surface. At around 55% RH, the tubes are filled and the liquid water-ice transition characterized by very strong H-bonds takes place. Despite its hydrophobicity, IMO-CH_3 welcomes up to 5% of total water inside the tube but the corresponding H-bonds are weak. Therefore, the hydrophilicity of the inner walls controls water confinement in imogolites.



Under irradiation with an electron beam, radiolysis of water and of –OH groups leads to the production of dihydrogen. The dihydrogen production is measured by gas chromatography. The H_2 radiolytic yield (in mol.J^{-1}) is calculated by depositing increasing quantities of energy (in Gy, 1 Gy = 1 J.kg^{-1}) in the sample. In IMO-OH, the H_2 radiolytic yield increases sharply as soon as the imogolite contains water. This yield can be up to 2 to 4 times higher than in bulk water (figure 1). The maximum is obtained at 3% RH for which all the water molecules are closely interacting with the nanotube surface. Reactions leading to H_2 production are therefore highly promoted when water is confined and the tubes are not full. In IMO-CH_3, H_2 comes from the radiolysis of both water and the internal methyl groups. This accounts for the higher values measured as compared to IMO-OH. From the yields calculated at different RH values, and knowing the water adsorption properties in imogolites, radiolysis mechanisms can be provided. They depend on the amount and behavior of water in the nanotubes and will be discussed.

Figure 13: Radiolytic yields of H_2 production as a function of RH for both types of

The influence of organic contaminants on clayey soil plasticity and strength

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In the recent years, the investigation of processes of the chemical-mechanical coupling in a medium subjected to chemical alterations is becoming more and more relevant, not only for the characterization of polluted area, but also in the field of geo-environmental applications (e.g. implications of contaminant migration). Indeed, the literature shows that the geo-mechanical behaviour of clays is highly dependent not only on stress/strain condition to which the material is subjected, but also on the chemistry of both soil and of the pore fluid which affects the attractive and repulsive forces inside the porous medium which could markedly affect the index and engineering properties of soils (e.g. Santamarina et al. 2002). The contaminants, with their peculiar properties, may have a significant role in this process.

A specific testing programme was carried out on three standard monomineralic clays, namely kaolin, Illite and Smectite, and one marine clayey silt artificially contaminated by a congener of Polychlorinated biphenyls, PCBs, and a congener of Polyaromatic hydrocarbons, PAHs. These contaminants have been chosen since they are worldwide widespread organic contaminants related to the anthropogenic environmental pollution. The quantity and the type of congeners used in the mixture was selected based on the case study of a polluted marine basin located in Taranto (South Italy), named Mar Piccolo (literally Small Sea), where the sediments are severely affected by the presence of organic and inorganic contaminants (Vitone et al. 2016). After thoroughly mixing of clays with the organic contaminants at different concentrations, the aggregation state, the Atterberg limits and the undrained shear strength of each mixture were determined and compared with the values of the unpolluted mixtures.

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Probing the surface chemistry of nano-layered silicates: a combined experimental and theoretical approach

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Nano-minerals are of great educational and industrial interests because of their minute size which generate surprising physico-chemical properties compared to larger minerals. As example, the nano-layered silicate "synthetic talc" ($Si_4Mg_3O_{10}(OH)_2$) shows opposite properties to natural talc because of its hydrophilicity and high adsorption capacity.

In this work, the molecular structure and crystal-chemistry of synthetic talc were investigated to better understand its physico-chemical properties. To do so, ^1H and ^{29}Si Nuclear Magnetic Resonance (NMR) spectroscopies were used on a series of synthetic talc samples of various crystallinity to probe their local structure. The NMR spectra evidenced unusual contributions that were difficult to interpret. The combination with Density Functional Theory (DFT) calculations allowed to solve this problem by simulating the theoretical NMR chemical shifts of various structural configurations of the synthetic talc particles (simulation of defective layers with vacancy of Mg^{2+} or substitution of Mg^{2+} by Na^+ in the octahedral layer; compensation by H^+ or Na^+ in the interlayer space (Na^+ is the cation resulting from the co-precipitation of reagents with an amount <1wt.%)).

The results show that the nano-mineral is composed of an assembly of defective and non defective layers that generate different signals in NMR. The proportion of defective and normal layers varies with the sample's crystallinity. DFT also enabled to identify the edges contributions in the ^1H and ^{29}Si NMR spectra. Such a new approach is very promising for analyzing the surface chemistry of many nano-materials.

Mg and Si-K edge X-ray absorption study of synthetic talc with various crystallinity

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Synthetic talc, a layered silicate of chemical formula $Si_4Mg_3O_{10}(OH)_2$, is a mineral of great industrial interest because of its nano-sized dimension, hydrophilicity, chemical purity, and high adsorption capacity. In order to develop this material on an industrial scale, it is necessary to know the mechanisms of growth and transformation of the particles from the amorphous precursor stage to the pristine nano-sized particle stage.

X-ray Absorption Spectroscopy (XAS) was performed at the Mg and Si-K edge on a series of five synthetic talc samples of powders and gels of growing crystallinity elaborated under sub-critical hydrothermal conditions (300°C, 85 bar). The objective was to monitor the evolution of the ordering at the local and extended scales as the sample's crystallinity increases. Another sample of unknown crystallinity and elaborated under continuous supercritical conditions (400°C, 250 bar) was also used to situate it on the series.

The results of correlation between the samples' crystallinity and the XAS profiles will be presented (Figure 1). They evidence a diminution of the disorder as the particle crystallinity increases. The supercritical hydrothermal flow synthesis enables to produce particles of lower crystallinity than the subcritical one. Lastly, the influence of the particle stacking will also be discussed as the analyses were performed on the dried oriented synthetic talc powders and on the initial non-oriented colloidal gels.

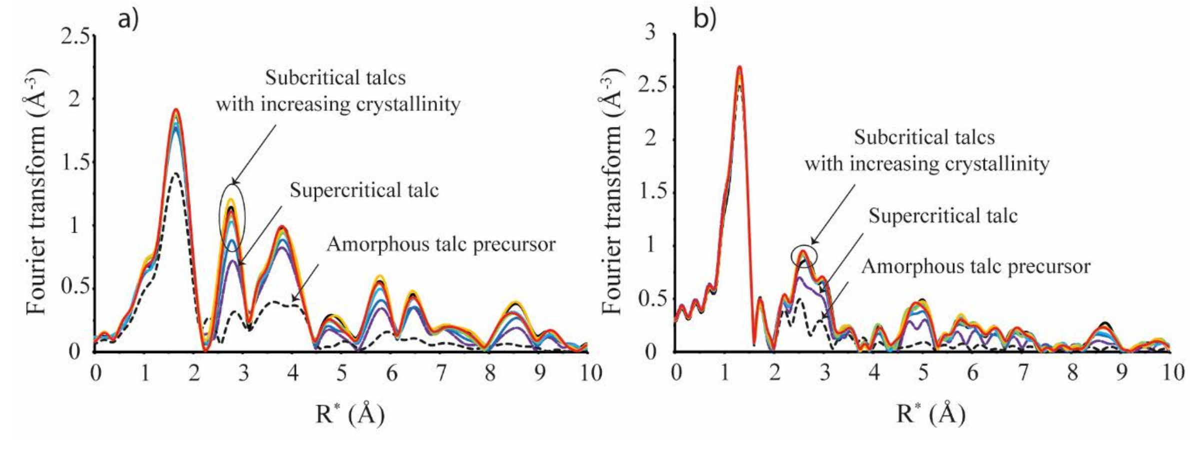

Figure 1. Magnitudes of Fourier transforms of the k^2-weighted EXAFS oscillations of the synthetic talc samples recorded at the (a) Mg-K edge and (b) Si-K edge.

Mechanisms of oxytetracycline oxidation by Fe(III)- and Mn(IV)-containing minerals

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Oxytetracycline, a broad-spectrum antibacterial agent, is being used extensively for veterinary purposes as well as for treatment of infections in humans. The parent compound and its metabolites are introduced to the environment via manure or sludge application, and irrigation with untreated or treated wastewater or runoff. As a result, oxytetracycline is found in a wide variety of environmental samples, and due to its low stability, it decomposes under a range of environmental conditions to form transformation products (TPs). Though adsorption and transformation of oxytetracycline by soils and minerals has been studied previously, detailed mechanisms of transformation by redox-active minerals were not investigated. This work provides comprehensive investigation of the mechanisms of oxytetracycline oxidation by redox-active minerals- Fe(III)-montmorillonite and birnessite (δ-MnO_2).

Kinetics of oxytetracycline adsorption and transformation was studied during 7 days. Transformations products were identified using liquid chromatography mass spectrometry (LC-MS). In the presence of both minerals, oxytetracycline was completely removed from solution, its transformation was induced and accompanied by reductive dissolution of the minerals. However, kinetics and redox behavior of Fe(III)-montmorillonite-oxytetracycline and δ-MnO_2-oxytetracycline systems were different. Oxytetracycline was oxidized by birnessite within minutes, its transformation involved radicals and resulted in the formation of 54 TPs in solution. X-ray photoelectron spectroscopy (XPS) demonstrated the accumulation of highly oxidized carbon on mineral surfaces with time. Mn(II) was released in large quantities from mineral surface to solution. Oxytetracycline oxidative degradation by Fe(III)-montmorillonite was gradually developing with time. In this system, 29 TPs were identified, among them 13 were surface-bound. XPS results showed presence of Fe(II) and accumulation of Fe(II) and highly oxidized carbon species on the mineral surface after 96 hours.

This work showed that δ-MnO_2 behaves as a fast and efficient oxidizer, whereas Fe(III)-montmorillonite acts as an effective sorbent, with redox reaction evolving with time. Based on the obtained results, detailed mechanisms of oxytetracycline oxidative transformation on both minerals are constructed.

This study demonstrates the impact of structure and reductive reactivity of iron- and manganese- containing minerals on oxytetracycline adsorption and oxidative transformation, which helps to predict possible scenarios of pollutant environmental behavior in the presence of redox-active minerals.

Adsorptive transformation of organic matter by mineral surfaces

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The importance of soil organic matter (SOM) as a carbon pool is widely recognized, but the mechanisms that control SOM transformation and sequestration at soil mineral interfaces are still debated. We studied interactions of organic matter with soil minerals involving various processes- adsorptive fractionation, transformation, esterification and polymerization of SOM components on mineral surfaces, and the role of iron-enriched minerals in these processes.

We investigated adsorptive fractionation of dissolved organic matter (DOM) isolated from biosolids by mineral soil. FT-ICR MS data showed DOM structural changes, accompanied DOM adsorption by mineral soil: preferential adsorption of polyphenols and highly oxidized, molecules. Enhanced adsorption of DOM phenolic components was attributed to the presence of iron-containing minerals in soil. Hence, to better understand the mechanisms of DOM transformation, we investigated the adsorptive transformation of various DOM components by montmorillonite saturated with Fe^{3+}. Aromatic-rich hydrophobic acid fraction (HoA) was isolated from DOM, to study its interactions with Fe^{3+}-montmorillonite. ^{1}H- NMR spectra of HoA –clay complexes indicated polymerization of amino acids on the Fe^{3+}-clay surface. XPS analysis of HoA-Fe^{3+}-clay complexes demonstrated formation of Fe^{2+} on the iron-enriched montmorillonite, which can be explained by the oxidation of HoA phenolic components, accompanied by reduction of surface iron. Interaction of various DOM components with Fe^{3+}- montmorillonite might result in both oxidative and non-oxidative polymerization. We observed oxidative polymerization of DOM phenolic components, investigating interactions of ferulic acid with Fe^{3+}-montmorillonite, which resulted in formation of dimers, trimers, and tetramers of ferulic acid, and reductive dissolution of the mineral. We detected non-oxidative polymerization of SOM components by iron-enriched minerals resulting from adsorptive transformation of model SOM aliphatic components- cutin monomers- on Fe^{3+}-montmorillonite surface. Though adsorption of cutin monomers was accompanied by their self-esterification, and oligomerization on both Ca^{2+}- and Fe^{3+}-montmorillonite, these processes were significantly more intense for Fe^{3+}- montmorillonite.

Our studies demonstrated variability of mechanisms of organic matter interactions with soil minerals, and emphasized particularly important role of iron-enriched minerals in the fate of soil organic matter.

The Influence of Soil Mineralogy on Soil Crust Morphology

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The studied soils are in a slope complex in the North of Thailand which is an intensive agricultural area. Soils are classified as Typic Paleustults. Soil parent materials are quartzite and slate. Soil textures are silty clay to clay. Soil pH ranges from 5.0 to 6.3. Thin sections of soil crusts were studied to investigate crust structure using micromorphological observations and pore characterisation with image analysis. Soil crust formation can be affected by soil mineralogy. Groundmass consists mainly of clay minerals, which are dominantly kaolinite and illite. Clay, organic matter, fine quartz grains and iron oxides combine to form soil aggregates. The wet aggregate stability of of the soils rangs from 27 to 66%. The crusts may be divided into two categories which are physical crusts and biological crusts. For physical crusts, clay and silt particles fill soil pores, coating and blocking porosity at the soil surface. For biological crust, moss-dominated biological soil crusts are present. A major function of the crusts is erosion control. Total porosity of both crusts was less than total porosity of non-crusted soils. Crusts have a strong influence on soil erosion, water use, and crop growth on this sloping farmland.

Aerosol approach toward functional nanostructured Layered Double Hydroxide microspheres.

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The chemical and physical properties of LDH make them candidates of choice for valorization in various fields. Nanostructured layered double hydroxide (LDH) materials with unique diffusion properties, large surface area along with desired functionalities have attracted great attention for a number of fields of applications ranging from the adsorption and photo- or bio-degradation of pollutants, heterogeneous catalysis to the controlled release of active principles. The efficiency of soft and hard templating approaches to prepare nanostructured LDH have been recently highlighted.[1]

In the laboratory, we are considering applying the aerosol route to produce functional microspheres from colloidal layered double hydroxide (LDH) suspensions. The aerosol drying widely used in the agri-food field consists in atomizing a suspension in micrometric droplets in order to dry them in a flow of hot air. In materials science, this process has been applied to the production of inorganic powders, multifunctional or porous organic / inorganic powders.[1]

In this presentation, we will show how aerosol drying allow to easily and quickly prepare LDH microspheres at low cost and in a large scale. The nanostructuration of platelets is maintained even during resuspension and anion exchange reactions.[2] We will also describe how, thanks to the self-assembly of LDH particles and other types of nanoparticles (TiO_2, latex) during this type of drying, functional nanostructured particles could be elaborated, giving rise to for example, LDH/TiO_2 heterostructures but also porous microspheres. The properties of the powders thus produced with respect to adsorption and photodegradation of orange II as a model pollutant will also be discussed.

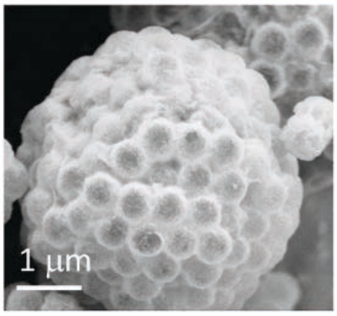

Fig.1 SEM image of macroporous LDH microsphere

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Preparation of NiAl Layered Double Hydroxide thin films and their electrochromic properties

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Electrochromic materials which display alteration of adsorption/color by electrochemically induced redox reactions, have shown great interest in electrochromic device development for potential applications in smart window, low-power display, anti-glare rearview mirror...Among the different electroactive species described such as metal oxides (WO_3, IrO_2, MoO_3, NiO), hexacyanometallates, viologens and conjugated polymer (Polyanilie, polypyrrole, poly(3,4-éthylènedioxythiophène) poly(styrène sulfonate) (PEDOT : PSS)...), Layered Double Hydroxides (LDH)[1] having a versatile chemical composition have also been described as potential candidates in the design of electrochromic devices.[2] Interestingly, the oxidation of NiAl-LDH is accompanied by a colour change from light to brown.

In this presentation, the structure and electrochromic properties of homogeneous thin films of NiAl layered double hydroxides (LDH) on FTO substrate will be closely described. The films were prepared from nano LDH aqueous suspension synthesised via one pot process from commonly available chemicals (metal chlorides, propylene oxide (PO) and, acetylacetone (acac)) in an aqueous solvent at a room temperature.[3] As prepared nano LDH lead to homogenous thin films with electrochromic behaviour evidenced by the relative transmittance measurements recorded in situ during potential scans. The influence of various parameters on the electrochromic properties of the films will be detailed such as the thickness of the layer, the nature of the electrolyte... The addition of a PEDOT:PSS layer into electrochromic films can modify the contrast between the bleached and coloured states due to an improved electronic transfer. Hybrid films based on the association of LDH and PEDOT:PSS following different approaches such as Layer-by-layer deposition or mixture have been investigated and will be discussed.

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Sulindac and Mefenamic acid intercalated into LDHs described by combination of DFT and classical MD simulations

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Layered double hydroxides (LDHs), also called as hydrotalcites or anionic clays, are very promising materials for applications in biomedicine due to its biocompatibility, low toxicity to human body, large palette of suitable intercalates and also due to possibility of surface or structure modifications. It was found that LDHs can increase the chemical stability of the resulting intercalated material and allow its sustained release in the body, and moreover can eliminate undesirable side effects of drugs.

We present computational description of two types of LDHs (Mg_2Al-LDH and Zn_2Al-LDH) intercalated by Sulindac and Mefenamic acid, where LDH serve as drug nanocarriers for sustainable drug release in the human body. Both drugs have anti-inflammatory and antinociceptive effects (anti conduction of painful stimuli).

The initial models as well as results of atomistic simulations were based and compared to experimentally published data for Sulindac [1] and for Mefenamic acid [2].

Comparison of calculated XRD patterns, basal spacings, concentration profiles, free volumes and mean square displacements will be presented for LDH supercell with the surface area of roughly 400 $Å^2$. DFT calculations were used for studying interactions between LDH surface and drugs. The whole complex structures were analyzed by MD calculation on nanosecond time scale. Results for combined CVFF and ClayFF in comparison with DFT substructure calculation and experimental results are presented.

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Bacteria-Clay Surface Interactions Mediated by Amyloid Fibers

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Clay minerals and oxides are key players in the physico-chemical interactions between bacteria and their environment and can impact their growth, mobility and ability to form biofilm. Many have explored the role of bacterial membranes and extracellular materials in soil-bacteria interactions, however, to date and despite their prevalence in environmental biofilm, the role of **microbial amyloids** in bacterial adhesion to clay surfaces has not been systematically studied.

Microbial amyloid fibers are strong, insoluble membrane appendages, ranging from 0.1 to10 µm in length and 4–12 nm in width. Presented here is a systematic study on the effect of curli (amyloid fibers formed by *E. coli*) on bacteria-clay surface interactions. The aggregation and adsorption of the curli-producing bacteria to clay minerals was followed using zeta potential measurements, lumisizer measurements, fluorescent spectroscopy and electron microscopy. Curli production and biofilm formation were both enhanced when *E. coli* were grown in the presence of montmorillonite but not with kaolinite or iron oxides. In terms of interactions, bacteria aggregation and sedimentation tests (without clay) showed that curli-producing *E. coli* sedimented within an hour as opposed to days for curli-deficient *E. coli*. In the presence of clays, large flocs were formed, and sedimentation time was reduced. The interactions of curli-producing *E. coli* alone and with clay did not follow the extended DLVO theory - sedimentation was fast even at low ionic strength and pH values. This was probably due to non-DLVO forces such as polymer bridging; the fibers effectively pierce through the energy barrier posed by the electrostatic forces. This mechanism was supported by the adhesion of curlin monomers and fibers to the clay minerals (without bacteria), even though electrostatic repulsion forces were present. Successive polymerization post adsorption was also found – suggesting the clay can act as an anchor for bacterial attachment.

The results of this study suggest that natural surfaces can enhance microbial curli production, clay-bacteria interactions and consequently biofilm formation. These findings will help shed light on important microscale processes at the aqueous-solid soil interfaces, such as biofilm formation, nutrient-cycling, pollutant and pathogen fate in the environment.

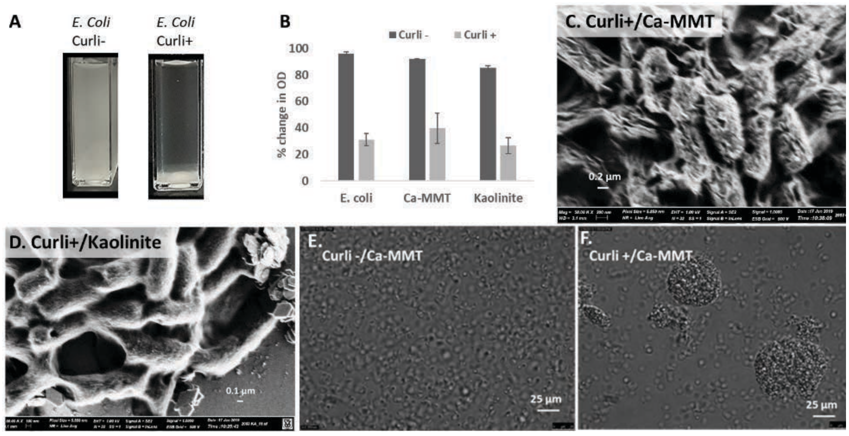

Figure. A. Curli deficient (-) and curli producing (+) *E. coli* left to settle for 1h. **B.** Settling after 1h of *E. coli* with montmorillonite (Ca-MMT) and kaolinite. **C-D**. SEM of curli+ *E. coli* with Ca-MMT and Kaolinite. **E-F.** Light microscope images of curli-/+ *E. coli* with Ca-MMT

Self-Regenerating Bio-Clays for Formaldehyde Wastewater Remediation

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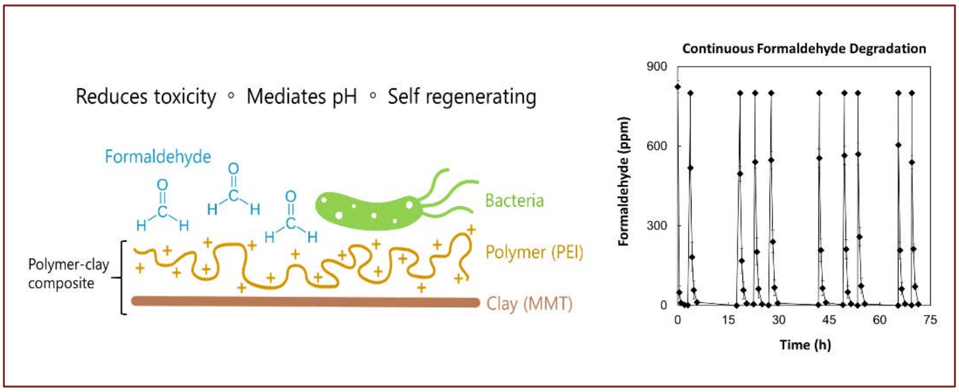

A multi-functional, self-regenerating clay-based material was designed to adsorb and biodegrade formaldehyde from industrial wastewater in a simple, one-step process. The material is based on montmorillonite, polyethyleneimine and formaldehyde-degrading *Pseudomonas putida* and has three functions which facilitate bioremediation: a. Selectively adsorbs formaldehyde to reduce cytotoxicity, b. buffers the solution to allow efficient biodegradation, and c. self-cleans through slow release of formaldehyde and subsequent degradation by the attached bacteria.

A polyethyleneimine-montmorillonite composite was optimized to carry a positive surface charge and a high concentration of functional amine groups, which facilitated formaldehyde adsorption and bacterial adhesion. Formaldehyde was specifically bound to the amines on the composite through the well-known Schiff base reaction. The binding was reversible and pH dependent and fit the Langmuir model with a q_{max} of 62 $mg \cdot g^{-1}$ composite. The formaldehyde degrading *Pseudomonas putida* strain was then immobilized on the positively charged composite and the bio-clay was characterized and optimized using X-ray diffraction, zeta potential measurements, BET, confocal and electron microscopy.

The efficiency of the resulting bio-composite was demonstrated for multiple successive treatment cycles, with degradation rates as high as 1600 ppm $FA \cdot h^{-1}$. This self-regenerating one-step process is a very promising solution to the challenging drawbacks of formaldehyde remediation but can also help design other clay-based adsorption-degradation platforms for wastewaters that demand complicated treatment strategies.

Gallic Acid Interactions with Iron-Coated Smectites

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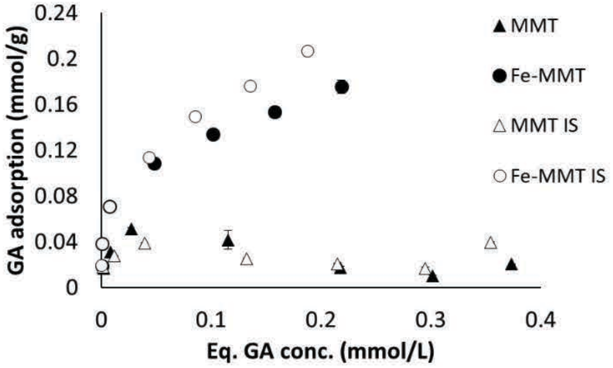
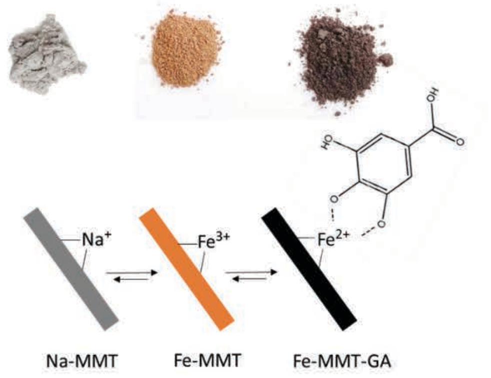
The occurrence of organic matter significantly effects pollutant fate in soils and aquifers and impacts efficiency of soil and water treatment processes. In that respect, a fundamental study was performed on the interactions between a prevalent quinone moiety in dissolved and solid organic matter, gallic acid (GA), and a smectite coated with amorphous iron oxides. Adsorption/desorption experiments revealed an increased affinity of GA to the Fe-MMT over the raw MMT. The adsorption was irreversible and only slightly affected by salinity indicating a strong inner-sphere complexation mechanism.

This Fe-MMT-GA complex was then characterized by UV-Vis, XRD, FTIR, LC-MS and XPS. The results showed further transformation reactions such as polymerization of the GA and reduction of the surface iron. The resulting complex also had increased adsorptive affinity towards PAHs and BTEX compounds due to increased hydrophobicity. Lastly, increased catalytic and conductive properties were shown and quantified using cyclic voltammetry and peroxide titration experiments.

These interesting and complex interactions can occur in soils and sediments under ambient conditions and can in turn significantly effect pollutant sequestration and transformation. Consequently, the findings are relevant not only in terms of predicting the fate of pollutants in the environment, but also for the evaluation of in-situ soil and sediment treatment processes such as in-situ chemical oxidation and reduction.





A toolkit for the characterization of kaolinite and smectite in the mining industry

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Kaolinite and smectite are very common minerals and occur in many commodities of economic importance. Kaolinite and smectite are either industrial minerals or notoriously problematic in the mining industry as they impact harmfully on many steps of ore mining and processing. Characterizing and identifying the three-dimensional variations of kaolinite and smectite abundance and composition can also be used to understand many mineral systems including the formation of the regolith. The location and abundance of kaolinite and smectite is also a critical parameter during mining and processing of the ore. A toolkit for the characterization of kaolinite and smectite has been developed with the ultimate goal of providing standards for mineralogical and chemical online sensors. X-ray diffraction (XRD) is the most common technique for recognizing and quantifying kaolinite and smectite. However, these minerals can also be identified directly or indirectly by a number of other technologies, ranging from satellite images to reflectance visible and near infrared (VNIR), shortwave infrared (SWIR) and mid infrared (MIR) spectrometers such as the HyLogging or Corescan automated System and Raman spectrometers to micro-XRF (X-ray fluorescence) or online XRF instruments. Using this toolkit, a number of kaolinite and smectite have been characterized, through a range of examples in commodities such as iron ore, bauxite and gold, demonstrating the potential of the combined methodologies. An example of the XRD trace and the reflectance spectra of the Western Australia Toolibin kaolinite is shown in Figure 1.

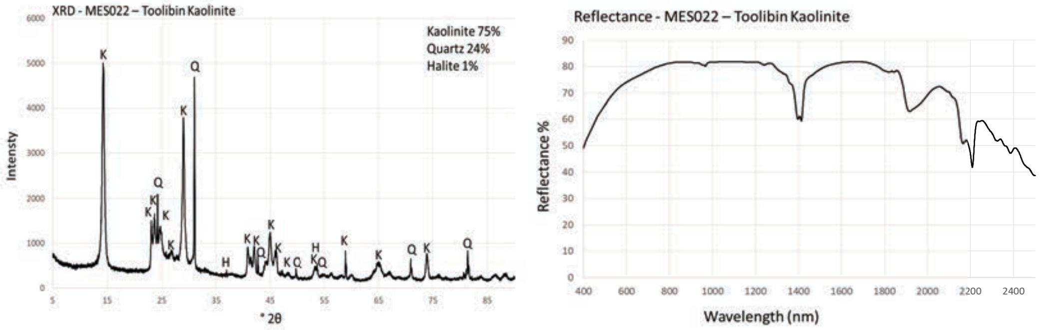

Figure 14 XRD trace and the reflectance spectra of the Western Australia Toolibin kaolinite.

Dehydration and intercalation behavior of the unique “Patch Clay” halloysite using in-situ XRD

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An unusual pale white-blue, semi-translucent plastic clay was received by CSIRO in the early ‘80s from the ‘Patch Pit’ of a nickel mine at Siberia, approximately 85 km NW of Kalgoorlie, Western Australia (Norrish, 1995). XRD patterns of the supplied air dry clay showed broad peaks indicative of halloysite, however several additional peaks at 1.65, 1.38, 1.11, 0.8, 0.75 and 0.698 nm were also observed. Subsequent re-sampling from twelve different locations within the mine (Patch A through Patch L) showed the material had a very high moisture content (47.8%). At concentrations as low as 1% by weight the clay dispersed in water forms a thixotropic gel. XRD patterns of some of the field moist samples showed unusual ripples in the low angle background and 1.0 nm peak of halloysite (Figure 15: Wet). These features were described as being due to interference between opposing walls of the highly uniform tube diameters of approximately 24.0 nm and tube wall thicknesses of 5-6 nm (Norrish, 1995).

Continuous collection of XRD patterns of oriented clay mounts whilst air drying (26°C and 40% RH) over 24 hours showed several stages of dehydration occurred. After approximately 7 hours the interference fringes gradually become less resolved as dehydration increases surface tension and the tubes begin to distort. Within 30 minutes the fringes disappear due to collapse of the tubes and the peak triples in intensity. After a further 30 minutes the 1.0 nm peak rapidly moves to 0.87 nm as the interlayer water is removed then gradually to 0.84 nm 16 hours later (Figure 1).

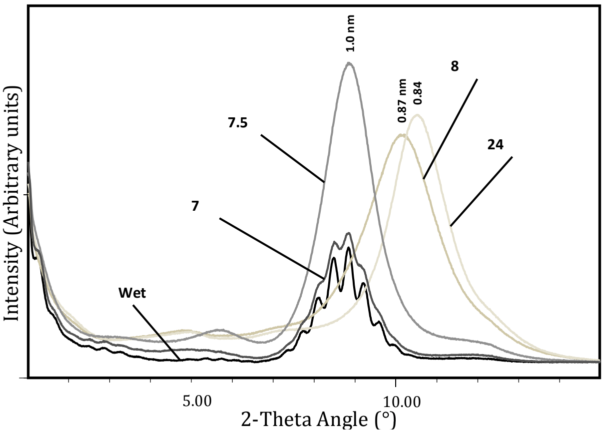

Figure 15 XRD patterns of Patch Clay

Intercalation experiments using formamide on the fully hydrated clay showed the 001 peak expand slightly from 1.00 nm to 1.04 nm, however, the interference fringes remained intact for over 24 hours. XRD patterns collected intermittently from 2 to 22 days showed a similar but slower progression with the dehydration experiment; (i) the fringes became less resolved after 8 days; (ii) at 9 days the fringes disappeared and the intensity increased 3-fold, (iii) at 14 days the intensity increased another 4-fold, and (iv) after 22 days the intensity decreased by half and the peak shifted to 0.84 nm.

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Theoretical and experimental investigation on the intercalation of metformin into layered clay minerals

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Metformin (MF) has been largely used for the treatment of type II diabetes. In addition, it has recently shown high efficacy in the treatment of prostate, colon and breast cancers (Aldea et al., 2014). However, it has several drawbacks caused by the low absolute bioavailability of 50-60% and a biological half-life of 6.2 h, which implies the administration of high doses for an optimal therapeutic effect that may produce gastrointestinal problems. In this context, drug delivery systems (DDS) can be suitable to offer a controlled release and, consequently, decrease these collateral effects. As we have initially reported (Rebitski et al., 2018), layered clays can serve as substrates of MF for this purpose. In this communication, we introduce results on the intercalation of MF in Laponite® XLG (Lap) and Wyoming-type montmorillonite (Mt) commercialized as Cloisite®Na, with CEC values of 63 and 93 mEq/100 g, respectively. The intercalation follows an ion-exchange mechanism in both clay minerals leading to interlayer distances of 0.36 nm and 0.39 nm for the Lap-MF and Mt-MF systems, respectively. The arrangement of MF as a monolayer in the interlayer space was studied by computational calculations at the molecular level, which were made using forcefields based on empirical interatomic potentials. The combination of molecular modeling and experimental characterization techniques, such as TG-DTA, FTIR, XRD, EDX and ^{13}C NMR, allowed the interpretation of this adsorption process and the final molecular disposition of MF in the interlayer region of the silicates. In addition, the release of the drug from the Lap-MF and Mt-MF intercalation compounds containing different amounts of MF has been evaluated simulating physiological media at pH values that mimic the gastrointestinal tract. The tested systems show a rapid release at low pH value (typical of the stomach), pointing out to the necessity to optimize this type of DDS in order to achieve a controlled MF release.

Aldea, M., Craciun, L., Tomuleasa, C., Berindan-Neagoe, I., Kacso, G., Florian, I.S., Crivii, C. (**2014**) Tumor Biol., 35, 5101–5110.

Rebitski, E.P., Aranda, P., Darder, M., Carraro, R., Ruiz-Hitzky, E. (**2018**) Dalt. Trans., 47, 3185–3192.

Description of bentonite textures and structural characteristics through 3D analysis

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Detailed investigations regarding bentonite genesis and subsequent alteration are utilised in enhancing conceptual understanding of the long-term behaviour of bentonite based engineered barrier systems (EBS) developed for geological disposal of radioactive waste. This is of special interest in the field geological disposal of long-lived hazardous waste (e.g. spent nuclear fuel) where the behaviour of the used materials needs to be understood over geological timescales (up to ~1 Ma). A specific term, natural analogues, i.e. studies on natural bentonite occurrences, have been used to describe this particular field of research to understand the future behaviour of the disposal systems based on studying geological past. But, how similar the natural bentonites actually are to the EBS ones? This question is related to bentonite mineralogy, density and structural/sedimentary/volcanic features. Here, the focus is set on the textural and structural characterisation of bentonite.

Application of conventional methods of describing textures of bentonites (or any other clays) are often limited by the number of samples and lack of three dimensional understanding. Here, bentonite textures have been characterised using X-ray tomography (XCT), which is a non-destructive and relatively fast method employed in many fields of geological investigations.

The benefits are evident for increasing the spatial coverage in textural description in deposit scale. Sampling of bentonite and related disturbances mainly on density are described and their significance are discussed. In addition, XCT provides a good point of reference for subsequent analyses of mineralogical, chemical, microbial and physical properties of bentonite clay.

Clay based engineered barrier systems can be either compacted homogenous bentonite materials, pellet based materials or bentonite mixtures with sand or crushed rock aggregates. The use of XCT imaging helps in assessing the analogy of natural bentonites to the processed EBS materials listed above. In this presentation, bentonites with various textures are presented (including homogenous, lapilli tuff, sedimentary and faulted) to provide new information on the analogous nature of various bentonites to EBS materials, and how the geological data could be used in more specific way.

On the key role of palygorskite on monitoring the phase composition of Ag_2CO_3 in palygorskite-based nanocomposites and correlation with their visible photocatalytic activities

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This study reports an original remarkable effect of fibrous palygorskite clay mineral in the stabilization at the ambient of the metastable hexagonal β (H_β) phase along with the stable monoclinic (m) phase of Ag_2CO_3 evidenced by in situ XRD versus temperature and TEM-EDS analyses. The m phase seemed to be formed in solution between free Ag^+ and CO_3^{2-} ions according to homogeneous germination whilst H_β structure likely aroused by heterogeneous germination onto the surface of palygorskite fibers between CO_3^{2-} (in aqueous solution) and the solid surface of Ag^+ exchanged palygorskite (Ag^+-Pal). The formation of H_β phase was favored by short digestion time (1 h) of Ag^+-Pal in Na_2CO_3 solution. By contrast, long digestion time (24 h) seemed to be sufficient enough to provoke reverse ion exchange of Ag^+-Pal into Na^+-Pal and hence the release of Ag^+ ions in bulk solution where, along with those already existing, react with CO_3^{2-} ions to form pure monoclinic Ag_2CO_3. Appropriate thermal cycling under CO_2 atmosphere ($P \approx 1$atm) carried out on fresh Ag_2CO_3-Pal composite noticeably increased H_β proportion at the expense of monoclinic structure. This proportion further reached 100% by mean of the same heat treatment performed on the composite after undergoing several months of ageing. The visible photocatalytic activity towards the removal of Orange G dye revealed that the composite formed of 100% of monoclinic structure was more active than the one containing 100% of H_β. Nevertheless, the composite containing a mixture of both the phases in a ratio of 32% H_β / 68%m was found to be interestingly the most photoactive in the visible due likely to the synergy of both the phases in the photodegradation of the dye like anatase and rutile in TiO_2.

Microporous Organically Pillared Layered Silicates (MOPS) – A versatile class of functional porous materials with structural flexibility

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The efficient, energy saving and environmentally benign separation of gas mixtures is of particular significance in industry for production of bulk chemicals[1]. In conventional porous materials the pore walls lack specific chemical binding sites, wherefore the pore sizes and shapes essentially dictate the performance of adsorptive separations. Consequently, it is a demanding task to achieve high selectivity between gases of similar physical properties and size like CO/N_2 or CO_2 /C_2H_2. In this context, porous solids owing structural flexible frameworks have attracted much interest, since they are able to specifically respond to guest molecules.[2] However, structural dynamism for controlling the adsorption properties is no longer a unique characteristic of so-called Soft Porous Crystals (SPCs). Pillaring charge homogenous synthetic clays with organocations or metal complexes, provides access to a largely unnoticed class of microporous hybrid materials. These Microporous Organically Pillared Layered Silicates (MOPS) are conceptually similar to SPCs and combine the concepts of functional porosity and component modularity with a continuous porosity tuning in the sub-Ångström range[3, 4]. The disposal of the building blocks in MOPS opens up new distinctive properties while their inherent characteristics remain untouched. It was found that the adsorbent recognition in MOPS could be specifically set to discriminate very similar gases (CO_2/C_2H_2 or CO/N_2) by a new fully reversible and selective gate-opening mechanism[5, 6]. Contrary to conventional gate-opening as observed for SPCs the additional adsorption sites in MOPS are mostly created without macroscopic framework displacements as it is triggered solely by freezing pillar dynamics. The gate-opening is restricted to CO_2 and CO. We found that the selectivity of this new type of gate-opening is primarily attributed on polarization effects. Tuning the electrostatic interaction among pillar and silicate by reducing the charge density of the latter alters therefore the present type of gate-opening. A decrease of the pillar density reduces simultaneously the Coulomb attraction between pillars and host layers modifying he gate-opening mechanism to a conventional structural gate-opening involving an increase in volume. The structural flexibility of MOPS in respect to systematic variation of charge density of the host, equivalent area of the pillar and their chemical functionality are the building blocks for a rational design of microporous materials tailored for separation of various industrially relevant gas mixtures.

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Multifunctional carrier based on clay minerals for drug delivery applications

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The goal of modern research is to use environmentally preferable materials. In this context, clay minerals are emerging candidates for their bio- and ecocompatibility, low cost and natural availability. Clay minerals present different morphologies according to their layer arrangements. The use of clay minerals, especially in biomedical applications is known from ancient times and they are regaining attention in recent years.[1,2] Among them, halloysite nanotubes are emerging materials with appealing properties for biological applications.
The present communication will be focused on some carrier systems based on halloysite nanotubes, for the delivery of biological molecules into cells.[3]

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[2]Rizzo C., Arrigo R., D'Anna F., Di Blasi F, Dintcheva N.T., Lazzara G., Parisi F., Riela S., Spinelli G., Massaro M. (**2017**) J. Mater. Chem. B, 5, 3217-3229.
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Fate of α-isosaccharinic acid in Callovian-Oxfordian clay-rich rock studied by *in situ* experiment

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When emplaced in deep geological disposal cells, intermediate-level long-lived radioactive waste and their cement-based packages can potentially release high amounts of anthropogenic organic matter. For example, isosaccharinic acid (ISA) was quantified as main degradation product of cellulose-containing waste, potentially released in large amounts and having an ability to form soluble complexes with radionuclides (Rout *et al.*, 2015). The behaviour of ISA strongly depends on the environmental conditions, *e.g.* abiotic conditions in laboratory experiments or biotic *in situ* conditions. In this context, α-ISA was chosen to be studied in an *in situ* diffusion experiment in the Meuse/Haute-Marne Underground Research Laboratory (East of Paris Basin, France). The fate of α-ISA in Callovian-Oxfordian (COx) clay-rich rock will depend on its transport properties, which have been assessed by means of batch and diffusion experiments (Dagnelie e*t al.*, 2018), but also on possible microbial degradation at circumneutral conditions (Kuippers *et al.*, 2015).

To design the experiment, the solubility of α-ISA in the COx pore water has been determined experimentally and predictive reactive transport modelling computations were done to evaluate the relative influences of diffusion, adsorption and biotic degradation of α-ISA. A gas chromatography-mass spectrometry (GC-MS) analytical method was developed and allows the quantification of α-ISA down to micromole per liter.

The experiment, to be implemented in 2019, consists in injecting 20-25 L of pore water with an initial concentration of 4 10^{-3} mol/L of α-ISA. The fluids will then circulate in contact with the rock, through the 5-m long packed-of interval at the far end of a 15-m long descending borehole. The water circuit is connected to a water sampling module, placed in the gallery, that allows air-protected samples to be taken for further chemical and microbiological analyses. Potential biodegradation products of ISA will be searched for, in order to discriminate the contributions of various mechanisms, *e.g.* adsorption or biodegradation, responsible for α-ISA content evolution in the pore water.

Dagnelie R.V.H. *et al.* (**2018**) Chemosphere, 213, 472-480.

Kuippers G. *et al.* (**2015**) Mineralogical Magazine, 79(6), 1443-1454.

Rout S. *et al.* (**2015**) Plos One, 10 (3), e0119164.

Functionalized clay minerals as "smart materials" for corrosion inhibition in paints

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The development of new corrosion inhibitors for paints is currently a hot topic to replace toxic pigments based on Cr(+VI) compounds (or others heavy metals) and to avoid the problematic release of phosphate ions caused by the degradation of widely used aluminum or zinc phosphate pigments. Actually, most of the current anticorrosion act by a dissolution process in the paint. Besides the potential toxicity issue, this raises also the problem of the organic protective layer integrity which can be impacted by holes or cracks.

In this framework, the objective of the present study is to present investigate anticorrosion pigments incorporated in a polymer coating, based on functionalized beidellite clay isolated from a raw clay picked up from Agadir basin (Morocco). Beidellite is herein used to store corrosion inhibition compounds in the interlayer space and added to the paint. Thus, the corrosion inhibitor can be progressively released in response to physico-chemical stimuli such as chloride or Na^+ concentrations or pH modifications.

The main advantages of clay minerals and especially beidellite are their ionic exchange capacity, their dimension stability in polymer coating, providing the opportunity to develop "smart materials" as corrosion inhibitors.

In this respect, two kinds of functionalization were performed on beidellite herein: the first one by direct intercalation of cationic inhibitors, and the second one with anionic inhibitors after cationic polymer grafting on beidellite sheet surfaces.

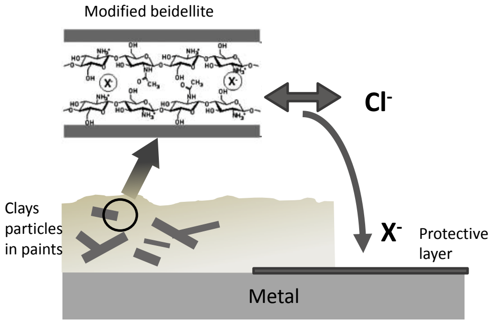

Figure : Principle of action of functionalized clays in paints (case of anionic corrosion inhibitors X^-)

Chemical analyses of functionalized clays were carried out by X-ray diffraction, thermogravimetry and scanning electron microscope. The physico-chemical conditions and kinetics of intercalation/deintercalation processes were characterized in aqueous solution. Then the corrosion inhibition and its mechanism were investigated by different electrochemical measurements without and with the polymer coating containing the functionalized clay minerals.

Using multivariate techniques to assess the effects of raw materials source and manufacture of Rammed-earth and Coating on conservation: the case of Badii Palace (Marrakech, Morocco).

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The city of Marrakech contains some of the most prestigious monuments of Islamic art, being Badii Palace (16th century) one of them. A project between Universities of Aveiro (Portugal), Cadi Ayyad (Marrakech, Morocco) and Liège (Belgium) has been developed aiming to provide accurate scientific diagnosis on the status and causes of damage found on the materials used for the construction and restoration this Palace. The approach consists to characterizing the various materials used in the construction, followed by comparison with local materials in order to assess the provenance of the earths and to identify suitable materials for restoration.

On a first stage, 30 samples of rammed-earth and coating materials collected from selected parts of the Badii Palace wall and local raw materials were studied for particle size distribution, chemical and mineralogical compositions. Differences in compositions between the rammed-earth and coating materials have been evidenced (Daoudi *et al.*, 2018). Samples from well-preserved wall places show a perfect compatibility between the coating material and the corresponding rammed-earth. However, the incompatibility of these 2 types of materials is clear in many wall parts where the original coated materials have deteriorated by natural weathering and by the corrosive action of polluted atmospheres. Obtained results also point to 2 local raw materials deposits.

On a second stage, multivariate statistical analysis were performed, using Cluster, Principal Components and Discriminant Analysis. Cluster analysis separated rammed-earth materials and plasters showing also relationships between them and different raw materials. Principal Components analysis stressed the influence of compositional parameters on provenance and conservation status. Discriminant analysis established the hierarchy of the groups according to their similitudes and differences, as well as which parameters are most relevant for these discriminations. These analysis allowed to better establish the internal homo(hetero)geneities, the relations between different building materials and their possible raw materials and, finally, the influence of textural, mineralogical and chemical characteristics on their relative compatibilities and conservation.

Daoudi L.; Rocha F.; Costa C.; Arrebei N.; Fagel N. (**2018**) Geoarchaeology, 33, 529−541.

Alkaline activation of rammed earth material – properties improvement for sustainable conservation and rehabilitation.

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The earth construction is the oldest technique and was once the most used by man, representing one of the first uses of geological resources. Adobe is an extremely simple form of earth construction and with this technique the shrinkage associated with the construction of large structures is avoided. In Portugal, earthen materials have been used in load-bearing walls in the form of adobe or rammed earth for the construction of buildings especially in the southern and central coast. Rehabilitation of adobe buildings must be sustainable, considering that one of the great advantages of the earth buildings is low energy consumption; thus, priority must be given to materials and processes taking advantage of low energy (without thermal processes) components as well as reduction of transport costs of the material, due to its availability in situ or at short distance.

Most conventional consolidation treatments used in the past have not succeeded in providing a long-term solution because they did not tackle the main cause of degradation, the expansion and contraction of constituent clay minerals in response to humidity changes. Clay swelling and posterior retraction could be reduced significantly by transforming clay minerals into non-expandable binding materials with cementing capacity using alkaline activation. To reach these aims, we developed adobes with water, submitted to alkaline activation with NaOH and KOH.

Alkaline activations were performed at room temperature and evaluated during the curing time (28, 60 and 90 days) for mechanical resistance and water absorption by capillarity. The formulations were made with materials used in traditional adobe constructions, thus seeking greater compatibility for a future use for historic buildings rehabilitation. In general, an increase in mechanical strength was observed in comparison with common water adobes.

The success of the formulations depended on the interaction of raw materials with the type of alkaline activator, being controlled by grain-size distribution, mineralogical composition and texture. The obtained results allowed to conclude that the adobes with both NaOH and KOH have an increase of its properties. However, NaOH activated adobes showed higher increase on mechanical properties whereas KOH activated ones showed lower water absorption. This approach can be a starting point for future solutions for rehabilitation of old adobe buildings and in sustainable adobe construction.

New routes of synthesis to obtain hybrid pigments based on carminic acid

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Different applications of natural dyes by mankind have been reported since ancient ages such as manufacturing of painting inks, cosmetics, dying of tissues and food coloring. Among the natural dyes, carminic acid (CA) is highlighted as a red pigment derived from cochineal with multiple uses.[1,2] Nevertheless, several works reported that CA presents light and temperature vulnerability when applied in its pure form. In this sense, the development of hybrid pigments has been pointed out as an alternative to solve these problems.[3,4] Given that, this work intent to synthesize new stable pigments based on CA and clay minerals. Three different systems were prepared with CA: raw saponite/dye; aluminum based pillared saponite/dye; and hydrogels of saponite or montmorillonite/dye covered by organosilanes n-hexadecyltrimethoxysilane (HDTMS) and tetraethoxysilane (TEOS). The solids were characterized by X Ray diffraction (XRD), thermal analysis (TG-DTA), infrared and nuclear magnetic resonance spectroscopies and transmission electronic microscopy (TEM). They were then submitted to chemical stability and photodegradation tests. We observed that Al-pillared saponite presented a greater stability compared to the raw saponite, once the dye is strongly binded on the aluminum pillars. The pigments obtained from hydrogels presented the greatest light stability due to the coverage with TEOS/HDTMS that acts as a protective layer. The versatility of inorganic matrixes with the photochromic properties of the organic dye allowed the preparation of stable pigments for possible applications in oil formulations.

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Amino-imine functionalized bentonites: from environmental remediation to new pigments

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In recent years, the presence of dyes in wastewater is an environmental problem. Synthetic dyes may cause damage not only to aquatic life, but also to human life.[1] Among various techniques used to remediate dyes, adsorption is one of the most applicable technologies worldwide.[2] However, the destination of the final solids and/or their reuse after the process have also to be investigated.[3] Therefore, in this work amino-imine functionalized clay minerals were synthetized to produce new pigments from dye-saturated solids. Amino bentonites were firstly synthetized by silylation over microwave irradiation for 5 min in presence and/or absence of ethylene glycol. Then, the silylated samples were reacted with glutaraldehyde to produce imino moieties immobilized on the surface. Infrared spectroscopy was used to monitor the grafting process, while the functionalization degree was estimated by using CHN elemental analysis. X-ray diffraction and transmission electron microscopy suggested the formation of intercalated hybrid compounds without exfoliation of the layered structure. The new solids were used for adsorption of violet 5R at pH 3, 7 and 10. The fixation of the dyes on the functionalized bentonites was then investigated by structural and spectroscopic techniques. The stability/photodegradation of the dye-amino imine bentonites was performed by using spectrophotocolorimetric analysis in solid state and in oil paints formulations samples. The data showed that all modified solids fixed the Violet 5R dye. The amount of dye increased in acidic medium resulting in more intense color at pH 3. Other parameters such as the absence or presence of ethylene glycol used as solvent in the synthesis of the solids and the presence of amino-imine groups in functionalized bentonites influenced the colors of the prepared pigments. The oil paints formulations presented less color differences than solid pigments and can simulate a real formulating inks for paintings. The aging tests revealed the high stability of the prepared pigments even after 450 h of light exposure. The results highlighted the dye/amino-imine bentonite hybrids as new stable pigments and presented an alternative to reuse of the loaded adsorbents.

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Atomically-Resolved Transformation Pathways of Ferrihydrite to Goethite

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Fe(III)-(oxyhydr)oxides are critical secondary minerals in soils and sediments that control iron bioavailability and the cycling of coupled elements. The nanomineral ferrihydrite is a poorly crystalline and metastable initial form, typically resulting from aqueous Fe(II) oxidation during meteoric recharge of otherwise stagnant suboxic pore water. Because it is metastable, ferrihydrite will spontaneously transform into more crystalline and persistent bulk phases such as goethite or hematite. However, in the absence of a redox catalyst such as Fe(II), this transformation tends to be kinetically hindered, consistent with both 1) the extremely low aqueous solubility of Fe(III), which restricts the dissolution/reprecipitation pathway, and 2) the extremely low solid-state diffusivity of lattice iron expected at room temperature, which restricts the topotactic transformation pathway. Particle-based recrystallization to goethite has been proposed, but this cannot transform ferrihydrite without recruiting one or both of these two slow pathways. Furthermore, in the presence of millimolar aqueous Fe(II), the goethite product and its physical characteristics are essentially unchanged, but the kinetics are, intriguingly, about 1000x faster.

We report a comprehensive experimental/computational investigation into this transformation at suboxic conditions and circumneutral pH, resolved at the iron site occupancy level. In the absence of added Fe(II), two-line ferrihydrite aged over two years was periodically characterized using *in situ* mXRD with detailed line shape analysis, electron microscopy, and synchrotron Fe *L*-edge and O *K*-edge XAS/XMCD spectroscopy quantitatively analyzed using MRCI *ab initio* calculations. The results are compared to DFT calculations of the relative thermodynamic stabilities of several possible ferrihydrite structure models as a function of hydration state, and goethite, along with activation energies for solid-state diffusion of iron along hypothetical topotactic channels. Tetrahedral Fe(III) is clearly resolved in 2 d ferrihydrite, diminishing concomitantly with increasing octahedral Fe(III) and decreasing net magnetic moment until the first appearance of goethite at ~ 100 d. Calculated iron diffusion activation energies are as low as 1 eV per unit cell. In the presence of Fe(II), the accelerated transformation kinetics appear to involve facile mass transfer of a labile Fe(III) pool created on ferrihydrite surfaces during oxidative adsorption of Fe(II). The findings are being assembled into transformation kinetics models that will help resolve the relative importance of dissolution/reprecipitation vs. solid-state pathways, to lay out the first atomically-resolved mechanism of this important Fe(III)-(oxyhydr)oxide mineral transformation.

Mineral- and Ion-Specific Effects at Clay−Water Interfaces: Structure, Diffusion, and Hydrodynamics

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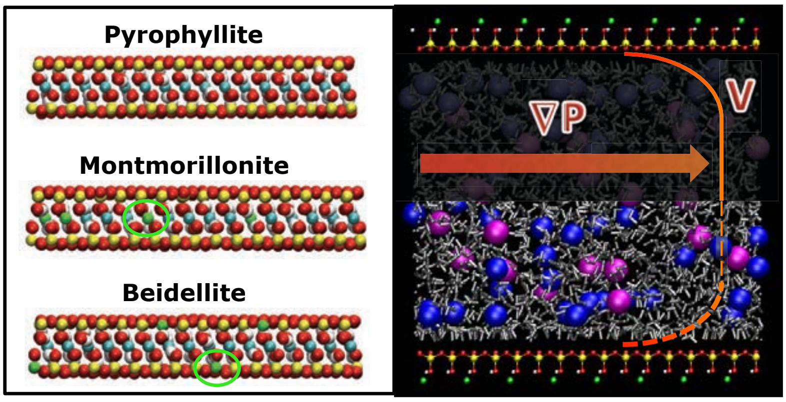
We use molecular dynamics to investigate how the structure, diffusion, and hydrodynamic properties of clay interfaces with aqueous solutions depend on the nature of the clay, the nature of the counterions, and the salt concentration in the solution. Specifically, we study water-filled nanopores between uncharged (pyrophyllite) and charged (montmorillonite and beidellite, with substitutions located in the octahedral and tetrahedral layers, respectively) clays, with sodium or cesium as counterions, in the absence and in the presence of added salt. We discuss how the balance between solvation and attraction of the cations to the surface results in various distributions between inner- and outer-sphere complexes, and how this influences the dynamics of water near the surface, as well as the hydrodynamic flow in the presence of an external force. In the latter case, the discussion based on mapping the molecular velocity profiles to a continuous description (parabolic Poiseuille flow) shows that the larger effects come from the presence/absence of charge in the mineral, as well as the localization of substitutions within the clay layer. The salt concentration and the nature of the counterions have a comparatively less important impact far from the surface, even though some differences are observed in its close vicinity, which are not properly captured by the continuous description.



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Structural and phosphate adsorption properties of nano-sized ferric oxyhydroxides produced by oxidation of Fe^{II}-Fe^{III} layered double hydroxides (green rust)

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Phosphorus (P) is an essential nutrient for growth of all organisms. Excessive supply of P to freshwaters from agricultural, industrial, and household activities causes eutrophication of fresh and coastal waters typically seen as algal blooms [1]. Nano-sized ferric oxyhydroxides such as ferrihydrite are well known to be suitable materials for removing phosphate from water. Other types of nano-sized iron oxides may be produced from Fe^{II}-Fe^{III} layered double hydroxide precursors, more commonly called green rusts (GR) [2, 3]. A three-dimensional ferric oxyhydroxycarbonate, called ferric green rust (FGR), was synthesized by the controlled oxidation of the carbonate interlayered form of GR, GR(CO_3) [2]. Another oxidation product of GR, a bi-dimensional single sheets of iron oxides (SSI), was produced by an oxidation/alkalization process using dodecanoate interlayered GR as precursor [3]. The structural and surface properties of FGR and SSI have been compared using several techniques such as XPS, Mössbauer and Raman spectroscopies. Similarities between FGR and SSI are observed in the O1s XPS spectra, and also between the temperatures of magnetic transition measured by Mössbauer spectroscopy [4]. The P adsorption kinetics and isotherms were recorded at pH 7 for FGR synthesized by different pathways [2]. The phosphate removal capacities of FGR, ferrihydrite and SSI were of the same order of magnitude; however SSI exhibited a particularly fast P adsorption kinetics [5]. In conclusion, bi- and three-dimensional nano-sized ferric oxyhydroxides are very promising compounds for phosphate removal and may be used to design new types of nanocomposites useful for water dephosphatisation.

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Stevensite-geofilter effectifivity for antibiotics sorption in wastewater treatments

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Antibiotics, such as tetracycline and sulfonamide families, are widely consumed for human and veterinary use. Many antibiotics are not inherently biodegradable and some of them can persist in soils for long periods of time at significant concentrations. These compounds that are released to the soil system can subsequently be transported to surface water or groundwater and, therefore, have a negative effect on ecosystems, crops and water quality.

Current water treatment technologies are not efficient enough for the removal of antibiotics contained in wastewaters [1]. Recent studies have showed that antibiotic drugs families, as sulfonamide, tetracycline and macrolide, have been detected worldwide in most of the high development countries. Residues of antibiotics in the environment are problematic as they are responsible of the proliferation and transmission of resistant pathogenic and commensal bacteria and their gens.

In the present study, a natural tri-octahedral smectitic clay, stevensite subjected or not to thermal treatment at 200 ºC, has been used to study the adsorption of sulfonamide and tetracycline from aqueous solution with the objective of designing a filter able to efficiently adsorb these kind of antibiotics from the sewage.

To carry out the study, batch experiment and laboratory columns packed with quartz sand have been used to test the effects of pH on their retention and transport of these antibiotics. The results showed that both, sulfamethoxazole and tetracycline hydrochloride, have a different behavior in similar conditions. Stevensite has been demonstrated to be an interesting material for tetracycline adsorption in a broad pH (4-8) range with maximum values at pH around 7 [2], in spite of the change form cationic positive to neutral polarity of the molecule. However, the preliminary tests that have been carried out with sulfonamide show how sorption capacity is restricted to lower pH (<4) values. Other material solutions are being considered to improve the adsorption efficiency under environmental pH conditions.

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Humic acids influence on the thallium-potassium cation exchange behavior of illite

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The influence of humic acids (HA) on the mechanism of cation exchange of K^+ by Tl^+ in IMt-2 (Silver Hill, Montana) illite clay was investigated. For this purpose, Tl^+ sorption isotherms in purified samples of the K^+-illite were performed in the absence and presence of HA at pH values of 3, 7 and 9.

In the absence of HA, the sorption of Tl^+ increased with increasing pH, which demonstrates the important contribution to its net electrostatic charge of the variable charge behavior at the clay particle edges. In addition, a possible contribution to the decrease in Tl^+ sorbed was identified at pH 3, by predicting a certain degree of dissolution of the illite.

In the presence of HA, since its dissolution is considerable at pH values as low as 3 and increases until complete dissolution at pH 9, the total Tl(I) sorbed concentrations on the illite decreased considerably at all pH values, suggesting the formation of a strong aqueous Tl(I)-HA complex. Tl(I) sorption was highest at pH 7, intermediate at pH 3, and lowest at pH 9. At this latter pH a high concentration of the dissolved complex is expected, and therefore the highest competition against Tl sorption. At the other two pH values, the differences in Tl sorption may be explained by similar reasons as in the absence of HA, adding the respective sorption decrease arising from the HA aqueous complex formation in both.

All isotherms were successfully simulated through the combination of a surface complexation and cation exchange model (1pKa/CE model), using the PHREEQC code, and the selectivity coefficients for the Tl-K exchange in illite were obtained using appropriate optimization procedures. Implications of the different selectivity coefficients obtained will be presented.

Carbon-sepiolite nanostructured materials incorporating Pd nanoparticles as improved catalysts for hydrodechlorination processes

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In recent years carbonaceous materials and clay minerals have been combined to produce a large variety of carbon-clay hybrid materials whose interest included applications as components in electrochemical devices, additives in polymer nanocomposites, adsorbents or as catalysts (Darder et al., 2018). In this context we have reported the use of sonomechanical treatments to produce diverse functionalized graphene-based materials by assembling graphene nanoplatelets (GNP) to clay minerals (Ruiz-Hitzky et al., 2016). When the implied clay mineral is sepiolite of rheological degree (e.g., Pangel S9, Tolsa SA) the resulting dispersions are very stable and allow the combination with other species (e.g., carbon nanotubes, biopolymers,..) for producing diverse multifunctional conducting materials.

The present communication will introduce results on the characteristics and properties of various carbon-sepiolite/Pd catalysts prepared by direct assembly of sepiolite fibers, graphene nanoplatelets and multiwall carbon nanotubes, also *in situ* synthesized Pd nanoparticles (Ruiz-García et al., 2018). Characteristics such as porosity, surface area, electrical conductivity as well as catalytic performance will be discussed on the basis of their composition. The catalytic activity has been evaluated in the hydrodechlorination reaction of 4-chlorophenol showing exclusive selectivity to phenol. Differences in activity and activation energy values depend strongly on the composition of the materials. The study confirms that the presence of sepiolite affords some valuable advantages: increasing the specific surface area, acting as capping agent and stabilizing the produced Pd nanoparticles, and acting as adsorbent of the HCl generated in the reaction helping to reduce the Pd poisoning.

Acknowledgements: financial support from MINECO (Spain): MAT2015-71117-R, CTQ2012-32821 and CTQ2015-65491_R projects and BES-2013-06608 5 C.R.-G. pre-doctoral Grant.

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Health impact of sepiolite fibrous clay mineral

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Diverse attempts to compare the behavior of sepiolite and palygorskite fibrous clays against asbestos minerals regarding health risks have been carried out in the last past decades with controversial results. The initial basis of that comparison can be mainly related with morphology, texture and composition of both types of silicates. However, sepiolite and palygorskite frequently show short length fibers that significantly exhibit different aspect ratio than asbestos and at the same time the structural and textural features are also different, the fibrous clays showing inherent porosity and easy dissolution in acidic environment contrarily to typical behavior of asbestos. *In vitro* and *in vivo* tests, as well as epidemiological studies, have confirmed that at least sepiolite from Taxus Basin deposits in Spain does not constitute a health risk (Denizeau et al., 1985; Carretero León & Pozo Rodríguez, 2007). Studies carried out on humans exposed to sepiolite seem to bear out the fact that exposure to this mineral involves no risk (Baris et al., 1980; McConnochie et al., 1993).

This communication will introduce new insights on toxicity of sepiolite from Tagus Basin deposits in Spain, considering aspects such as fiber length and other characteristics particularly when interacting with mammalian cells. For instance, we have observed spontaneous internalization of disaggregated sepiolite bundles in this type of cells without damage except in high concentration of clay dispersions. This behavior significantly differs from that observed in bacteria where the Yoshida effect could take place.

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Clay minerals as a key to seismic hazard assessment for a New Nuclear Build: Wylfa Head, Anglesey, North Wales

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Constraining the age of most recent fault movement and identifying potential 'capable' faults is part of the critical external hazard assessment for new build nuclear projects. The UK Atlantic margin is often underlain by Precambrian and early Palaeozoic rocks that preserve a history of late Palaeozoic, Mesozoic and Cenozoic basinal subsidence and inversion which culminated in the opening of the Atlantic Ocean. Constraining the age and duration of tectonic events remains problematic given that individual faults are inherently weak and repeatedly reactivated. An opportunity to examine Atlantic margin fault rocks was provided through studies commissioned by Horizon Nuclear Power Ltd. to evaluate the sesmic risk for a proposed new nuclear power plant at Wylfa Head on Anglesey, North Wales.

Detailed core logging and a comprehensive petrographic study were used to establish a history of relative movement and mineralisation from onshore faults cutting Lower Palaeozoic host rocks. Analysis showed local evidence of authigenic illite in fault gouges associated with the last phase of movement (Fig. 1). These findings informed fault gouge sub-sampling for K-Ar dating. This study also yielded, we believe, the first identification of palygorskite in an Anglesey fault rock.

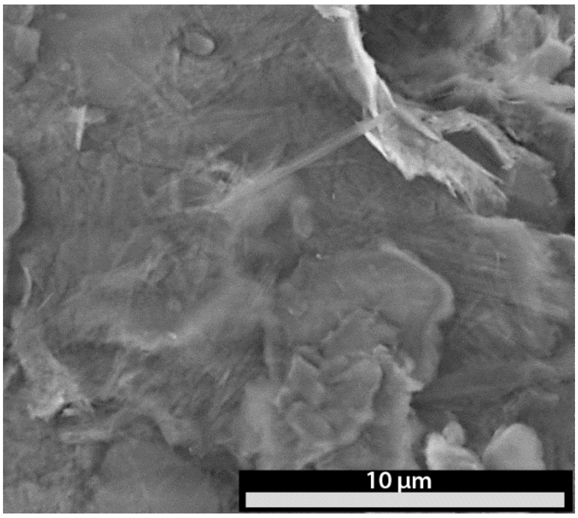

Figure 16 : SEM image showing

X-ray diffraction (XRD) was used to identify and quantify the illite polytypes in the fault gouge samples, which are a mix of host rock ($2M_1$), and authigenic (1M) illite. Using the XRD data together with the K-Ar dating results, we have been able to constrain the youngest clay mineralization episode (~38 Ma) and demonstrate a history of multiple illite growth episodes going back to ~180Ma. These illite ages are used as a proxy for fault reactivation from which a history of fault movement is proposed. Subsequent U-Pb dating of gouge-associated authigenic carbonate has yielded slightly younger ages (30.9-23.5 Ma). Taken together, we can be confident that no fault movement has occurred in the last 20 Ma.

Australian palygorskite for treating Pb (II) contaminated water

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In Australia, palygorskite deposits are primarily located in Lake Nerramyne (Western Australia) and Garford (South Australia). This presentation summarised the research performed on Australian palygorskite as a potential adsorbent in removing lead Pb(II) from contaminated water. Modifications of raw palygorskite into polymer-clay and magnetic nanocomposites to enhance their physico-chemical characteristics were achieved through facile synthesis route. Characterisation of raw and modified palygorskite was carried out using techniques like FTIR, XRD, SEM, TEM, TGA and XPS. Adsorption experiments were performed in synthetic and simulated contaminated water. Overall, significant efficiencies enhancement in Pb(II) removal from aqueous solution by palygorskite nanocomposites was recorded. A maximum adsorption capacity, q_{max}, of 201.5 mg g^{-1} and 58.5 mg g^{-1} was recorded by polymer-clay composite and magnetic palygorskite nanocomposite, respectively. High adsorption capacities, easy separation and high magnetic stability were demonstrated by the magnetic palygorskite composites. This study has shown that Australia's natural palygorskite could serve as a reliable and efficient adsorbent for the remediation of heavy metals in contaminated waters.

Arsenic speciation in trioctahedral clays: insights from a serpentine synthesis study

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The occurrence of arsenic in minerals and amorphous solids is one of the main controls on its behavior in groundwater, sediments, soils and hydrothermal-metamorphic systems. The oxidation state of arsenic ranges from 3- to 5+, where the low oxidation states tend to occur in sulfides and arsenides and the higher oxidations states – As(III) and As(V) – in oxides, hydroxides and silicates. Arsenic in antigorite and chlorite occurs as As(III) or As(V) in tetrahedral coordination and potentially as As(III) in octahedral coordination. Both minerals are sources of elevated As in groundwater. Considering charge and radius of ions in silicate minerals, the occurrence of As in in phyllosilicates is predictable. As(V), with a crystal radius of 0.48 Å, is a better fit in the tetrahedral sheet than Al(III) with (crystal radius of 0.53 Å), and the 0.54 Å crystal radius of As(III) is nearly identical to Al. Paired substitutions to balance charge may include:

$$\mathrm{As(V)} + \mathrm{As(III)} = 2\ \mathrm{Si(IV)}$$

$$\mathrm{As(III)}_{tet} + \mathrm{Al(III)}_{oct} = \mathrm{Si(IV)}_{tet} + \mathrm{Mg(II)}_{oct}$$

To study incorporation of As into trioctahedral clays, we synthesized serpentine minerals at 200 ^{o}C over 10-day periods in alkaline solutions including varied amounts of Si, Mg, Al, As(III) and As(V). XRD data from synthesized powders lacking Al (and with or without As) indicates 00*l* peaks at 7.5, 3.66, 2.47 and 1.84 Å with broad weak peaks at ~ 9.5 14 Å suggesting small amounts of interstratified or physically mixed talc-like 2:1 layers. 020 and 060 peaks indicate b-axis of 9.1 to 9.2 Å. Al-bearing solutions (with or without As) produced powders with a sharp 7.2 Å 001 as well as broad weak peaks at ~ 9.5 Å. FTIR data for As-bearing serpentines are consistent with those of naturally occurring chrysotile, especially peaks at 3696, 980 and 600 cm^{-1}, whereas specimens that include Al (with or without As) are more similar to naturally occuring antigorites. TEM data from As-bearing synthesized serpentines shows tubular crystal form, consistent with XRD and FTIR evidence for chrysotile, whereas Al-bearing synthesized serpentines have platy morphology, consistent with antigorite. These relationships are consistent with the presence of octahedral Al that reduces the T-O mismatch and allows planar crystals to form. As in tetrahedral sites would preserve the mismatch and foster tubular crystals. Elemental analysis by EDX analysis in the TEM and by ICPMS analysis of dissolved powders reveals average compositions of As-bearing chrysotile-like crystals of $\mathrm{Mg_{2.8}(Si_{1.8}As_{0.2})O_5(OH)_4}$, and of platy antigorite-like crystals of $\mathrm{(Mg_{1.8}Al_{0.7})(Si_{2.0})O_5(OH)_4}$. Syntheses using both As(III) or As(V) indicate that either, or possibly both, enter the serpentine structure. Low octahedral occupancy relative to tetrahedral occupancy is consistent with interstratified talc-like layers, and HRTEM reveals interstratified 9.5 Å talc-like layers within crystals mainly comprised of 7 Å layers, including lateral transitions between these two layer types. To decipher questions of As(III) vs. As(V) and to assess speciation of As into tetrahedral (predicted) vs. octahedral sites, powders also will be analyzed by EXAFS and XANES.

Physico-chemical studies of Mg/Fe and Mg/Al Layered Double Hydroxides obtained via transformation of minerals

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Layered Double Hydroxides (LDH) represent a large class of phases which exhibit a brucite-like structure intercalated with anions. According to the general formula $[M^{II}_{1-x} M^{III}_{x} OH_2]^{x+} [A^{n-}]_{x/n} \cdot y H_2O$, the LDH structure consists of divalent (M^{II}) and trivalent (M^{III}) metals that form positively charged layers where the charge is balanced by interlayer anions. The LDH display a wide range of unique physical and chemical properties which makes them perfect candidates in a variety of industrial applications, including wastewater treatment [1]. These minerals can be rarely found in nature and represent a hydrotalcite-pyroaurite group [2], however their synthesis is easy to carry out in laboratory conditions. Nevertheless, the exclusive use of chemical reagents for their synthesis is relatively expensive. This implies a demand for other low-cost sources of metals e.g. metal-bearing minerals forming widespread deposits.

The aim of this research was to investigate the quality of Mg/Fe and Mg/Al LDH obtained by the transformation of magnesite [M] and dolomite [D]. These minerals were sources of M^{II} (Mg^{2+} and Mg^{2+}+Ca^{2+}, respectively) and $AlCl_3$ or $FeCl_3$ were used as a source of M^{III}. The M and D were dissolved in the appropriate chloride solution, where acidic hydrolysis enabled the release of M^{II} cations. This approach is an alternative to the use of strong acids e.g. HCl which is not desired in industry due to corrosive properties [3]. The solution containing M^{II} and M^{III} was added dropwise to the 2M NaCl solution with the pH=10 set by an aqueous NaOH and controlled constantly during the synthesis. The obtained slurry was aged (2 or 24 h), washed with water and dried at 60°C overnight. For comparison the samples of pure LDH from chemicals were synthesized in analogical conditions. Several variations of LDH in terms of M^{II}/M^{III} ration and ageing times were obtained.

The XRD confirmed presence of LDH in all samples as compared to the ICDD standards of hydrotalcite and pyroaurite. In the samples derived from minerals additional phases: gibbsite, calcite and akaganeite were formed. An increasing M^{II}/M^{III} molar ratio induced structural changes revealed by peak shifts in the XRD patterns. This was due to changes of unit cell parameters as well as change of interlayer distance. It was observed that an increase of ageing time affected the crystallinity of the obtained phases. The LDH morphology was depicted by the SEM and showed characteristic layered structures differing from the starting minerals. The surface chemistry and thermal behaviour of the materials varied as attested by DTA/TG and XPS methods.

Acknowledgement: This research was supported by the National Science Centre, Poland under the project no. 2017/27/B/ST10/00898.

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Synthesis and Study of Layered Double Hydroxides with Magnetic Properties

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One of the areas of application of layered double hydroxides (LDHs) is water purification [1]. Recently, special attention has been paid to the synthesis of magnetic layered double hydroxides [2] or composites based on them [3] and using them for water decontamination treatments.

In the present study multicomponent LDHs with hydrotalcite structure containing doubly charged magnesium and cobalt cations and triply charged aluminum and iron cations in the brucite-like layers have been synthesized by co-precipitation at variable pH. Formation of hydrotalcite structure has been confirmed by XRD (Fig.1) though a presence of extra phase has been detected in the sample with high cobalt and iron content as well. It was the sample that exhibited room temperature magnetism. Sorption capacity of the LDHs towards anionic Congo red dye at room temperature was estimated (Fig.2). Dyes concentration in the solutions was determined spectrophotometrically.

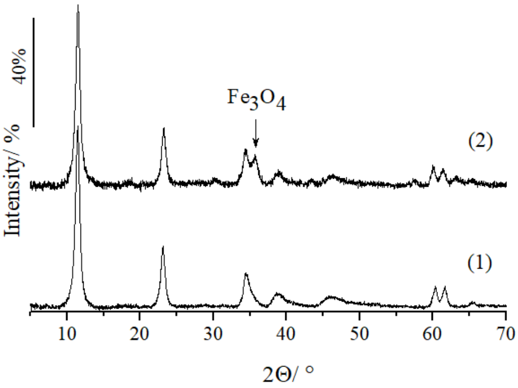

Fig.1. XRD pattern of LDHs:
$Mg_{0.497}Co_{0.225}/Al_{0.205}Fe_{0.073}$ (1);
$Mg_{0.289}Co_{0.366}/Al_{0.159}Fe_{0.186}$ (2)

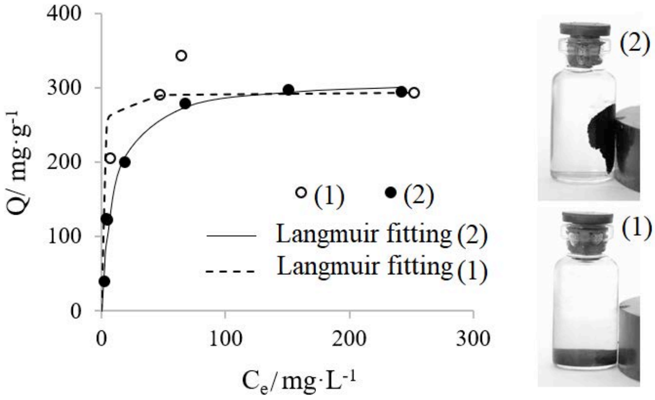

Fig.2. Isotherms of sorption of Congo red on LDHs:
$Mg_{0.497}Co_{0.225}/Al_{0.205}Fe_{0.073}$ (1);
$Mg_{0.289}Co_{0.366}/Al_{0.159}Fe_{0.186}$ (2)

The sorption isotherms for all samples in a given concentration range were described by Langmuir model. It was determined that the presence of extra phase did not influebce the sorption capacity towards anionic dye (Fig.2).

This work was supported by the Russian Foundation for Basic Research, grant № 18-29-12103.

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Adsorption of pharmaceutical compounds confined in clay nanospaces by molecular modelling

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Phyllosilicates have a nanometric interlayer space accessible to water molecules and other compounds. This interlaminar space represents about 90% of the mineral total surface yielding a high adsorption capacity. These properties make phyllosilicates suitable for environmental applications, such as the retention of organics residues in soils, or their use as nanocarriers for controlled release of pharmaceutical drugs. However, it is difficult to know how is the molecular structure of these organo-silicate nanocomposites. Several cases will be showed where experimental investigations showed discrepancies and molecular modelling has helped to find the solution. Besides, the intermolecular interactions are important for organic crystal polymorphs. Some examples of organic molecules with pharmaceutical interest confined in phyllosilicates with layered structure such as montmorillonite, with fibrous structure, such as palygorskite, and tubular forms such as halloysite, will be showed. Complementary between experimental and theoretical calculations results will be presented for several surfactants and pharmaceutical drugs in clays. Different theoretical methodologies with force fields based on empirical interatomic potentials and quantum mechanics methods based on Density Functional Theory (DFT) level calculations along with Molecular Dynamics simulations have been used to study the adsorption of organic molecules on models of crystal surfaces of silicates.

Aluminum silicate tubes by chemical gardens formation, new insights in the formation of tubular halloysite

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Halloysite is a dioctahedral 1:1 phyllosilicate similar to kaolinite with no significant charge generating cation substitution in tetrahedral or octahedral layer with high adsorptive properties. The siloxane surface is oriented to the external part of the tube whereas the aluminol surface is oriented to the internal part of the tube. Its main morphology is the tubular one, formed by concentric tubes with layers of internal tetrahedral silicate sheet with internal octahedral sheet. The mechanism of formation of the tubular morphology in halloysite is not well understood yet. Some authors have suggested the bending of flat kaolinite sheets as a possible mechanism (Singh, 1996). On the contrary, other authors reported that halloysite and kaolinite are formed independently because no transition phases (between these two minerals) are found as ageing progresses (Kirkman, 1977). Using chemical gardens from aluminium salts, tubes were formed where the external surface is formed mainly by silicate and the inner surface is mainly aluminum oxide-hydroxide. Although the crystallization and chemical composition of these chemical gardens are not the same as the nature halloysite formation, our laboratory experiments can be extrapolated to geological times. Therefore, we propose a possible mechanism for formation of tubular halloysite based on the chemical garden phenomenon. Besides, some molecular modelling simulations of adsorption of organics in the halloysite nanotubes will be presented.

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Effect of organic acids and ammonium ion on the dissolution kinetics of natural and K-saturated montmorillonite.

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Natural smectites undergo diagenetic transformations under surficial conditions, due to temperature, pressure, pH and fluid circulation. As the stratigraphic column deepens, the smectites become saturated in potassium, this element coming from the decomposition of potassium feldspars, favoring the transformation of smectite to illite. The changes produced in diagenetic conditions can increase or inhibit the dissolution of clays (Rozalen et al, 2009).

In basins rich in organic matter, diagenetic processes will promote their decomposition into simple molecules such as ammonium ion and organic acids, which will influence the dissolution dynamics of clay minerals (Golubev et al., 2006; Ramos et al., 2014).

To further our understanding of the process of smectite alteration in diagenetic conditions, we have studied the dissolution of natural (Na-Ca-Mg) and K-saturated montmorillonite under neutral pH conditions and different temperatures in the presence of ammonium acetate and ammonium oxalate. We performed flow-through experiments, using a typical concentration range reported for natural media, i.e. from 0.0001 to 0.5 M ammonium acetate and from 0.0001 to 0.25 M ammonium oxalate. The material used was montmorillonite from the Cortijo of Archidona deposit (Cabo de Gata, Almería, Spain). Stirred flow-through cells were submerged in thermostatic baths at a temperature of 25, 50 and 70ºC. The input solution was introduced into the cells at 0.02 mL/min, and the output solutions were sampled every 48-72 h.

The results obtained indicate that under steady-state conditions, the natural and potassium smectites experience an increase in dissolution rate with increasing temperature. Furthermore, the variation of the concentration of ammonium in the solution is not a fundamental factor in this process. At 25 ºC the dissolution rate of natural smectite is higher than K-saturated, this tendency decreases with increasing the temperature. At 70 ºC there are no differences in dissolution rates between both types of smectite. Compared with acetic acid, oxalic acid enhances montmorillonite dissolution rate probably due to formation of stronger surface and/or aqueous cation-oxalate complexes.

Smectite-to-illite transformation in the two types of montmorillonite depends of the alteration conditions, such as temperature a solution composition.

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Surface reactivity in cement mortars/bentonite interface experiments for the upscaling to an in-situ demonstration of nuclear waste clay barrier

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In the context of nuclear waste isolation, it has been studying the surface reactivity promoted by the contact between three types of cement mortars based on ordinary Portland cement formulations (CEM I, CEM II and CEM I + silica mixture, named low-pH) and bentonite. Laboratory experiments were performed during 6 and 18 months with the aim to obtain the main early perturbations and their evolution in a short time scale. Both types of materials were put in contact separated by a PTFE membrane casted in a methacrylate cylinder constrained in a stainless steel cell designed for flow-through tests. All experiments were duplicated. The system was exposed to a groundwater flow at 23±2ºC simulating the conditions foresee in a deep geological repository. Then, the effluent was collected at the end of bentonite and the flow rate, major chemical ions, alkalinity and silica were determined by means ion chromatography, potentiometric titration and Vis-spectrophotometry. The solid phase was cut and studied by scanning electron microscopy coupled to energy dispersive X-ray (SEM-EDX), random powder and grazing incidence X-ray diffraction (GI-XRD), specific surface area (SSA) and Infrared (FTIR) spectrometry analyses.

Hydraulic conductivity decreased the first month and tend to stabilize at $2.3\pm0.8\cdot10^{-13}$ m/s. The pH (8.1±0.2) and silica (13.6 ±2.6 mg/L), showed characteristic values of bentonite.

SEM-EDX analyses provided an Mg increase in the bentonite nearby (<400 µm) cement mortar, which is more pronounced in the bentonite-CEM I contacts. In the cement mortars, a Ca enrichment was found next to the interface (<200 µm) with high development in the CEM I and CEM II materials. Low-pH cement mortars presented precipitation of brucite mixed with calcium carbonate. These perturbations were determined at 6 months and were kept at 18 m.

XRD analyses show a slight modification of the montmorillonite basal spacing due to small changes in the exchangeable cations distribution and the development of a wide reflection in a~7.4 Å in the interface surface of bentonite related to Mg anomalies and the detection of tri-octahedral Mg-OH stretching IR bands. The 7.4 Å effect was found to enhance its development from 6 to 18 months for the bentonite exposed to CEM I and CEM II, and appears later (at 18 months) for the bentonite in contact with low-pH. Despite of this reactivity, the dioctahedral character of bentonite was kept because characteristic (hk0) reflections of montmorillonite were preserved. This suggests the coexistence of a brucite-montmorillonite complex with presumably Mg-tri-octahedral clay mineral according to the XRD reflections found at 1.52-1.53 Å.

These results can be compared with previous findings from larger scale experiments. In fact, they are discussed to evaluate their potential for upscaling the time and scale evolution applied to a reliable Engineered Barrier System required for the nuclear waste isolation issue.

This research has been supported by The European Union's Horizon 2020 Framework EUROATOM (H2020-NFRP-2014/2015) under subvention agreement Nº. 662147 (CEBAMA).

Drugs adsorption by hydrotalcite-like compounds synthesized from aluminium saline slag wastes

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In the secondary aluminium melting process, hazardous materials in the form of aluminium saline slags are generated. Due to their heterogeneous composition, which varies depending on the materials used for the recycling treatment, they have limited application. On another note, the increase consumption of drugs has generated awareness on the need for an effective operating procedure concerning the disposal and control of pharmaceutical waste. There is an increasing presence of emerging contaminants and, particularly, non-steroidal anti-inflammatory drugs (NSAIDs) in the aquatic environment.

In this study, aluminium from saline slags was extracted with a NaOH aqueous solution and used as an alternative aluminium source to form hydrotalcite-like compounds. The aluminium was combined with titanium chloride, zinc nitrate an sodium carbonate by the co-precipitation method, aged for 24 h, centrifuged and washed with distilled water until the excess NaOH was removed, dried at 60 ºC for 16 h and calcined at 400 °C for 4 h. The hydrotalcites were synthetized in varying concentrations of Ti-Al in order to test their salicylic acid and diclofenac adsorption capacity. The effect that several operational parameters, such as pHs, initial concentration of drugs, mass of adsorbents and contact time, may have on the sorption behavior was evaluated. The kinetic data were fitted to several adsorption models. The equilibrium adsorption data were analyzed using the Freundlich, Langmuir and Toth isotherm equation models. The results show an increment in the adsorption capacity with the increase of aluminium in the samples. For a 75 µM diclofenac concentration and 0.4 g/L of hydrotalcites, the sample with no aluminium (Zn_6Ti_2) did not adsorb any diclofenac, and the sample with no titanium (Zn_6Al_2) adsorbed 83% of the diclofenac, reaching equilibrium in around 200 min. Salicylic acid adsorption was once again non-existing for Zn_6Ti_2 while Zn_6AlTi and Zn_6Al_2 were able to adsorb 18% and 39%, respectively.

Acknowledgements: This work was funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (ERDF) through the project MAT2013-47811-C2-R.

Analysis of TGA-MS investigations on oil compounds adsorption on kaolinite and pyrophyllite

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It is a well-known fact that low salinity enhanced oil recovery (LSEOR) techniques work by altering the wettability of pore-lining minerals in an oil reservoir towards a more water-wet state. Therefore, to gain an understanding of the nanogeochemical mechanisms behind LSEOR, it is crucial to establish what drives this wettability change, particularly on clay minerals, which are the most common minerals in the pore space. In this work, we aim to understand how physical different chemical parameters (pH, salinity, cation type, Na^+: Ca^{2+} ratio, ionic strength) of aging water (representing formation water) affects the wettability of two clay minerals (kaolinite and pyrophyllite) with respect to polar model oil (decanoic acid dissolved into dodecane) mixtures. To this end, we used thermogravimetric analysis coupled to mass spectrometry (TGA-MS) to quantify and provide the type of adsorption and desorption of organic matter on solid surfaces, which are indicative of the wetting state. Results show that increasing the pH from 6.5 to 8 lead to smaller oil adsorption on kaolinite, while pyrophyllite shows similar oil sorption at both pH. This effect is probably mostly related to the combination of the protonation state of the polar oil molecules (decanoic acid) in the oil, which will be affected by pH, and the charge state on the aluminol face. At pH 6.5, a significant number of decanoic acid molecules are still protonated, which increases the possibilities of forming hydrogen bonds, in addition, the aluminol surface of kaolinite will be close to its point of zero charge. At pH 8, on the contrary, decanoic acid groups will be fully deprotonated (limiting any bonding to cation bridging) and the aluminol face will be negatively charged (again, limiting any bonding on this face to cation bridging). Changing the cation type also lead to variations in the oil sorption, with $CaCl_2$ inducing a larger amount of oil to be sorbed on the clays than an equivalent NaCl solution. In addition, there was a more pronounced concentration effect on the experiments performed with $CaCl_2$ where higher concentrations lead invariably to a higher oil retention. This effect was, again, less prevalent on the experiments performed with NaCl. Although there are slightly different amount of sorption on the effect of pH both kaolinite and pyrophyllite, all cases presents the similar trend on salinity effect which is high concentration of $CaCl_2$ related to high adsorption, but not NaCl. The effect of the divalent cations on increasing oil sorption can be explained by the development of cation bridges between the clays and the deprotonated polar oil molecule. Consequently, higher concentration of Ca^{2+} directly relates to be more oil adsorption whereas the presence of NaCl results in lower oil adsorption. This effect could also be observed in the experiments performed with different Na^+:Ca^{2+} ratios, where higher amounts of Ca^{2+} present in the mixture lead to increasing oil sorption. Finally, experiments performed with varying values of ionic strength (and a fixed Na:Ca ratio) show almost no effect of this parameter. Overall these results indicate that surface complexation and protonation/deprotonation effect are the dominant process determining oil adhesion, with double layer effect only playing a limited role.

Synthesis of Sepiolite/g-C_3N_4/Pd Nanoparticles Composites for Surface Plasmon Resonance Enhanced Visible-Light-Driven Photocatalytic Degradation of Rhodamine B

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The degradation of organic pollutants by using photocatalytic process under the visible light irradiation has attracted interest for dye wastewater treatment due to its effective use of solar light radiation. In this work, sepiolite/g-C_3N_4/Pd composites were successfully synthesized for photodegrdation of rhodamine B (RhB). Sepiolite was utilized not only as a space controller to accommodate g-C_3N_4, which is a metal-free photocatalyst, but also as an electron carrier between RhB and g-C_3N_4 due to the positive charge of RhB. Decoration of Pd(0) nanoparticles on g-C_3N_4 further enhanced the photocatalytic degradation of RhB, since Pd(0) supported to avoid the recombination between photogenerated electrons and holes in g-C_3N_4. Added amount of Pd was optimized to 1wt% Pd in the composite by photocatalytic degradation of RhB, which was consistent with decrease in photoluminescence intensity. The photocatalytic degradation mechanism was proposed in relation with the electron transfer from conduction band of g-C_3N_4 to the surface of Pd(0) nanoparticles though the heterojunction through the scavenger tests. The sepiolite/g-C_3N_4/Pd(0) composites can be a potential catalyst for degradation of positively charged organic pollutants in wastewater under the visible light.

Impact of pore size and surface charge on precipitation processes in clay systems: Case of barite precipitation in compacted kaolinite and illite

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Argillaceous formations are the focus of many studies concerning the development of geological facilities for the disposal of radioactive waste and the storage of anthropogenic CO_2. One scientific challenge is the understanding and the modelling of how far the mineral precipitation/dissolution processes that could take place at pore scale in these facilities could deviate from results given by aqueous phase chemistry and impact the containment properties of the clayey barriers.

In this framework, a classical counter diffusion approach was used to study barite precipitation in two types of clay, namely kaolinite and illite. For the kaolinite case, reactive diffusion experiments were performed at two degrees of compaction in order to investigate the impact of the pore size on barite precipitation. For illite, two ionic strengths were used to vary the thickness of the double layer and thus, the pore accessibility to reactants. For all of these experiments, diffusive parameters of water tracer (HTO) and anionic tracer ($^{36}Cl^-$) in the porous media were determined before and 70 days after the start of the reactive experiment. X-ray tomography images were acquired at different migration times and the evolution of the chemistry in the solutions was monitored.

Results clearly show how barite precipitation is affected by the local physical structure and the charged surfaces. In kaolinite, barite precipitated as spherical clusters (Figure 1), and led to a decrease of the HTO diffusivity by a factor of 1000, compared to the value determined before the reactive experiment. Moreover, a total blocking of the $^{36}Cl^-$ diffusion was observed, indicating that newly formed barite possesses negative surface charges. Contrary to the kaolinite case, barite sparsely precipitated in illite as a thin layer (Figure 1), without any impact on the tracer diffusivity.

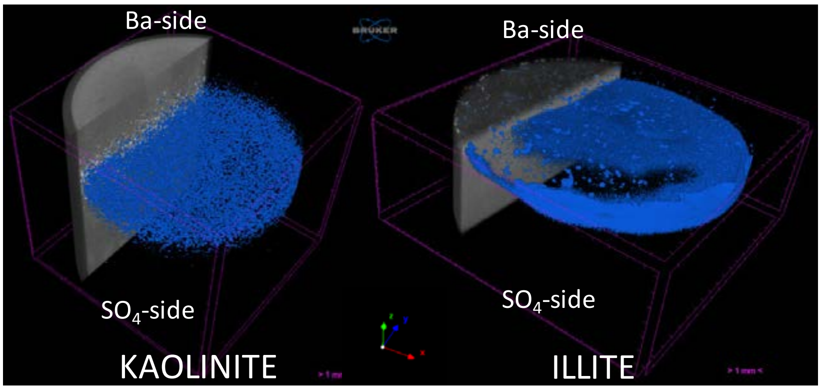

Figure 1. µ-CT images of kaolinite (left) and illite (right) 30 days after the start of experiments

Composition and properties of Westerwald bentonites and their usage for high swelling pressure sealing in underground mining and nuclear waste deposits

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In the famous Westerwald clay mining area, more than one million cubic meters of overburden are removed each year. The overburden consists predominantly of altered basaltic tuff stones and volcanic ashes. Until the early nineties of last century, there was no application for these raw materials. A more precise characterization of the overburden during the last 20 years has shown that some of these altered volcanic materials have been transformed into bentonites with smectite contents up to 90 percent. According to XRD analysis, the smectites are a blend of dioctahedral and trioctahedral phases.

However, it was found out that these bentonites could not be activated by sodium carbonate for applications in foundry industries or civil engineering due to low swelling volume and very poor binding strength. There have been some first successful developments and applications in usage of non-activated natural calcium bentonite for horticulture and agriculture over the last decades.

In spite of the low performance in swelling volume, recent studies show that the Westerwald bentonites in their natural calcium layer form are able to present an impressively high swelling pressure of up to 17,5 MPa by dry density of 1.84 t/m³ which even exceeds the well-known Bavarian bentonites. Therefore, some bentonites with high smectite content were singled out, further developed and established as a new product under the brand **Securso® UHP**. Securso® UHP is actually used in several research studies for underground seals in mining industries and nuclear waste repository research. According to latest developments in practice, it is possible to stow Securso® UHP pneumatically and emplace the material underground without compacting, achieving dry densities higher than 1.45 t/m³, corresponding to more than 2 MPa swelling pressure.

The history of research and development as well as first results of the recent studies are shown in this study.

Tunable thermoelastic anisotropy in Bragg stacks with extreme polymer confinement

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Heat management is increasingly being recognized as a key technology to fuel the growth of our technology-driven society. Controlling the elusive flow of heat is a complex challenge across multiple materials, length scales, and ultimately devices. This results in stringent requirements for achieving a directional control over the heat flux based on advanced material design. In practice, hybrid materials are employed and structured using various assembly techniques, where thermal control is achieved by choosing constituents with large thermoelastic contrasts, such as combinations of soft and hard materials or amorphous and crystalline materials. In dielectric, (partially) crystalline hybrid materials, phonons are the main energy carriers in heat transport, and thermal studies could benefit a great deal from a deeper understanding of nanomechanics, which provides sound velocities and mechanical properties.

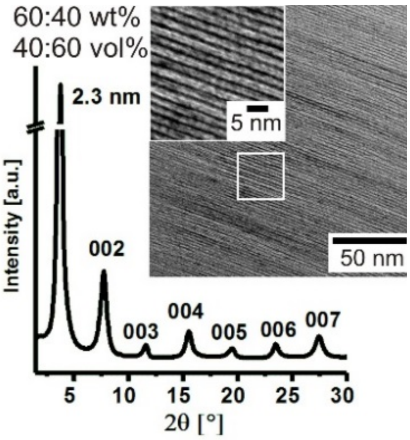

Figure 1. XRD of the hybrid film with Hec:PVP = 60:40 wt%, showing intense *00l*-reflections representing a rational series of basal reflections up to the seventh order. The cross-sectional TEM images show perfect stacking periodicity over long range.

Exploiting various degrees of liberty offered by hybrid systems, such as geometry, dimensionality, symmetry, and confinement, has been reported to drastically alter the materials' mechanical and thermal transport properties. Surprisingly strong thermal insulation has been shown for (disordered) hybrid stacks of two-dimensional materials. Such layered structures inherently exhibit anisotropy, and understanding anisotropy requires not only model systems possessing tunable anisotropy but also analysis techniques capable of direction-dependent measurements.

Here we report on synthetic Na-hectorite/polyvinylpyrrolidone (Hec/PVP) nanocomposite films that allow achieving concomitantly long-range, periodic nanosheet spacing, which can be tuned with Å precision in discrete volume fractions. The discrete nature of the accessible composition states raises questions about the validity of continuum mechanics theory in describing the films' thermoelastic properties, and how those properties vary as a function of direction. Fortunately, these nanocomposite films are transparent and allow for measurements of their mechanical tensors by Brillouin light scattering. The films show high thermal conductivity anisotropy, being highly insulating and fairly conductive in the cross-plane and in-plane directions, respectively.

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Linking faults, fractures and clay minerals occurrence with fluid transport in the accretionary prism of the Nankai Trough, Japan

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In the Nankai Trough subduction zone offshore Japan, the Philippine Sea Plate moves underneath the Eurasian Plate, with a plate boundary megathrust fault as a possible source of devastating earthquakes. In the framework of the International Ocean Discovery Program (IODP), the NanTroSEIZE project (Nankai Trough Seismogenic Zone Experiment) was performed in order to improve our understanding on the mechanics of stress accumulation and rupture propagation along the seismogenic portion of the Nankai accretionary prism. Expeditions 338 and 348 allowed drilling into the inner accretionary prism of the Nankai Trough down to 3058.5 m below seafloor (mbsf) at Site C0002.

In this study, we are linking the abundance of fractures and faults with localized amounts of clay minerals in the deep section of the Nankai Trough inner accretionary prism. In fact, mineral precipitation can easily occur in such faults and fractures and are often mixed with detrital clay minerals off-scraped from adjacent subducting sediments. The interpretation of logging while drilling (LWD) resistivity oriented images and geophysical logs revealed a complex structure characterized by steep bedding and abundant folds, as well as fault and fracture zones, indicative of specific areas of deformation within the clay-dominated accretionary prism sediments. Local faults were undoubtedly interpreted on images from Hole C0002P (2162.5-3058.4 mbsf), whereas folds were identified in both Holes C0002P and C0002F (860-2005.5 mbsf). The clay mineral analysis of rock samples (cuttings) shows that clay mineralization occurs within the range of the faulted and fractured zones. This linkage between local deformation and clay mineralization can have implications for enhanced fluid flow and localized fluid-rock interaction within the highly fractured areas of the accretionary prism.

Based on our combined mineralogical and microscopic analyses, together with the interpretation of LWD oriented images and geophysical log data, we conclude that dissolution and neomineralization of illite and smectite phases within fractures and faults is a process that probably continues during active creep and fault reactivation and plays a key role in influencing weak fault and creep behavior within the Nankai Trough, and likely in shallow fault systems elsewhere.

Molecular mechanism of dissolution, growth and ion uptake at the clay mineral/water interface

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Clay minerals and clay rich rocks are widely used as backfill material at disposal sites to protect the environment from toxic waste. The interplay between adsorption and desorption, crystal growth, dissolution and changes in pore water chemistry is of key importance for the prediction of the pollutants' transport and their retention time. Atomistic simulations can help us to obtain deeper understanding of the underlying reaction mechanisms and kinetics. A complete and consistent description of these reactions has not been achieved yet. While the cation exchange or the adsorption at the basal planes are well understood[1], the knowledge of the sorption mechanisms at the edge sites is limited[2]. The latter is known to be pH dependent, due to different protonation states of the surface oxygen sites that change the surface affinity towards adsorbed ions. Furthermore, the dissolution and growth of clay platelets can modify the surface topography and the availability of sorption sites[3]. These processes are responsible for a durable entrapment of contaminants since they involve direct structural incorporation.

In this study we investigated the molecular mechanism of clay mineral dissolution at edge sites by ab initio MD simulations. We use the Metadynamics (MtD) approach[4] to obtain activation energies for step-by-step detachment and attachment of mineral building tetrahedral and octahedral ions at the edge sites. Simulations are performed for pyrophyllite that serves as a reference model of an uncharged phyllosilicate. We choose (110) edge face as the most energetically stable. The system size and the amount of water between the edge surfaces were chosen to minimize the interaction between opposite surfaces. Coordination numbers for different atomic pairs were used as collective variables (CV) for the MtD.

The simulation results in pH neutral water show that dissolution of the silicon (Si(t)) and aluminium (Al(o)) polyhedrons are going through at least four reaction steps including breaking and building O-bridges to neighbouring Si(t) and Al(o) forming bi- or monodentate structures, allowing for H_2O molecules to alter the remaining bonds. Activation energies were obtained through the minimum energy pathways between the global minimum and local minima on the free energy surface plotted with CVs as reaction coordinates. The mechanisms and energies have extreme importance for the parametrisation of the kinetic Monte Carlo developed on the basis of a previous approach[3]. The combination of detachment and attachment reactions allow us to build a model of montmorillonite particle dissolution and growth as a function of saturation state. In particular, we demonstrate the influence of the activation energies for Si-O-Si and Al-O-Si bond breaking on the step edge morphology.

Acknowledgements:
This study was financed by SNSF grant 200021_165548, simulations have been performed at Swiss Center of Scientific Computing (CSCS).

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Influence of pH, carbonate and calcium concentration on U(VI) retention by clay minerals at (hyper)alkaline conditions – A batch sorption and spectroscopy study

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Clays are considered as potential host rocks and backfill material for deep geological repositories for radioactive waste. Therefore, profound understanding of radionuclide retention processes at clay mineral surfaces is essential for a long-term safety assessment. As a result of the degradation of concrete within such a repository, hyperalkaline cement pore waters can evolve. Since the U(VI) sorption behavior at alkaline conditions is still poorly understood, batch experiments were combined with spectroscopic investigations in order to gain insight into the underlying retention processes on the molecular level.

U(VI) batch sorption experiments (pH 8-13) with various clay minerals at different carbonate concentrations (absence, 0.5 and 100 mM) showed a decreased U(VI) retention in the presence of carbonate up until a certain pH (pH 9.5 or pH 11, depending on $[CO_3^{2-}]$) due to the formation of weakly sorbing uranyl carbonate complexes in aqueous solution, confirmed by time-resolved laser-induced fluorescence spectroscopy (TRLFS). This is in accordance with previous studies [1]. However, also in the presence of carbonate, U(VI) retention is increased in even stronger alkaline solutions, which is attributed to the preferred formation of hydrolyzed U(VI) species.

In order to clarify the mechanisms responsible for the very strong U(VI) retention in the pH range 10-12 (absence and 0.5 mM CO_3^{2-}), uranyl complexes on Ca-bentonite surfaces were examined directly, using site-selective TRLFS and extended X-ray absorption fine structure (EXAFS) spectroscopy (ESRF, Grenoble). Both techniques showed the presence of two different U(VI) surface complexes and no indication for U(VI) precipitation. Consequently, under the given conditions, adsorption is the dominant retention process despite the negative mineral surface charge and the anionic character of prevailing aqueous U(VI) species (i.e. $UO_2(OH)_3^-$). The retention could be realized by mediating cations, which adsorb to the mineral surface in the first place, leading to a local compensation of negative surface charge. Experiments with different calcium concentrations confirmed that the presence of calcium significantly enhances the U(VI) retention between pH 10 an 12.

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Tropical paleo-weathering and variations in clay mineralogy in the Ramså Basin, northern Norway.

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The Ramså Basin is situated on Andøya, at the eastern flank of the Andfjorden Basin in northern Norway. Its basement consists of rotated and tilted fault blocks of Mid-Proterozoic granodioritic and ultramafic rocks. A preserved saprolite sequence in the basement at the southern part of the basin suggests deep meteoric weathering prior to being covered by Jurassic sediments.

Four boreholes (BH1-4), up to 230 m deep, were drilled in the Ramså area to investigate the Mesozoic sediments and define the basement boundary. Geochemical and mineralogical analyses on drill cores were carried out at the Geological Survey of Norway to reveal the nature of the Jurassic and Cretaceous sediments and the underlying bedrock. The cores from the lower part of BH 1 are dominated by a 60 m thick sequence of ultramafic debris flow conglomerates, having angular clasts which mainly consist of plagioclase (45 wt%), talc (<20 wt%), chlorite (<15 wt%) and occasional biotite. In the upper 120 m of BH1, the lithology is dominantly siliciclastic sediments comprising quartz (30 wt%), K-feldspar (<10 wt%), illite/muscovite (<10 wt%) and abundant (up to 50 wt%) kaolinite. Cores from the deepest parts of BH 3 revealed strongly weathered granodioritic basement as evidenced by high contents of kaolinite (30-50 wt%) and illite/muscovite (up to 15 wt%).

A strongly dipping basement allowed sampling of the entire ~30 m thick saprolite section and the overlying Jurassic sediments by digging ditches along the shoreline at Ramså. The saprolite consists of minor amounts of K-feldspar, plagioclase and illite/muscovite (each <10 wt%) and is dominated by quartz (>30 wt%) and kaolinite (>50 wt%). In thin sections, this 'kaolinite' shows a peculiar growth habit with elongated and twisted brownish filaments. Its 7/4.45 Å ratio indicates a severe b-axis disorder which contrasts with the well-crystallized kaolinite in the Jurassic sediments above. The saprolite seems to have been influenced by humic acids from meteoric water percolating through swamps, now preserved as coal layers. It is suggested that these acid fluids have led to the formation of leverrierite, a mineral intermediate between kaolinite and illite. The brownish staining is characteristic of the interaction with humic acids during its formation.

Tetraalkylphosphonium beidellite intercalates – structural stability by DFT method

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Clay minerals modified by organic cations are a subject of a great interest because of possibility to develop new materials with specific properties for new technological applications e.g. polymer-clay nanocomposites, active sorbents of pollutants, drug release retardation from biocomposite hydrogels, storage of radioactive waste, etc. In a recent time, closer attention is also paid to phosphonium-based organic cations that could be used at the sorption of pollutants due to better properties and higher stability than conventional organoclays with alkylammonium cations (Scholtzová&Tunega, 2019).

Structural properties and stability of four models of beidellite (Bd) clay mineral intercalated with tetraethyl-, tetrabutyl-, tetrahexyl-, and tetraoctylphosphonium cations (4PX-Bd; X= 2,4,6, 8) are examined by *ab initio* density functional theory (DFT) method. Beidellite, a smectite group member, is layered aluminosilicate with predominant Si/Al substitutions in the tetrahedral sheets (e.g. montmorillonite has substitutions mainly in octahedral sheet). The different type of the substitutions affects a charge distribution in the clay layers. In beidellite, the charges are localized at the Si/Al sites in comparison to montmorillonite expecting improved stability of the beidellite-based organoclays (Scholtzová et al., 2018).

Calculated results show a good agreement of the predicted d_{001}values of models (~14.5 Å) with experimentally determined values of the prepared organoclays (~14.2 Å). The structural sability grows with the size of alkyl chain of phosphonium cations. Further, the *ab initio* molecular dynamics (AIMD) calculations will help in a detailed analysis of the experimental FTIR spectra of the 4PX-Bd organoclays.

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Quantification of mixed-layer clays in multiple saturation states using NEWMOD2: Implications for the potassium uplift hypothesis

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Hydrous 2:1 and 1:1 layered phyllosilicates offer multiple structure sites that can uptake/release nutrients under different biogeochemical conditions. We examined the clay fraction (<2 µm) of Ultisols from hardwood, pine, and cultivated sites in the Calhoun Critical Zone Observatory, located on Piedmont of South Carolina, United States. Shallow (< 1m) and deep (>5m) samples were examined with X-ray diffraction (XRD) as oriented mounts in Mg- and K-saturated (Mg-sat and K-sat) states in both ethylene glycol (EG) and heated (110°C) conditions. Calculated XRD patterns were forward modeled using NEWMOD2. Model results can attribute the variable low angle XRD responses to a combination of differences in a) preferred orientation (i.e., s* as defined by Reynolds, 1986) and b) the presence of mixed layer clay structures (layer types and abundances) (Reynolds, 1980). In general, K-sat/EG has the effect of increasing low-angle scattering (<5° *2Q*) relative to Mg-sat/EG, while 110°C has the effect of increasing scattering of both K- and Mg-sat relative to EG. The increase in low-angle scattering can be ascribed to commensurate increases s*. Scattering differences in the range of 5 to 15 °*2Q* can be ascribed to changes in 1) layer dimensions, 2) relative number of layer types, and 3) distribution of coherent scattering domains. Layer types used in NEWMOD2 included: kaolinite (K), illite-like (I), vermiculite (V), and smectite (S). Interlayer cation and octahedral iron abundances for 2:1 structures were adjusted based on independent electron microprobe observations of large grains.

Mixed layers of varied proportions where exhibited in all samples. For example, the deep pine site progressively had in the Mg-sat/EG (IS73, IV74, IV64, KI90, KI50); K-sat/EG (IV85, IV72, KI90, KI34); Mg-sat/110° (IS68, IV79, IV64, KI96, KI47); K-sat/110° (IV85, IV72, KI34, KI90). XRD patterns for shallow samples exhibited less variability across all treatments because they contain lower abundances of vermiculite layers (smectite layers are not detected). Subtle changes in the intensity and peak position of the kaolinite (001) peak exhibited in the K-sat/110° pattern suggests that there are multiple combinations of mixed layered phases, possibly including three component mixed layered structures but are not able to be modeled using NEWMOD2 two layer only algorithms.

The demonstrable presence of mixed layer structures and their variability in response to cation saturations, hydration states, and location within the weathering profile suggests that these minerals can play an important role in the cycling of base cations in the critical zone. The added observation that there was a change in K-bearing layer types progressing from cultivated to pine forested to hardwood forested locations hints that these mixed layer phases play an important role in the uplift and cycling of K in vegetative ecosystems.

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ZnTi layered double hydroxides as photocatalysts for salicylic acid degradation under visible light irradiation

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A series of ZnTi layered double hydroxides (LDHs) with different Zn/Ti ratios are prepared and used as catalysts for photodegradation of salicylic acid (SA) under visible light. The catalysts are characterized by X-Ray diffraction, diffuse reflectance infrared Fourier transform spectroscopy, UV-vis diffuse reflectance spectroscopy, thermogravimetry, electron paramagnetic resonance and N_2 adsorption-desorption. The results show that SA anions bind to the LDH surface and that an electron can be excited from the HOMO in the adsorbed molecules to the conduction band of the LDH under visible light illumination. This charge transfer further leads to an effective photodegradation and mineralization of SA with better conversion results than on P25 titania.

Key factors influencing the charge-transfer process in LDH are the high surface area and the Ti/Zn ratio of the LDH materials. The combination of highly dispersed Zn^{2+} and Ti^{4+} cations in the brucite-like sheets of the LDHs allows for a better charge separation, which also accounts for the high photocatalytic activity.

The present results show that superoxide radicals play a role in the visible-light induced degradation of SA on LDH, while no $^{\bullet}OH$ radicals are formed. In contrast to LDH, the light-induced degradation pathway of SA over P25 titania leads to the formation of CO_2^-, a relatively stable anion that may hamper further conversion to CO_2 and hence limit the photocatalytic performance. The introduction of an electron acceptor, such as peroxydisulfate, further improves the degradation and mineralization of SA over LDHs, but care should be taken not to use an electron acceptor that can easily adsorb to the LDH surface, such as H_2O_2.

ZnTi LDHs are thus very promising alternatives to TiO_2 for the photodegradation of colorless organic pollutants, such as SA, under visible light irradiation.

Sorption of metal oxyanions from complex solutions by layered double hydroxide (LDHs) type anionic clays

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The present study focuses on the selective recovery of metal oxyanions, e. g. chromates and vanadates, from complex leachate solutions by sorption onto anionic clay type layered double hydroxides (LDHs).

Layered double hydroxides (LDHs), are a family of naturally occurring anionic clays having positive layers and negative exchangeable interlayer species. They are represented by the empirical formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+} (A^{n-}_{x/n}) \cdot mH_2O$, where: M^{2+} are divalent cations (Mg^{2+}, Zn^{2+}, Ca^{2+}, etc.), M^{3+} are trivalent cations (Al^{3+}) and A^{n-} are interlayer anions (CO_3^{2-}, NO_3^{-}, etc). These materials can be used in oxyanion sorption due to their large surface areas, high anion-exchange capacity, and flexible interlayer region accommodating various anionic species. Moreover, their chemical composition can be easily tuned allowing not only a high ion exchange capacity but also selectivity towards specific ions.

Sorption tests are conducted for both uncalcined and calcined LDH-type materials in order to determine the optimum parameters for increased sorption performance, such as initial oxyanion concentration, chromate/vanadate ratio, time and pH. Characterization of the LDHs before and after sorption tests as well as sorption mechanism are demonstrated by X-ray diffraction analysis.

This work is part of the European H2020 project CHROMIC which aims to develop new recovery processes for critical (Cr, Nb) and economically valuable (Mo, V) by-product metals from secondary resources, based on the smart integration of enhanced pre-treatment, selective alkaline leaching and selective metal recovery across the value chain.

Acknowledgements: The authors acknowledge the Horizon 2020 CHROMIC project (more information on www.chromic.eu) Grant Agreement n° 730471.

Clay-based structured composites for oxyanions uptake from aqueous waste effluents

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Powder materials, sorbents or catalysts, are difficult to handle in large scale applications. Thus, powder active materials shaped into porous granulates/microspheres facilitates their applicability in a relevant industrial environment (e.g. column installations). The use of granulates/microspheres will minimize the mass transfer limitations in column or packed bed reactors, lower the pressure drop and will be easy to handle and recover at the end of the process.

Clays are known for their ability to effectively uptake heavy metal species by specific adsorption and ion exchange depending on their structure.

Given by the layer composition and charge as well as interlayer ions identity, two complementary types of clay systems may be identified: layered double hydroxides (LDHs) and smectite type clays. These are naturally occurring or synthetized layered minerals often referred to as anionic and cationic clays, respectively: in LDHs, the host layers are positively charged, thus requiring the presence of interlayer anions to maintain overall charge neutrality, whereas in smectite clays the host layers are negatively charged and interlayer cations are required.

The present study focuses on the potential of natural and/or synthetic mixed clays structured into ceramic microspheres for heavy metal uptake (such as Cr) from complex leachate solutions.

This work is part of the European H2020 project CHROMIC which aims to develop new recovery processes for critical (Cr, Nb) and economically valuable (Mo, V) by-product metals from secondary resources, based on the smart integration of enhanced pre-treatment, selective alkaline leaching and selective metal recovery across the value chain.

Acknowledgements: The authors acknowledge the Horizon 2020 CHROMIC project (more information on www.chromic.eu) Grant Agreement n° 730471.

Formation of Eogenetic Chlorite in Verdine Facies Sedimentary Rocks from the Gabon Basin in West Africa

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Clay phases numbering odinite-like minerals (OLM), chlorite, illite, and smectite along with interstratified odinite-chlorite (O-C), illite-chlorite-smectite (I-C-S), and illite-smectite are ubiquitous in sediments of the Gamba Formation. The formation itself stems from the Gabon coast of the western African margin where multiple Cretaceous sedimentary basins came into existence prior, during and after the opening of the South Atlantic Ocean. Analyzed core material is siliciclastic and petroleum bearing, originating from the fluvio-lacustrine-deltaic environment drilled at depths of ~1500 m. The OLM and O-C occur as grain coatings but are more common as pore fillings rendering the characteristic honeycomb texture. Chlorite emerges at the contact of OLM and O-C flakes as a particulate authigenic mineralization.

This study aims to find the mineralogical and geochemical clues to explain diagenetic changes that enabled nucleation of low-grade diagenetic chlorite in the verdine sedimentary facies. Inferring from a detailed scanning electron microscopy and X-ray diffraction with spectra modelling, OLM appears to form in shallowly buried sediment from the alumosilicate and Fe-oxyhydroxide debris brought as a riverine influx. Peculiar geochemical conditions induced a partial chloritization of OLM at practically syn-sedimentary conditions through the solid-state transformation of 7 Å to 14 Å layers. With increasing burial, at peak diagenetic conditions (50°C, ~1.5 km depth), the OLM and O-C both recrystallized to form the eogenetic (monocomponent) chlorite most likely following the Ostwald ripening mechanism.

Trioctahedral smectite in the upper part of the Gamba Formation also served as source for chloritization, where dissolution must have been complete resulting in a series of I-S-C intermediates. However, the I-S-C intermediates did not reach the composition of monocomponent chlorite.

Interaction between a bentonite barrier and a dilute groundwater – flocculation and the impact of gravity

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The uptake of water and the resulting swelling of the bentonite buffer in a nuclear waste repository are hindered by the walls of the deposition hole, and thereby a swelling pressure develops in the bentonite. If fractures intersect the deposition hole, there are no rigid swelling restrictions at intersection surfaces. The swelling then continues into the fractures until equilibrium or steady-state conditions are reached. This free swelling may lead to separation of individual montmorillonite layers (dispersion). The maximum free swelling of bentonite is strongly dependent on the charge and concentration of the ions in the interlayer spaces. At low concentrations of solutes in the groundwater, the interlayer distance between the individual montmorillonite layers may increase so much that the clay/water system takes on a sol character, i.e. single or small groups of montmorillonite layers behave like colloidal particles.

The sol can then be transported away with the flowing groundwater. This issue has been extensively studied in the past and can be reasonably well bounded. However, recent experiments have shown, if the sol is exposed to gravity, for example in a vertical or sloping fracture, it may flocculate and form something that can be described as a secondary gel. This secondary gel is affected by gravity and may sediment in fractures. The mass loss from gravity may be substantially higher than from the flowing water.

The effect of gravity on clay colloids has been studied in an experimental program. The approach has been to simulate fractures by using parallel acrylic glass plates with spacers and a cylinder of compacted bentonite in the middle. This equipment enables studies of the effect of clay composition, water salinity, fracture aperture and roughness, water flow, and fracture slope. Flocculation sedimentation only occurs if the water in contact with the clay has a salt content below the critical coagulation concentration (CCC). There is a clear difference between the behavior of natural bentonites compared to purified and washed montmorillonite fractions. The main reason for this is that even a small residual content of salt in the bentonite will have a large impact on the water composition in a narrow fracture at stagnant conditions. There is a clear effect of fracture aperture, which could be attributed to surface interaction, but also to a more rapid salt exchange. The rheological properties of the secondary gel change with time and the gel becomes more stable. However, the formation of a secondary gel is reversible and it reverts back to a sol if the movement stops.

Agates in the low-grade metamorphic volcanic rocks: “bearing”, “existence”, “extinction”

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Agates are rhythmic-bedded and figured aggregates of calcedony. Its structure is close to α-quartz, in which [OH] replaces a number of O-atoms in tetrahedra [SiO_4] and [AlO_4] replaces some of [SiO_4]. The substitution degree changes from one pyramid of growth to another, therefore, calcedony crystals have filamentous habitus and contorted structure. Agates in volcanites fill out geodes, hydraulic fracture cracks and vesicles of desalination. They are divided into the Brazilian type with concentric zonal texture and the Uruguayan type with parallel and layered pattern. It was considered that thermal springs circulating in volcanics after eruptions evoke cavity fillings and appearance of mandelstones. Owing to the conducted studies, volcanics of Quarternary and Late Tertiary age have total porosity and no secondary minerals. Neither mandelstones, nor agates arise after the completion of volcanoes eruptions. The time gap between formation of fresh volcanics and mandelstones with zeolites and agates is not less than 3-6 Ma years and reaches 180 Ma. Therefore, mandelstones with agates are not diagenetic, but epigenetic. Agate-bearing volcanics appear because of the low-grade metamorphism of immersion and overburden stress. Agates in metavolcanics are the products of metamorphogenic-hydrothermal differentiation at the elevated fugacity of CO_2. The Uruguayan type agates had formed under the conditions of metamorphism of poorly flooded volcanic series, whereas for agates of the Brazilian type the strongly flooded conditions are more typical. Agates’ "bearing" starts at the beginning of zeolite facies when fresh volcanics turn to greenstones with celadonite, albite, chlorite, carbonates and zeolites. Slightly coloured, delicate agates with moire texture occur under the conditions of low-temperature band of zeolite facies. Bright delicate agates develop under the conditions of medium temperature band. Agates are partly recrystallized and lose the «play of colours» under the conditions of high temperature laumontite band of zeolite facies. In metavolcanics of prehnite-pumpellyite facies agates “extinction”, - agates are transformed into jaspers and quartzites.

Work has been completed with support of Russian FBR (grant 19-05-00490).

Assessment of reduced environmental impact of a novel clay-based herbicide formulation: release and volatilization tests

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This abstract has to be considered confidential before publication of the book of abstracts (a patent application is currently being prepared on the reported content)

Dicamba (3,6-dichloro-2-methoxybenzoic acid) is a moderately volatile and highly soluble broad-spectrum herbicide. Due to its volatility, dicamba is usually applied in the field at higher doses than those strictly necessary, causing a waste of this active ingredient (AI). Moreover, this high dosage may increase the possibility of leaching, thus potentially resulting in a greater pollution risk for soils and groundwater. The use of nano- and micro-sized carriers could help facing some issues related to the AI's chemistry, such as low solubility in water, photodegradation, interactions with other compounds.

In this study, dicamba was adsorbed on montmorillonite, a soft phyllosilicate, using an aqueous dicamba solution, with a C_0 concentration near the saturation value, and without any surface modification of the clay. During the dicamba loading process, the AI aqueous solution can stream between the layers and physisorption of the AI occurs. FTIR analyses pointed out hydrogen bonds between dicamba and montmorillonite surface, proving a reduced volatility of the AI.

Adsorption tests showed a moderate value of Encapsulation Efficiency (EE%, in general it is the percentage of drug that is successfully entrapped into a nanoparticle) of a 25% wt. of the initial concentration of dicamba. After a centrifugation of the suspension, the supernatant could be used to carry out another loading of the herbicide on the clay, to reduce any waste.

Batch tests permitted the quantification of the AI volatilization from the nanoformulation. A simple evaporation test was carried out to confirm the reduced volatility of the herbicide. Results highlighted a negligible weight loss of dicamba, compared to the pure AI where the weight loss is around 20% within 2h from the beginning of the test.

Release tests in batch showed a constant amount of dicamba released in water, after an initial burst, within 24 hours of test.

Selected formulations were then coated with biodegradable carboxymethylcellulose CMC, to investigate any variation in terms of dicamba's release.

All the tests with the novel herbicide formulations were compared to same protocol tests with both the pure active substance and a commercial dicamba based product to assess the effective reduction on volatility by adsorption on montmorillonite clay.

Laponite® Family of Synthetic Clays: History, Present Status, and Trends

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Laponite® materials are a growing family of commercial synthetic clays with over five decades of history and a wide variety of technological applications. Already great and constantly increasing number of patents, research articles and reviews is a testament of the enduring legacy of Laponite® in industry and academia.

In this presentation, we would like to touch upon the history of Laponite® technology, starting with its discovery by Dr. Barbara S. Neumann[1-5].

The key properties of the Laponite® materials will be briefly reviewed, together with some of the established technological applications. We shall also include some emerging applications such as Pickering emulsion stabilisation and Laponite® as a synergist in complex systems with organic molecules, polymers and other particles.

A brief overview of the current trends in Laponite® applications will be presented, with particular emphasis on the recent developments in the biomedical field [6] and other, higher-end industrial uses of these materials [7-11].

Finally we are going to share some of the latest advances in the analysis of the Laponite® synthetic clays, in particular, the AFM visualisation of the individual platelets, which has been a major challenge for several decades.

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Free energy of interaction of two smectite clay nanoparticles in liquid water

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Clay minerals are one of the most important constituents of soils, sediments, and sedimentary rocks. The aggregation and swelling of clay nanoparticles, in particular, strongly influence porosity and permeability and is highly sensitive to both short- (hydrogen bonding, ion solvation) and long-range (charge screening) geochemical interactions. Simulation predictions of clay aggregation and swelling, to date, have relied almost exclusively on coarse-grained simulation technique (Monte Carlo or Brownian dynamics simulations) that rely on effective inter-particle potential models. Most such models are based on the DLVO theory of long-range colloidal interactions and they neglect the short-range interactions that stabilize the crystalline hydrates (1-, 2-, and 3-layer hydrates). All-atom molecular dynamics (MD) simulations have the potential to help inform existing coarse-grained models, but have focused almost exclusively on the crystalline hydrates. To bridge this gap, our research uses all-atom MD simulations to examine the energetics of a pair of smectite clay nanoparticles suspended in bulk liquid water. In particular, we use the metadynamics methodology to elucidate the free energy of swelling over a range of interparticle distances that includes the transition between crystalline and osmotic swelling (*d*-spacings between 1 to 3.5 nm). Results are compared with the predictions of DLVO theory as illustrated in Fig.1. Different solutions are used to study the effect of water chemistry, including counterion type (K^+, Na^+, Ca^{2+}) and salinity, on the interaction between clay particles.

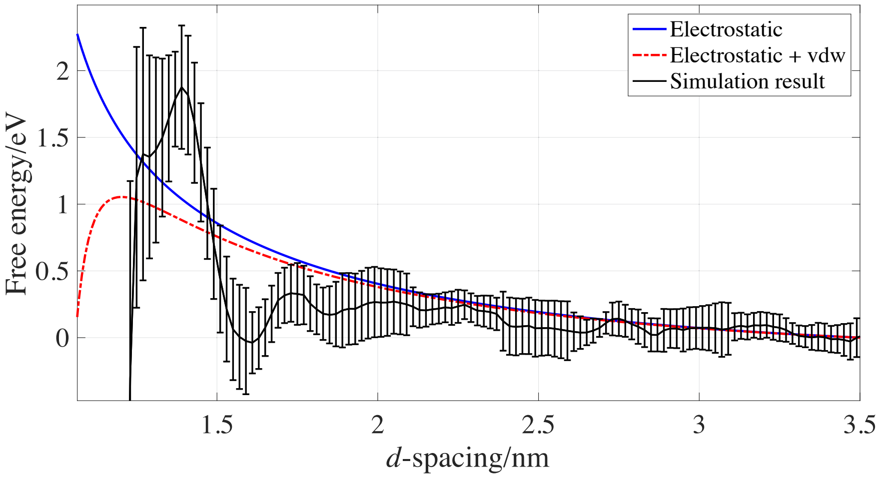

Figure 1. Free energy profile for the interaction of two smectite nanoparticles in pure water, calculated using MD simulation with metadynamics. The red line shows the DLVO theory prediction.

Stimuli-responsive colloidal assembly consisting of imogolite, cylindrical clay

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Imogolite (IG) is a single-walled alumino-silicate type rigid cylindrical clay with the formula of $(HO)_3Al_2O_3SiOH$.[1] The external and internal diameters are approximately 2 and 1 nm, respectively. In contrast, their length ranges from several ten-nm to several µm. The outer and inner surfaces of IG are covered with aluminol (Al-OH) and silanol (Si-OH) groups that give the dispersibility of IG in polar solvent. When dissolved in neutral to acidic and relatively low-ionic strength aqueous media, synthesized IG with adequately purification gives opaque colloidal dispersion containing individual nanotubes or thin bundles.[2]

Here, IG colloidal assemblies with stimuli-responsiveness are described.[3] Crosslinking of IG nanotube in its dispersion via hydrogen bonding between Al-OH on IG and dicarboxylic acid (DA) gives a gelated IG colloidal assembly in which IG nanotubes form network structure.[4] The mixture of IG and DA consisting of nanotube's network (later denoted as IG-DA mixture) exhibits keen thixotropy, a reversible solid/liquid phase transition behavior in response to mechanical shock.

After flow-orienting and subsequent standing the liquid-state IG-DA mixture, the uniaxial alignments of IG nanotubes with cm scale were realized in the recovered solid-state mixture. The self-standing interpenetrated network gels with the desired shapes can be prepared by the *in situ* polymerization of polymer network in the uniaxially IG oriented gels. The confinement of the IG nanotubes with the uniaxial orientation induced some anisotropic physical properties to the IG-DA mixture such as proton conductivity and mechanical strength.[3] Furthermore, an addition of chirality to DA induces cm-scale spiral alignment of IG nanotubes in the IG-DA mixture with uniaxial orientation that is reflected a helical arrangement of Al-OH on the IG nanotube.[5]

The mixture of IG, DA, and ionic liquid (IL) gives thixotropic gel with ionic conductivity that has potential applications in free-moldable conductive coatings and electrolyte.[6] Furthermore, IG colloidal dispersion exhibits an electrorheological (ER) effect in which assembly/disassembly of IG nanotubes in response to applying/removal of direct-current electric field causes reversible viscosity change of dispersion.[7] The electron conductivity of IG-DA-IL mixture and the ER effect of IG colloidal dispersion is encouraged us to use IG colloidal assembly as an electro-responsive materials. According to this hypothesis, an electro-responsiveness of IG-DA mixture at its various structural condition as a change of its polarization property will be also presented.

This work is financially supported by the JSPS KAKENHI (26870179, 16H04199 and 18K05252).

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Estimation of fault moving sense at Yangsan fault zone in Pohang area, using the Shape Preferred Orientation(SPO) analysis

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The Shape Preferred Orientation (SPO) of the quartz particles in the fault gouge is affected by the force acting after the fault activation. Assuming relatively rigid quartz particles are rigid body rotations surrounded by a relatively ductile clay matrix, the SPO of these particles reflects the fault-moving sense of the last stage. The Yangsan fault zone is located in the southeastern part of the Korean peninsula where the two largest earthquakes in South Korea, the Pohang and Gyeongju earthquakes, occurred. According to the previous studies, the Yangsan fault has been activated more than a few times, and Bokyeongsa area, which is a study area, is a region where fault gouge created by such activity is typically revealed. In this study, 3D-μ-CT images of a fault gouge samples were used to measure the fault-moving sense by capturing a 2D-image at 15-degree intervals between a fault plane and a plane perpendicular to the fault plane. And we tried to obtain reliable SPO data by classifying grain size and aspect ratio of quartz grains. Oriented sample images were taken from the 6C BMI beam line of the Pohang Accelerator Laboratory (PAL).

The results of the SPO measurement showed a tendency toward the P-shear direction of the field observation. 00,045 direction and 70, 155 direction are dominant, which are about 20 degrees different from the fault plane 90→155, as a result of measurement in two planes perpendicular to the fault plane. The grain size was not affected by the size more than 10μm, and the larger the aspect ratio value, the closer the SPO value was to the P-shear direction. Also, it is considered that the plane with high frequency of grains with a large aspect ratio is close to the P-shear direction. For the fault plane identified in the outcrop of the Bokyeongsa area, some reverse fault and dextral type strike-slip fault were observed in the fault zone. In this way, it is possible to estimate reliable fault moving sense from grains of several tens of μm in size, and it is possible to obtain various information about fault moving sense at brittle fault zone by classifying the aspect ratio value of rigid grains. Furthermore, it is possible to accumulate fault moving sense data and use it as a basic data for estimating the shear sense of the fault zone.

The role of clay minerals in the preservation of organic carbon in the soil

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Useful properties of clays and clay minerals have been known since pre-historic times. Clay minerals possess several unique properties, such as fine particle size, large specific surface area, permanent and variable surface charge, which make them ideal for many environmental applications. Additionally, clay minerals are widely available, occur in vast amounts and are relatively inexpensive. The environmental applications of clay minerals are extensive and wide ranging, e.g. industrial processes, agriculture, construction and environmental protection. In the last few decades the relevance of clay minerals in soil carbon storage and carbon capture have been recognised. Soil is the largest terrestrial carbon pool containing more than twice the carbon of the atmosphere. Globally, soil organic carbon has been estimated between 3,500 and 4,800 Pg C (1 billion t = 10^{15} g C) in the top 0 − 100 cm soil. Soil organic carbon is continuously recycled and approximately 59 Pg C is released from the soil organic carbon pool. There has been significant increase in the flux of soil carbon in the last few decades that has contributed to increased CO_2 concentrations in the atmosphere and associated global warming. Mineral associated carbon accounts for over 90% of the total soil carbon and thus plays an important role in the cycling and storage of carbon in soils. This presentation will explore the processes and mechanisms of organic carbon and mineral associations in soils in relation to carbon sequestration in soils. The factors that affect the mineral-carbon associations in soils will be discussed using laboratory and field examples.

NMF-intercalated kaolinite: a comparative vibrational and XRD investigation

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Kaolinite, $Al_2Si_2O_5(OH)_4$, the most abundant mineral of the kaolin group, has been frequently studied as an inexpensive potential template for advanced functional materials synthesis. Only a few organic compounds, and among them N-methyl formamide (NMF), can populate spontaneously the interlayer by disrupting the dense H-bonding network that holds the asymmetric neighboring layers together. Numerous organic compounds (including chromophores, pharmaceuticals etc.) can enter the interlayer by displacement of the previously intercalated species.

Intercalation leads to interlayer expansion. For this reason, the presence and extent of intercalation is conventionally studied by X-ray diffractometry (XRD), by comparing the intensity of the *001* reflections of the intercalated and pristine kaolinite populations.

On the other hand, vibrational spectroscopy is not directly sensitive to interlayer expansion. Instead, intercalation is monitored by recording signal due to the bonding between the intercalated species and its new local environment, against that of the unperturbed system. Interactions between the confined species and the layers of kaolinite ought to be weak. This is because the intercalated species must diffuse in two-dimensions from the edges and towards the center of the platy particle for the intercalation reaction to proceed.

In this report we compare the structure and dynamics of NMF intercalation in low-defect kaolinite (KGa-1b) by means of *in situ* and *ex situ* XRD and vibrational spectroscopy (NIR, ATR and controlled H_2O/D_2O exchange). Both techniques record sigmoidal kinetics from kaolinite/NMF slurries in real time, which are more densely sampled by spectroscopy (see a separate submission by Andreou *et al.* in the same session). In agreement with the literature, XRD indicates that the transition to the fully-expanded state involves no interstratification of pristine and expanded layers. Commonly, the extent of intercalation is determined by the ratio $A_{exp}/(A_{exp}+A_o)$, where A_{exp} and A_o are the integrated intensities of the expanded (~1.06 nm) and pristine (~0.71 nm) kaolinite reflections, respectively. This approach is based on the assumption that the ratio of diagnostic A_{exp} and A_o intensities equals the relative ratio of their populations. This approximation is not supported by the present complementary vibrational and XRD investigation.

This work was supported by a) project "Advanced Materials and Devices" (MIS 5002409) of TPCI-NHRF, funded by the Operational Program "Competitiveness, Entrepreneurship and Innovation" and co-financed by Greece and the European Union, and b) the Applied Spectroscopy Lab at TPCI.

Structural properties and spectroscopic characterization of choline-beidellite and acetylcholine-beidellite intercalates

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Beidellite mineral intercalated with different types of organocations is comprehensively investigated due to their excellent properties and various chemical interactions using theoretical and experimental methods (Ezquerro et al., 2015). Beidellite is, for example, extensively used as a potential sorbent of waste and pesticides (Aggarwal et al., 2006).

In this work are summarized the theoretical calculations and experimentally obtained measurements of four types of organoclays – beidellite (Bd) intercalated with acetylcholine (AC) and choline (C) in hydrated (hAC-Bd and hC-Bd) and dehydrated (dAC-Bd and dC-Bd) form, respectively. The beidellite models were investigated using the density functional theory (DFT) method. DFT calculations were performed with dispersion corrections using D3 scheme due to the weak interactions between the layers and intercalated compounds (Grimme et al., 2010).

From the structural point of view, all organic cations had a flatty arrangement and were located approximately in the middle of the interlayer space of beidellite clay. For dehydrated models, sodium cations (Na^+) were situated in the centre of the hexagonal hole due to strong Coulombic interactions with a negative layer charge localized on the surface of basal oxygen atoms. The analysis of interactions in the interlayer space of Bd mineral has shown that $[Na(H_2O)_4]^+$ and AC/C cations create weak hydrogen bonds for both, dehydrated and hydrated forms. The vibrational modes of hAC/C-Bd and dAC/C-Bd were identified from calculated spectra and compared with experimental measurements.

Acknowledgments:

This work was supported by the Slovak Grant Agency VEGA (Grant 2/0021/19) and the Slovak Research and Development Agency under the contracts No. APVV-15-0741, APVV-15-0347 and APVV-15-0479.

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Effect of chain length and surfactant loading on the self-assembly of primary alkylammonium cations on montmorillonite

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Organoclays are employed in a wide variety of industrial applications such as adsorbents of organic pollutants or fillers for polymers. The properties of organoclays strongly depend on the structure and arrangement of the intercalated surfactants, most often alkylammonium cations. The objective of this paper was to investigate the effect of the alkyl chain length and surfactant loading on the arrangement/conformation of the primary alkylammonium surfactants in the montmorillonite interlayers. Organo-montmorillonites (O-Mts) were studied by XRD and near-infrared (NIR) spectroscopy. Two series of O-Mts were prepared from montmorillonite Jelšový Potok (JP-Mt, Slovakia): 1) C*n*-JP with increasing length of the alkyl chain (*n* = 4 - 19) and surfactant concentration ~100% of the CEC of JP-Mt, and 2) C18-$JP_{\%CEC}$ with the increasing concentration of C18 cation from 20% to 200% CEC of JP-Mt.

The XRD showed almost the same basal spacing (d_{001}) for C4-JP – C8-JP (~1.33 – 1.37 nm) suggesting a monolayer arrangement. With further increase of the chain length the d_{001} values gradually increased from 1.41 nm (C9-JP) through 1.75 nm (C14-JP), 1.83 nm (C16-JP) to 1.95 nm (C19-JP), indicating consecutive transitions from monolayers to bilayers and pseudotrimolecular layers. Further information on the arrangement of surfactants was obtained by NIR spectroscopy. The position of the first overtone of the methylene groups ($2\nu_{as}CH_2$) was found to be very sensitive to the local conformation of the intercalated surfactants. The gradual shift of the band to lower wavenumbers, i.e. from 5830 cm^{-1} (C4-JP) to 5786 cm^{-1} (C19-JP), revealed a wide range of molecular environment varying from liquid-like to solid-like. The NIR spectra showed three groups of the O-Mts with different population of the disordered *gauche* and ordered *trans* conformers in the chain. The first involved samples with shorter chain surfactants (C4-C10) for which the position of the CH_2 overtone suggested dominance of disordered *gauche* conformers. For the second group (C11-JP – C14-JP) a comparable population of ordered *trans* and disordered *gauche* conformers was proposed while for the third one (C15-JP – C19-JP) the wavenumbers in the 5790 to 5786 cm^{-1} range indicated dominance of ordered all-*trans* conformers, characteristic for long chain alkylammonium surfactants.

The arrangement of alkyl chains were found to be also dependent on the surfactant concentration. With the growth of loaded C18 cation the d_{001} value increased from 1.35 nm (C18-$JP_{20\%}$) through 1.74 nm (C18-$JP_{80\%}$), 1.81 nm (C18-$JP_{100\%}$), 2.19 nm (C18-$JP_{160\%}$), to 2.34 nm (C18-$JP_{200\%}$) indicating consecutive transitions from monolayers, bilayers to pseudotrimolecular and paraffin-type of arrangement. Continuing increase of the basal spacing found for samples with surfactant content above 100% CEC confirmed the presence of C18-salt molecules in addition to C18-cation in Mt interlayers. In the NIR region a gradual shift of the $2\nu_{as}CH_2$ from 5789 cm^{-1} (C18-$JP_{20\%}$) through 5784 cm^{-1} (C18-$JP_{100\%}$) to 5774 cm^{-1} (C18-$JP_{200\%}$) reflected the increase of ordered *trans* conformers. Rather small shift (by 5 cm^{-1}) at the C18 concentration change from 20 – 100% CEC reflected small increase of *trans* conformers. In contrast, further increase up to 200% CEC moved the $2\nu_{as}CH_2$ band by 10 cm^{-1} revealing clear increase of highly ordered conformers.

Acknowledgments:
The financial support of the Slovak Research and Development Agency (APVV-15-0741 and APVV-15-0347) and the Slovak Grant Agency VEGA (2/0141/17) is gratefully acknowledged.

Adsorption of fulvic and humic like acids on surfaces of clays: relation with SUVA index and acidity

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In the context of sustainable development, economic and environmental issues encourage the valorization of local materials such as clay and agro-industrial waste. One of the major problems nowadays is the management of municipal waste. The degradation of this waste produces leachate rich in humic-like substances which can be valued for the consolidation of earth bricks. The characterization of the interaction between humic-like substances with clay minerals could provide a better understanding of the consolidation mechanism. In this respect, the adsorption behavior of fulvic and humic like acids on surfaces of distinctive raw clays has been studied. Five types of products were tested: green waste extract, municipal solid waste extract, two commercial products and one product synthetised from xylose. The quantities of fulvic acids adsorbed by the surfaces of raw clays (expressed in mg per g of clay) are greater than the quantities of humic acids. A raw clay with a large specific surface area and a large amount of iron compounds adsorbs a higher quantity (expressed in mg per g of clay) of fulvic acid than a raw clay, rich in kaolinite, containing less iron compounds and with a lower specific surface area. In alkaline conditions, the adsorbed quantities are lower than in alkaline conditions, and the surface area or the presence or iron compounds influence less the adsorption capacity than in acid conditions. It is interesting to note that if the adsorbed quantities are expressed in mg divided by the specific surface area of the clay, it appears that a kaolinite rich clay adsorbs more fulvic or humic like substances than a lateritic clay which is rich in iron oxides. Lastly, in acid (resp. alkaline) conditions, the parameter which governs the adsorption is the acidity (resp. the Specific Ultra-Violet Absorbance, SUVA index): the lower (resp. the higher) the parameter, the greater is the adsorption capacity. The interest in these adsorption reactions is the possibility to use these acids in the building sector for the manufacture of clay bricks at low temperature (compared to fired clay bricks).

Gouré-Doubi H.; Martias C.; Smith A.; Villandier N. ; Sol V. ; Gloaguen, V. ;Feuillade G. (**2018**) App. Clay Sci., 154, 83-90. doi.org/10.1016/j.clay.2017.12.036

Modeling the effect of ionic strength on diffusion. The DR-A experiment in Opalinus Clay at Mont Terri.

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Solute diffusion in compacted clays depends on ionic strength through its control on the thickness of the electrical double layer (EDL) on the charged clay surfaces. In the DR-A field experiment (Mont Terri rock laboratory, Switzerland), synthetic porewater (NaCl-dominated, I = 0.36) was circulated through a borehole for 189 days, leading to the out-diffusion of a variety of tracers into the Opalinus Clay. The borehole solution was then replaced with a higher-salinity solution (0.50 M NaCl + 0.56 M KCl) and for an additional 540 days, leading to the diffusion of Cs^+, Ca^{2+}, Mg^{2+} and Sr^{2+} back into the borehole and to an increase in the out-diffusion of anions (I^-, Br^-) and also, to some extent, of ^3H (HTO). The experimental results were interpreted using the CrunchClay code, which includes a mean electrostatic potential model for the EDL. The EDL corresponds to a second continuum domain in addition to bulk electrically-neutral porewater. Species-specific diffusion (Nernst-Planck equation) occurs through both domains. A 1D radial model considered a single pore diffusion coefficient (D_p = 10^{-9} m^2/s) for cations and HTO in the bulk porosity, and a smaller D_p (3×10^{-10} m^2/s) for anions. D_p values in the EDL were smaller (10^{-11} m^2/s), except for Cs^+ and K^+ (5×10^{-10} and 2×10^{-10} m^2/s, respectively). Well-established multisite cation exchange was used to calculate sorption of cations on the clay.

The model reproduced the experimental results well. The increase in ionic strength caused the increase in the out-diffusion of I^-, Br^- and HTO, due to the decrease in the thickness of the EDL. The high K^+ concentration in the high-salinity solution caused the displacement of Cs^+, Ca^{2+}, Mg^{2+} and Sr^{2+} from the cation exchange complex in the clay and their diffusion back to the borehole. And the calculated tracer distribution profiles in the rock are consistent with the measured profiles. Differences in D_p in the rock between bulk and EDL porosities may be caused by the different geometries of the tortuous diffusion pathways near the clay surfaces (EDL) and those in the centers of the pores (bulk). Pore throats where EDLs from opposite walls overlap may be the reason for the smaller D_p values for anions in the bulk porosity.

The model has shown the capability to consider changes in geochemical conditions affecting the transport and retention of potentially important radionuclide contaminants (e.g. $^{137}Cs^+$, $^{90}Sr^{2+}$, $^{129}I^-$) in underground geological nuclear waste repositories. Non-Fickian diffusion together with the electrostatic properties of the charged surfaces are essential in the development of predictive models for ion transport in clays.

Influence of Polyelectrolyte Mono- and Bilayer Formation on the Charging and Aggregation of Layered Double Hydroxide Nanoparticles

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Self-assembled multilayers have been a point of interest for many groups due to their versatile utilization in sensors, membranes and smart coatings. Polyelectrolytes are often used to form multilayers on nanoparticles with the sequential adsorption method. Applying this method, thin films can be obtained after deposition. Even though this is a popular technique, there are limited number of publications about the colloidal stability of the nanoparticles after polyelectrolyte multilayer formation.

In this study layered double hydroxide (LDH) particles were synthetized with the co-precipitation method followed by hydrothermal treatment. The latter process resulted in low polydispersity in the size of the nanoplatelets. The first polyelectrolyte layer adsorbed on LDH was negatively charged poly(styrene sulfonate) (PSS) and the adsorption occurred due to electrostatic attraction (LDH-PSS, see Figure 1). A second polyelectrolyte layer was also applied by adsorbing poly(diallyldimethyl ammonium chloride) (PDADMAC) on the surface of the LDH saturated with PSS. The effect of polyelectrolyte dose on the colloidal stability and the resistance against salt-induced aggregation was investigated in electrophoretic and light scattering measurements. The results indicated that the obtained LDH-PSS-PDADMAC material shows excellent colloidal stability once the polyelectrolyte doses are adjusted accurately. The highly stable dispersions are excellent candidates as feeding materials in film formation processes, where guest molecules can also be immobilized in the sequential adsorption procedure.

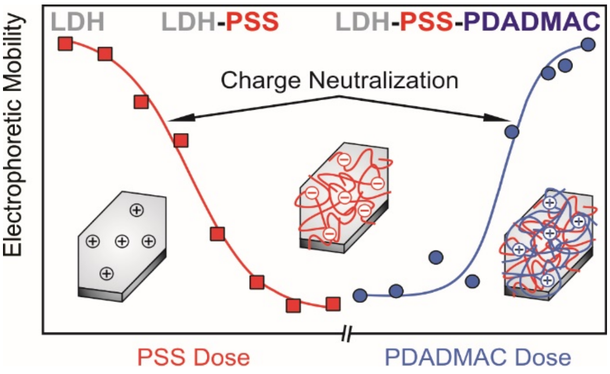

Figure 1. Effect of adsorbed PSS and PDADMAC on electrophoretic mobility.

Preferred format: Oral
Session number and name: D5. Frontier and new applications of clay colloids

Acknowledgement
This research was financially supported by the Lendület program of the Hungarian Academy of Sciences (project 96130) and by the Ministry of Human Capacities, Hungary through grant 20391-3/2018/FEKUSTRAT.

Reaction Mechanism of Layered Double Hydroxide as the Cathode Material of Nickel Secondary Battery

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Ni-hydrogen battery (NHB) has high energy density next to lithium ion battery. For this high energy density and safety, NHB is currently used for Hybrid electric vehicles and portable batteries. The weak point of this battery is limited theoretical capacity of its cathode electrode material: β-$Ni(OH)_2$. The reaction mechanism of cathode is expressed as follows.

β-$Ni(OH)_2$ +OH^- $\Leftrightarrow$ β-NiOOH + H_2O + e^- (1)

The theoretical capacity of reaction (1): 289 $mAhg^{-1}$ limits the energy density of NHB. To extend the energy density, much attention is payed to the following reaction that expands the theoretical capacity to 433 $mAhg^{-1}$.

α-$Ni(OH)_2$ +OH^- $\Leftrightarrow$ γ-NiOOH + H_2O + 1.5e^- (2)

However, cycle stability of reaction (2) is low owing to instability of α-$Ni(OH)_2$. As the substitute of α-$Ni(OH)_2$, we focused on the layered double hydroxides (LDH) with the similar structure to α-$Ni(OH)_2$.

In the present study, we have examined the electrochemical property of Ni-Fe and Ni-V LDHs and its reaction mechanism was investigated using the ex-situ XRD and XAFS measurements.

Ni-Fe and Ni-V LDHs were synthesized by a solvate thermal method [1]. Ni, Fe and V *K* edge XAFS spectra were measured at BL-11S2 of Aichi synchrotron center.

From the Ni *K* edge XANES measurement, it was confirmed that Ni ions in Ni-V LDHs and $Ni(OH)_2$ are oxidized to 3.5 valence state by charging to 0.5 V vs. Hg/HgO reference electrode. Ni-V LDH showed reversible capacity of 249 $mAhg^{-1}$ and its structure was sustained after 30 cycles of charge-discharge process, whereas the capacity of $Ni(OH)_2$ was 142.8 $mAhg^{-1}$and its structure degradated after 10 cycles.

From the EXAF spectra of these compounds, it became clear that the structural change of LDHs is reversible with small volume change during charge-discharge process, whereas that for $Ni(OH)_2$ indicates irreversible structural change from the first charge-discharge cycle with the 66% of volume change.

In the present study, it was demonstrated that LDHs show excellent performance as the cathode material of Ni rechargeable battery.

Reference

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Synthesis and Electrochemical Properties of Layered Double Hydroxide Coated Electrodes Fabricated by Electrodeposition Method

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Layered double hydroxide (LDH) is well known layered materials that has similar structure of natural cray. In LDH, divalent and trivalent metal ions are randomly locating in the metal ion site of brucite structure, and anion are inserted between metal hydroxide layers for the charge compensation. For this structure, LDHs are known to have various function such as drag delivery system, anion exchange, catalysts and so on. Recently, LDHs are also applied to the electrochemical device for its high activity for electrochemical reaction. However, LDHs are difficult to coat on the surface of electrode materials for its insolublility to various solvents and instability under the high temperature. Electrodeposition coating method is one of the useful methods those coat functional materials on the surface of the electrodes. The characteristic advantage of this method is uniform coating even on the rugged surface of porous electrodes, because coating proceeds uniformly at the interface of the electrolyte and electrode surface. [1] In spite of this advantages, the reports of formation of LDH films are limited to few kinds of LDHs. The reason for limited kinds would be that the condition for crystal growing of LDHs is different from that for electrodeposition, in other words the formed seed crystal of LDHs does not grow under the condition of electrodeposition. In this paper, we have synthesized various LDH films on Au and carbon paper electrodes by electrodeposition and subsequent crystal growing method. We have obtained Ni-Al, Ni-Fe, Ni-Mn, Zn-Al and Mg-Al LDHs with this method. Films are deposited on the surface of the anode electrodes, a flat Au (10 × 10, *t*=0.2 mm) substrate or a carbon paper (Toray, TGP-H-120 : 10 × 10, *t*=0.3 mm) at the constant current of 17 mA with a Au sheet as a counter electrode. The total electrolysis time was 10 min. As the electrolyte solution containing nitrate of M_{II} and M_{III} ions and $NaNO_3$ with the content of 0.05, 0.025 and 1.0 M, respectively. The electro-deposited films are dipped in the solution with the same component with its electrodeposition bath. After adjusting the pH of solution to 9.0 by addition of NaOH solution, films are left at 80˚C with stirring for 3 days.

In the XRD patterns of Ni-Mn LDH films on Au substrate after electrodeposition and subsequent crystal growing, 003 diffraction at 11˚ that is distinctive for LDH comes to be clearly observed after crystal growing, whereas clear diffraction was not observed only electrodeposition. This suggests that the seed crystal of LDH formed in electrodeposition grew in the crystal growing process. The surface SEM image of Ni-Al LDH deposited carbon paper electrode is shown in Fig. 1. The uniform coating of LDH on the carbon paper is confirmed.

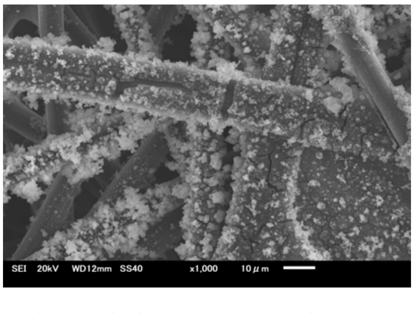

Fig. 1 NiAl LDH deposited on carbon paper substrate

Reference
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Low-grade metamorphism on the East Siberian Platform as ore preparation, ore-forming, ore-transforming process

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One of the poorly studied problem posed by H. Schneiderhöhn, the largest specialist in the field of ore deposits for more than half a century, is the problem of regenerated deposits. Essentially, this is the problem of the interconnections between metamorphism and the process of ore-forming, and the origin of metamorphogenic-hydrothermal ore concentrations. Below we present the results of the study of these processes on the example of the plate cover of the East Siberian Platform. It was proven the role of epigenetic post-trap (after 251 Ma) regional low-grade burial metamorphism LGM in the conditions of zeolite facies ZF (Rb/Sr age - apophillite, calcite, metabasalts, 232-212 Ma, T~200→300°C, P~1→2 kb), then the prehnite-pumpellyite facies PPF (212-198 Ma, T~330-350° C, P~2-2.5 kb) and again under the conditions of ZF (at the beginning - 187-164 Ma, T~290→150°C, P~2→0.5 kb; at the end 164-122 Ma, T~150→<100°C; P~0.5→0.1 kb) - as ore preparation, ore-forming and ore-transforming.

Ore-transforming LGM. A significant part of igneous Au-Ag-Pt-Pd-Co-Ni-Cu pentlandite - cubanite - chalcopyrite - pyrrhotite ores of giant Noril'sk deposits was converted into aggregates of pyrite, valleriite, bornite, bravoite, millerite, heazlewoodite, chalcocite, godlevskite, hematite, hisingerite, chlorite, serpentine, hydrogarnet, calcite etc, which sharply worsened the technological characteristics of ores.

Ore-forming LGM. Numerous manifestations and deposits of native copper of the copper-zeolite formation were formed in the metabasalts and metadolerites of the trap formation. Numerous deposits of optical Iceland spar were formed in the deformed metabasaltic and metadoleritic sheets, dikes, and volcanic pipes of the trap formation; their isochronous Rb/Sr age is 122±1 Ma. Manifestations of the metamorphogenic-hydrothermal five-metal U-Ag-Bi-Co-Ni arsenide-antimonide formation, regenerative Sn-Pt-Pd-Ag mineralization, carbonate-anhydrite veins with sulphides and selenides Cu, Zn, Pb, Cd, Ag were formed within and around the low-grade metamorphosed magmatic Au-Ag-Pt-Pd-Co-Ni-Cu ores of the Noril'sk deposits.

Work has been completed with support of Russian FBR (grant 19-05-00490).

Geochemistry and mineralogy of REE in low-grade metamorphosed magmatic rocks and problems of their Sm/Nd dating

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It is commonly believed, that the isotope Sm/Nd age of magmatic rocks is in correlation with the age of their crystallization (For, 1988). The undertaken investigations established that it not always corresponds to the truth. Specifically, the REE are not mobile at processes of low-grade metamorphism in the conditions of zeolite facies; the age of magmatic rocks established by the U/Pb method evaluated with zircon or baddeleyite and the isotope Sm/Nd age are identical. At processes of low-grade metamorphism in the conditions of prehnite-pumpellyite facies PPF lanthanides mobilize and their own minerals form; the U/Pb age zircon or baddeleyite of metamorphosed rocks evaluated with their Sm/Nd age are significantly various.

The most ancient kimberlites of Kimozero, Karelia, Russia. The U/Pb age of kimberlites evaluated with zircon is 1919±18 Ma (Priyatkina et al., 2014). Kimozero's kimberlites are turned into PPF metakimberlites (antigoritic serpentine and tremolite-carbonate rocks). At the same time, there was almost full mobilization of REE and their metamorphogenic minerals appaired: allanite-(Ce), hydroxylbastnesite-(Ce) and -(La), hydroxylparisite-(Ce) and -(La), monazite-(Ce). Crystals' borders of REE minerals with antigorite and tremolite are the surfaces of conjoint growth. Therefore, the isochronal Sm/Nd age which is 1760 Ma (Makhotkin, 2003) corresponds to the time of epigenetic metamorphism of Kimozero rocks.

Gabbroids of the Yoko-Dovyrensky intrusive, Baikal region, Russia. The U/Pb age of rocks evaluated with zircon and baddeleyite is 728±4 Ma (Ariskin et al., 2018). The intrusive is notably tectonised and its rocks are partly metamorphosed. The main mineral is chlorfluorapatite, the REE carrier in gabbroids, is turned to hydroxylapatite without REE at processes of metamorphism in the conditions of PPF. Metamorphogenic REE-containing epidote, allanite-(Ce) and monazite-(Ce) associate with it. The Sm/Nd age of rocks is 673±22 Ma (Amelin et al., 1996), which answers to the age of epigenetic low-grade metamorphism.

Work has been completed with support of Russian FBR (grant 19-05-00490).

Clay minerals of some Paddy soils in the Southern of Thailand

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Soil fertility in the southern of Thailand has low level, because weathering process of soil parent material appear faster than the other region due to very heavy rain. The chemical properties of paddy soils in the Southern of Thailand is related with type of clay minerals and amount of clay . Anchalee *et al.*(1993) studies soil chemical property and mineral clay on paddy soil of Thailand; Bangnara series, Klaeng series, Ranote series and La-ngu series in Songkhla province, the Southern of Thailand. Those soil series are poorly drained, fine-textured (clayey texture). Most land uses have been contributed to paddy rice in rainy season and cash crops in dry season (after harvesting of paddy rice). **Problems:** Low fertility, strong acid in some places, lack of water in dry season and water logging in rainy season. Since it has a clayey texture, high water holding capacity, and low permeability, physical soil conditions are favorable for rice production. However, due to some adverse chemical conditions, these soils become less productive. The chemical conditions affecting crop growth include extreme acidity, aluminum toxicity, iron toxicity, hydrogen sulfide toxicity, low base status, and inadequate supply of nitrogen and phosphorus. Therefore, to use these lands for rice production the following amelioration measures are practiced in Thailand. Liming, Marl and lime dust at the rate of 13-25 t ha-1 have been used extensively in Thailand to increase the pH of the soil. Soils down to a depth of approximately 1.25 meters was found that the level that mineralogy of clay fraction would be an important factor controlling chemical properties of soil. There is kaolinite, a low activity clay. (Anchalee *et al.*, 1993) Soil properties is related with clay mineral type, such as exchagable and absorb soil nutrient. Most soils show low plant nutrition, moderate to high cation exchange capacity (C.E.C.) and high extractable acidity (H^+ and Al^{3+}). These show that soil have low base cation as plant nutrition, due to low acitivity clay to control soil properties, and cause to low soil fertility.

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Fe-smectites as the main products of basalt hydrothermal alteration: example from the Ediacaran flood basalts of the East European Craton

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Both on the Earth and on Mars, smectites are documented as ubiquitous alteration products of basalts. Their common characteristics are: high Fe content and trioctahedral or di-trioctahedral character. Trioctahedral clays with Fe>Mg are called ferrosaponites. For Fe<Mg clays, informal terms “Fe-smectite”, “griffithite”, or “oxysmectite” are used. Elevated concentrations of such smectites are found in dark accumulations of glassy-looking material, decribed by petrographers as “chlorophaeite”, “palagonite”, or “glass”.

In this contribution we report the investigation of basaltic smectites based on the bulk rock and clay fraction XRD, chemistry, Mössbauer spectroscopy, oxygen and iron isotopes. The object of our study is an Ediacaran basalt trap, which covers the western margin of the East European Craton (SW Belarus, NW Ukraine, N Moldova, NE Romania, and E Poland), and underwent a hydrothermal alteration.

All investigated basalt samples were found to contain smectite: from a few up to over 50% of the rock mass. Smectite is the most abundant basalt alteration product. Based on separate 02 and 06 XRD reflections, we identify this clay material, both in the chlorophaeite accumulations and in the host basalt, as a mixture of dioctahedral and trioctahedral smectite. During progressing basalt alteration, the amount of dioctahedral smectites increases at a constant rate, while the amount of trioctahedral smectites first increases, then levels of and starts decreasing. This pattern indicates transformation of tri-smectite into chlorite.

FTIR and chemical analysis of clay fractions confirm the di-trioctahedral nature of smectites. Mössbauer detects two components: di-smectite with only Fe^{3+}, and tri-smectite with Fe^{2+} and Fe^{3+}. The dioctahedral clay is Fe-montmorillonite, without Al^{IV}. It concentrates almost all REE present in the sample, its $d^{18}O$ is high, and its $d^{56}Fe$ is positive. The trioctahedral clay is Fe-saponite, without Al^{VI}, Fe<Mg. Its $d^{18}O$ is lower and its $d^{56}Fe$ is negative.

The chlorophaeite in least altered basalts is optically isotropic, then it becomes birefringent, loses some Fe and alters into smectite crystals. We assume that ferrosaponite present in isotropic chlorophaeite alters into a mixture of Fe-montmorillonite and Fe-saponite.

Such basalt alteration products are indicative of a process, which involves a convection cell of oxygenated meteoric water, heated by the cooling basalt and bringing Mg into the alteration zone from deeper parts of the basalt body.

Authors acknowledge financial support from the Polish National Science Centre MAESTRO grant 2013/10/A/ST10/00050.

A mean electrostatic model for ion transport through heterogeneous clay

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We present here a new model, CrunchClay, that simulates multicomponent diffusion of ions through clay and clay-rock by taking into account the charge and transport characteristics of the electrical double layer (EDL). The model can be applied in 2-D to clay systems with heterogeneous distributions of mineralogical and surface charge properties. The model makes use of a set of newly developed routines that calculate accurately the fluxes between adjacent grid cells with differing charge properties. In addition, the model is able to consider time-dependent EDL lengths (or volumes) resulting from salinity changes. The more common use of the model, however, is to simulate ion transport through heterogeneous clay rocks, where the distribution of minerals and connected porosity is derived from microtomography or other means. The model is based on a global implicit solve of the reaction-diffusion equation with explicit consideration of two co-existing continua: a bulk water continuum and an EDL continuum in which electrostatic effects are treated. The global implicit or fully coupled approach, while requiring additional software development, offers the advantage of improved computational efficiency and convergence characteristics over operator split treatments of the diffusion-reaction equation. The model is used to simulate uphill diffusion of radiolabeled tracers as well as a reactive and non-reactive tracer in Opalinus Clay.

Crystal growth of an expandable layered silicate on fluorophlogopite surface

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Mica is a platy particle with a smooth cleaved plane, and has been used as a substrate for atomic force microscopy. Crystal growth of layered solids (e.g., layered metal chalcogenide1)) through epitaxy has been studied on a smooth cleaved plane of mica. Epitaxial growth on mica has recently attracted attention in metal enrichment processes at a molecular level based on weathering and diagenetic of mica.2) Here we present artificial growth of a layered clay mineral on the cleavage of a synthetic mica. Epitaxial growth of an expandable layered silicate (a hectorite-like layered silicate: abbreviated as Hect) was found to occur on fluorophlogopite when the sources of the layered silicate were allowed to react hydrothermally with fluorophlogopite ($KMg_3AlSi_3O_{10}F_2$) in a basic aqueous solution.

Fluorophlogopite was mixed with aqueous solution consisting LiF, $MgCl_2$, silica sol and urea. The slurry was transferred into a Teflon-lined autoclave, followed by heat-treatment at 373 K for 48 h. After the slurry was centrifuged, the precipitate was dried at 323 K. Sample was named as A when the molar ratio of LiF:$MgCl_2$:SiO_2:urea in the starting mixture was 1.4:5.6:8:51. Added amounts of LiF and $MgCl_2$ were increased to 2 and 3 times, being named as B and C, respectively. Methylene blue adsorption was used for estimating Hect contents in samples.

SEM images of the samples show that the surface of fluorophlogopite was rough with fine particles (Figure 1a). Whereas the XRD patterns included reflections ascribed to hectorite, reflection peaks ascribable to magnesium carbonate was observed in sample C. Considering that Hect contents in A, B and C were 18, 27 and 30%, respectively, B contained a larger amount of Hect without by-products. In TEM image shown in Figure 1b fine crystals of Hect adhered to the cleavage of fluorophlogopite. Because Hect was absent in the supernatant after the hydrothermal reaction, we elucidate to occur selective growth of Hect epitaxially on fluorophlogopite dispersing in water phase.

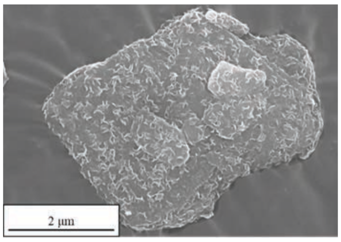

Figure 1a. SEM image of sample B

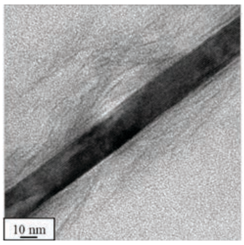

Figure 1b. TEM image of sample B

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Biomimetic Polymer/Clay Nanocoatings with Exceptional Mechanical, Barrier, and Flame Retardant Properties from One-Step Co-assembly

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Large-scale biomimetic organic/inorganic hybrid nanocoatings with a nacre-like microstructure were prepared via a facile co-assembly process. Different from conventional polymer nanocomposites, such nanocoatings contain a high concentration of nanosheets, which can be well aligned along the substrate surface. Moreover, the nanosheets and polymer matrix can be chemically co-crosslinked. As a result, the nanocoatings exhibit exceptional mechanical properties (high stiffness and strength), barrier properties (to both oxygen and water vapor), and flame retardancy, but meanwhile they are highly transparent (maintaining more than 85% of their original transmittance to visible light). The nanocoatings can be applied to various substrates and regular or irregular surfaces (e.g., films as well as foams). Because of their excellent performance and high versatility, such nanocoatings are expected to find widespread application.

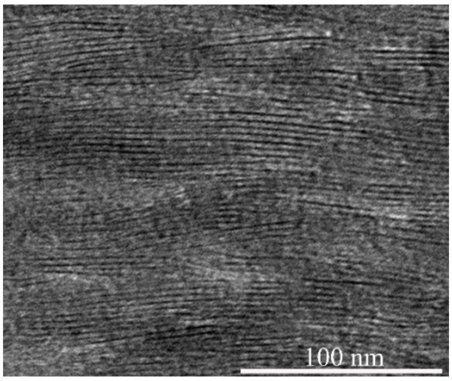

Figure 1. Transmission electron microscopy image of the cross-section of the nanocoating containing 50 wt. % clay nanosheets.

Session number and name: D1. Recent Progress on Nanotechnology and Nanomaterials from Clay Minerals

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The activity of sulfate reducing bacteria in bentonite as a function of water and lactate availability

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In the Swedish KBS-3 concept highly radioactive used nuclear fuel is emplaced in copper canisters embedded in compacted bentonite deep down (-500 m) in crystalline rock (designed lifetime is 100 – 1000 ka). The bentonite is protecting the canister chemically and physically from the surroundings. One of the main functions of the bentonite is to inhibit activity of microbes, e.g. sulfate reducing bacteria (SRB). During the right conditions SRB may reduce sulfate (S(VI)) from the bentonite or from the groundwater) into sulfide (S(–II)) that may corrode the copper canister. Current observations indicate that at the high swelling pressure that arise during water saturation (> 2 MPa), microbes become inactive. However, during the early period of the repository lifetime and before the bentonite is water saturated, there may be a window of opportunity where the bentonite is neither dry, nor wet, when a high enough relative humidity is present for SRB to potentially be active. This study aims at finding out if there is a moisture threshold limit for the bentonite when SRB may produce sulfide.

Several types of experiments were performed using (i) natural SRB in Wyoming bentonite, (ii) added commercial strain of SRB (*Pseudodesulfovibrio aespoeensis*) and (iii) enrichment from a natural groundwater from the Äspö underground laboratory borehole.

Natural SRB in Wyoming bentonite were activated by adding a layer of gypsum and lactate in the middle of a bentonite volume in a glass cylinder and liquid water was added. The cylinder was plugged with a rubber septum and placed in the laboratory (20 ^{o}C). After approximately 2 months gas had formed approximately 5 mm above the gypsum layer. A copper solution was added to the top and instantaneously CuS precipitated, as an indicator of formed hydrosulfide. SRB is naturally present in Wyoming bentonite as well gypsum. Hence, the presence of both indicates that SRB are restricted by the lack of available energy sources in the natural bentonite.

Tube experiments were performed in an anaerobic box (N_2-atmosphere) where an open glass tube was emplaced within a bigger closed plastic tube. In the smaller glass tube bentonite, gypsum, lactate, commercial SRB, and nutrients were emplaced and in some cases liquid water. In the outer plastic tube a solution was placed with either pure water or saturated salt solutions, and with a small addition of $CuSO_4$ salt as an indicator of formed hydrogen sulfide from the small tube. The different salt solutions gave rise to different relative humidities. Microbiological reduction of sulfate to hydrogen sulfide was detected to occur when the microbes had access to liquid water (in addition to gypsum, lactate, and nutrients and no swelling pressure), while no hydrogen sulfide production was detected when the microbes were restricted to a relative humidity of 75-100%. The amount of CuS formed was lower when bentonite was present compared to with no bentonite, which is compatible with previous experiments, where bentonite was found to react with hydrosulfide, possibly redox active Fe(III) in montmorillonite is responsible for oxidising the S(-II) to S(0).

Characterizations of attapulgite mbodiene for pharmaceutical trials preformulations

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Our study focused on the still attapulgite called palygorskite, a fibrous clay, locality Mbodiène located south of Dakar (Senegal) for testing pharmaceutical preformulations. Mineralogical and physicochemical characterizations have shown that our palygorskite was pure to 82%, the remainder being “ankérites” (cubic iron and calcium carbonate) and quartz. The major components were represented by silica (46.7%), alumina (4.74%), iron oxide (3.67%), calcium oxide (8.2%) and magnesium oxide (9.16%). The specific surface area of our palygorskite was 96.22m^2.g^{-1} and its 3-2.3g.cm^{-1} density. The determination of the density before settling (0.642g.ml^{-1}) and that of the tap density (0.746g.ml^{-1}) was used to calculate the compressibility index (CI) (13.94%) and index Haussner (IH) (1.16). Referring to Carr's classification, the sample showed good flowability. Finally, Atterberg limits, the sample attapulgite was a normal activity clay, highly plastic and hard consistency. Pharmaceutical trials preformulations were carried out with binary mixtures of attapulgite-mango kernel and attapulgite-zinc sulphate with respectively persistence of antioxidant activity up to 3 months and a binding rate of 35% of zinc. In addition, a comparative study with an attapulgite drug showed similar materials.

Crystallinity of hematite as a potential indicator of diagenetic grade

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During burial diagenesis (at temperatures above 120°C) sedimentary hematite undergoes structural reorganization, which results in significant changes of its powder diffraction pattern (Środoń et al., 2018). This effect is responsible for the reset of its magnetic properties below its Curie temperature (675°C), influencing the applicability of hematite for paleomagnetic reconstructions.

The main aim of this study was to investigate the reorganization mechanism of hematite by calculating crystallite size distributions (CSD) from the peak shapes of the powder diffraction patterns. The specific CSD shape can be qualitatively correlated with the crystal growth mechanism (Eberl et al., 1998).

A series of eighty bulk rock samples from the Ediacaran redbeds of the East European Craton, representing a wide range of diagenetic conditions, was analyzed as random preparations. The crystallite size ($L_{VOL\text{-}IB,}$ Topas ver. 5, peak shape based on fundamental approach) was calculated for three different crystallographic directions from (104), (110), and (300) reflections. Significant changes were observed for (104) and (300) peaks, while for (110) only small variation was visible. The results indicate that hematite formed during weathering has a platy shape and the main direction of growth is [001], accompanied by the decrease of micro-strain broadening in [100].

For further evaluation of CSD for selected samples, (104) peak was chosen. Three different models were implemented in the Topas ver. 5 software: (1) *irregular model*-without any assumption about the shape of distribution, (2) *lognormal* shape and (3) *Ostwald ripening* shape (Voorhees, 1985). The volume-weighted CSD with different shapes were obtained. For all the studied samples, the best fits (with the lowest R_{wp} factors) were observed for the first or the second model. The Oswald ripening growth was excluded, since in all cases the significant deterioration of fits were observed.

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Authors acknowledge financial support from the Polish National Science Centre MAESTRO grant 2013/10/A/ST10/00050.

PREFERRED FORMAT: POSTERMolecular dynamics simulations of interactions of organic molecules found in oil with smectite: influence of brine chemistry on oil recovery

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Clay minerals with smectitic type of mineral outer surface (smectite, illite-smectite, illite) are major constituents in many unconventional oil and gas reservoirs. Therefore, smectite was used as a model compound to test interactions of oil compounds with mineral surfaces. Natural crude oil is a complex mixture, which - for the purpose of simulating an influence of surrounding fluid on its interactions with smectite - needs to be simplified. Based on the protonation state at a close to neutral pH: decane, quinolone, quinoline cation, nonanoic acid, deprotonated nonanoic acid, benzamide and protonated heptylamine were selected as model compounds for oil - smectite interactions.

Our study employed molecular dynamics simulations to study the interactions between smectite and major oil constituents (model compounds), along with the impact of different brine chemistry (type of cation in a solution) and ionic strength on the compound desorption.

The first set of simulations showed remarkably different interactions of the selected organic molecules with the smectite surface. For a fully hydrated state of the model smectite, differences were readably visible between polar and non-polar organic molecules. Also, a degree of protonation was found to be a crucial factor affecting the molecules' affinity to the mineral surface. In the case of model compounds surrounded with cyclohexane as an approximation of the oil phase, there is a tendency of all tested model molecules to be adsorbed on the smectite surface, however in different quantities depending mainly on polarity. For a system which contains - additionally to the cyclohexane phase - also a monolayer of water, very similar tendencies as for fully hydrated smectite state were observed: organic molecules that are well cyclohexane (thus oil) - soluble formed droplets in water phase, whereas organic compounds miscible in water concentrated at the water-covered film on the smectite surface.

The second set of calculations was aimed at testing mobility of organic model compounds within wide-open smectite interlayer space (acting as a narrow pore model), under one-dimensional pressure. External pressure was exerted on the graphene walls limiting the box of calculations: 0.3 kbar at one and up to 6.6 kbar on the other wall, with pressure increasing stepwise as graphene layer moved. The results show significant differences in pressure that allows expulsion of organic molecules in different systems and different ions from a narrow slit. We conclude that the mobility of oil compounds depends mainly on differences in a type of molecules and the size of effective hydration sphere of the cations adsorbed on a mineral surface.

Buserite and asbolane type manganese-cobalt-nickel phases for supercapacitors

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Throughout the years, MnO_x in various forms has been widely studied as the electrode material in different energy storage systems, such as lithium ion or alkaline batteries and supercapacitors. In all these cases, MnO_x has been proven to be a reliable electrode material with high performance thanks to the various oxidation states of Mn. An innovative research track aiming at synergistically gathering in a same layer-based material, the pseudo-capacitive properties of manganese, the good electronic conduction properties associated to cobalt 4+, and the capacitive properties of nickel has been developed in the laboratory. To do this, we use an original synthesis method starting from the lamellar birnessite manganese phase, whose structure consists of sheets of edge-sharing MnO_6 octahedra with vacancies. In this type of phases, the manganese ions have a mixed valence 3+/4+. To compensate the resulting negative layer charge, some cations such as Na^+, K^+, H^+, together with water molecules are present within the interlayer space. The defined protocol involves an exchange of the alkaline cations present in the interlayer space by cobalt or nickel ions, leading to phases exhibiting similarities with asbolane. The structure of the materials obtained was studied by X-ray diffraction and their thermal behavior was evaluated by thermogravimetric analysis. Different mass losses associated with structural changes have been highlighted (see figure 1). Chemical analyzes were conducted to determine the composition of the materials obtained, as well as scanning and transmission electron microscopy. In the spirit to use these new phases as positive electrode in supercapacitors, the electrochemical properties have been studied in neutral (K_2SO_4/Na_2SO_4) and alkaline (KOH/NaOH) media. Manganese-Cobalt materials show promising capacity values up to 150 F/g in 5M KOH electrolyte.

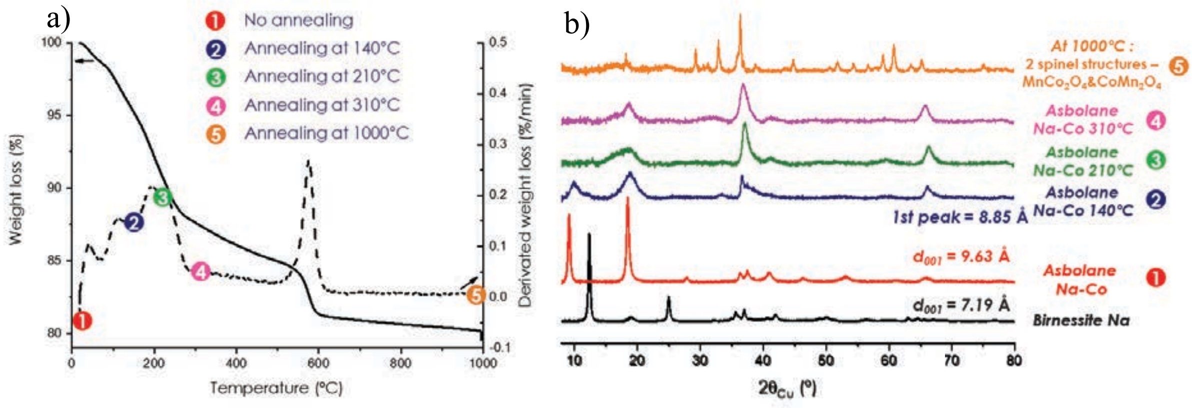

Figure 1 : a) Thermogravimetric analysis curve (solid line) and its time derivative (dashed line) obtained for the material exchanged with cobalt and b) X-ray diffraction patterns of the starting birnessite phase, of the cobalt exchanged phase (1), of the annealed phase at 140°C (2), of the annealed phase at 210° (3), of the annealed phase at 310°C (4) and of the phase obtained after annealing at 1000°C, at the end of thermogravimetric analysis (5)

Acknowledgments – The authors are grateful to Thales for their suppor

Iron oxidation and leaching with intense kaolinization -implication of the formation of sedimentary kaolin deposits-

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A zone of sedimentary kaolin deposits in the Seto-Tono district is the largest kaolin field in the Japan Arc. Although each deposit comprises an area smaller than 10 km^2, more than 20 deposits are distributed within a field of 10 x 30 km. The source sediments of these kaolin deposits, which accumulated in Pliocene under lacustrine or swamp environments, are mainly arkose sandstone (up to 10 m thick) and subordinate ligneous mudstone (up to 3 m thick). The arkose sandstone and ligneous mudstone were subjected to intense kaolinization, and altered to bleached kaolin + quartz ores (gaerome clay) and carbonaceous kaolin ores (kibushi clay), respectively. The kaolinization likely occurred in situ, because the gaerome and kibushi clay are unsorted with presence of carbonized snags in gaerome clay in places.

Formation of the kaolin deposits has been investigated using gaerome and kibushi clay from Akatsuki mine. Limonite crusts (up to 30 cm thick), comprising sand and pebbles concreted by goethite, are a common feature in the unconformity plane between the kaolin deposits and a Cretaceous granitic basement whose surface had gradually changed to green saprolite containing Fe-kaolinite (Jige et al., 2018 Am. Mineral., 103, 1126-1135). The field occurrence indicates iron in the source sediments leached out, mostly as ferric oxide, and precipitated due to change in the pH-dependent solubility and permeability at the unconformity plane. Minor amounts of Fe-Ti, Fe and Ti oxides present in gaerome and kibushi clay, are likely decomposed residue of mafic silicates in the source sediments. Fe-Ti oxides are ilmenite and secondary pseudorutile. The hematite component of ilmenite ranges widely from 0.2 to 21 %. Fe oxides are porous ferrihydrite whereas Ti oxides are fine-grained rutile or leucoxene. An assemblage of ilmenite, pseudorutile and leucoxene suggests successive oxidation and leaching of iron (Mücke and Bahadra Chaudhuri, 1991 Ore Geol. Rev., 6, 25-44) since ilmenite was partly altered to pseudorutile and leucoxene occurred as discrete grains. Trace amounts of gypsum and pyrite were also detected.

Source sediments had accumulated in inland lakes or swamps with abundant organic materials. Thus, aerobic oxidation of ferrous iron was unlikely to have occurred within the source sediments. Long-term acidic conditions are necessary for kaolinization of feldspars however, significant leaching of alkali elements in association with HCO_3^- would not occur below pH5 (Reuss and Johnson, 1986 Ecological Studies 59, Springer-Verlag). Based on these factors, biological nitrification of organic nitrogen is the most likely cause of the acidification and kaolinization. Furthermore, nitrate-dependent microbial oxidation of ferrous iron (e.g., Straub et al., 1996 Applied Env. Microbiol., 62, 1458-1460) is likely to have occurred under the anaerobic conditions. Iron oxidation brought about decomposition of mafic silicates and leaching of iron from the source sediments; those would have occurred simultaneously with intense kaolinization of feldspars.

A vision for transformation of iron oxides with organic molecules and their effect on soil aggregates

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Iron (hydr)oxides are widely present in nature and nano-particles of iron minerals are distributed throughout the atmosphere, oceans, groundwater, surface waters, soils, in and/or on most living organisms. The formation of iron oxide can be improved by employing Fe(II). Furthermore, some organic molecules with hydrophilic groups on the surfaces and specific space structures, such as polymers and surfactants, can be used as electron donor and template to promote the transformation of iron oxides. Meanwhile, organic molecules, adsorbed on the crystal plane of iron oxide through the selective adsorption or special adsorption as crystal growth, influence the minerals' morphology by the mineral's self-assembly, oriented attachment or Ostwald ripening mechanism.

Ascorbic acid instead of Fe(II) effectively catalyzes the formation of α-Fe_2O_3, and for the first time, spherical, ellipsoidal and elongated particles of hematite have been successfully obtained by just controlling the amount of ascorbic acid. Tartaric acid as both a reducing agent and a template also control particle size and morphology of hematite. The initial pH was a crucial factor to exhibit morphology of hematite. The products were corn-like at initial pH 7 through oriented attachment, but changed to be rounded by Ostwald ripening mechanism at high pH.

In addition, the dissolution of iron hydroxides induced by organic acids has been proposed as an important mechanism for colloid generation and removal. The inner- and outer-sphere complexes of oxalate are simultaneously present on the surface of ferrihydrite (Fh). The stabilization of Fh colloids was dominant over dissolution into dissolved Fe at a low oxalate solution concentration, driven by electrostatic repulsive forces from the unsaturated, strongly bound species. Outer-sphere complexes at a high oxalate solution concentration induced the dissolution of aggregates and colloids of Fh into dissolved Fe. Our results provided insight into the fate of iron hydroxide colloids in soils and aquatic environments.

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Lithium isotope systematics in coal

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Lithium has been shown to be a valuable trace element because of its mobility during surface weathering and under hydrothermal conditions (Pistiner and Henderson, 2003). Currently there is limited understanding of how Li-content and isotopic compositions vary among coals of different rank and depositional environments. The Li content of organic-rich rocks is high (tens to hundreds ppm) compared to seawater (0.2 ppm), and its content varies with depositional environment, organic maceral type, and thermal maturity. Lithium concentrations of bituminous coals from the Jungar Coalfield (Mongolia) have been reported over 500 ppm (Dai et al., 2012). However, the worldwide average Li content is 14-20 µg/g (Swanson, 1975; Ketris and Yudovich, 2009). In general, Li is reported to be hosted by silicates (ash) in coal, but Swaine (1990) sited evidence that Li was also associated with the organic constituents.

To better understand the Li distribution and isotopic fractionation in coals as they mature thermally, we analyzed coal samples from the Pennsylvania State Univ. Coal Repository and coal from two locations in CO (USA) where a dike intruded normal to bedding creating a thermal gradient away from the contact. The coal repository samples range from lignite to anthracite in rank, have varying ages and amounts of huminite, vitrinite, inertinite and liptinite. Analyses were made using Secondary Ion Mass Spectrometry (SIMS) and results show that low rank coals are ^{6}Li enriched (as low as δ^7Li –30.8 ± 3.5‰) compared to higher rank coals (up to –4.6 ± 1.5‰).

Previous measurements of Li content on coals/kerogen used acids to isolate the insoluble organic matter, potentially removing organic-Li along with dissolved silicates. Using Nano-SIMS to map the isotopic distribution of Li in coals mitigates the need for chemical isolation of organic and silicate phases. Preliminary results indicate that Li is correlated with areas of high C in immature samples but is higher in Si-rich areas as thermal maturity increases. Our hypothesis is that organic-Li may be released with increasing thermal maturity and taken up by silicates (e.g., clays). The timing (temperature) of Li redistribution in coals, and knowing the isotopic fractionation associated with this process, will lead to a better understanding of the contribution of organic-Li to the global geochemical cycle.

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The role of cation-vacancies for the electronic and optical properties of aluminosilicate imogolite nanotubes: a non-local, linear-response Time-Dependent Density Functional Theory study

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We report a combined non-local (PBE0-TC-LRC) Density Functional Theory (DFT) and linear-response time-dependent DFT (LR-TDDFT) study of the structural, electronic and optical properties of the cation-vacancy based defects in aluminosilicate (AlSi) imogolite nanotubes (Imo-NTs) that have been proposed on the basis of Nuclear Magnetic Resonance (NMR) experiments [1]. Following numerical determination of the smallest AlSi Imo-NT model capable of accommodating the defect-induced relaxation with negligible finite-size errors, we analyse the defect-induced structural deformations in the NTs and ensuing changes in the NTs' electronic structure. The NMR-derived defects are found to introduce both shallow and deep occupied states in the pristine NTs' band gap (BG). These BG states are highly localised at the defect site. No empty defect-state is modelled for any of the considered systems. LR-TDDFT simulation of the defects reveal increased low-energy optical absorbance for all (but one) defects, with the appearance of optically active excitations at energies lower than for the defect-free NT. These results enable interpretation of the low-energy tail in the experimental UV-vis spectra for AlSi NTs as being due to the defects. Finally, the PBE-TC-LRC-approximated exciton binding energy for the defects' optical transitions is found to be substantially lower (up to 0.8 eV) than for the pristine defect-free NT's excitations (1.1 eV).

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Interlayer hydration of clays depending on humidity

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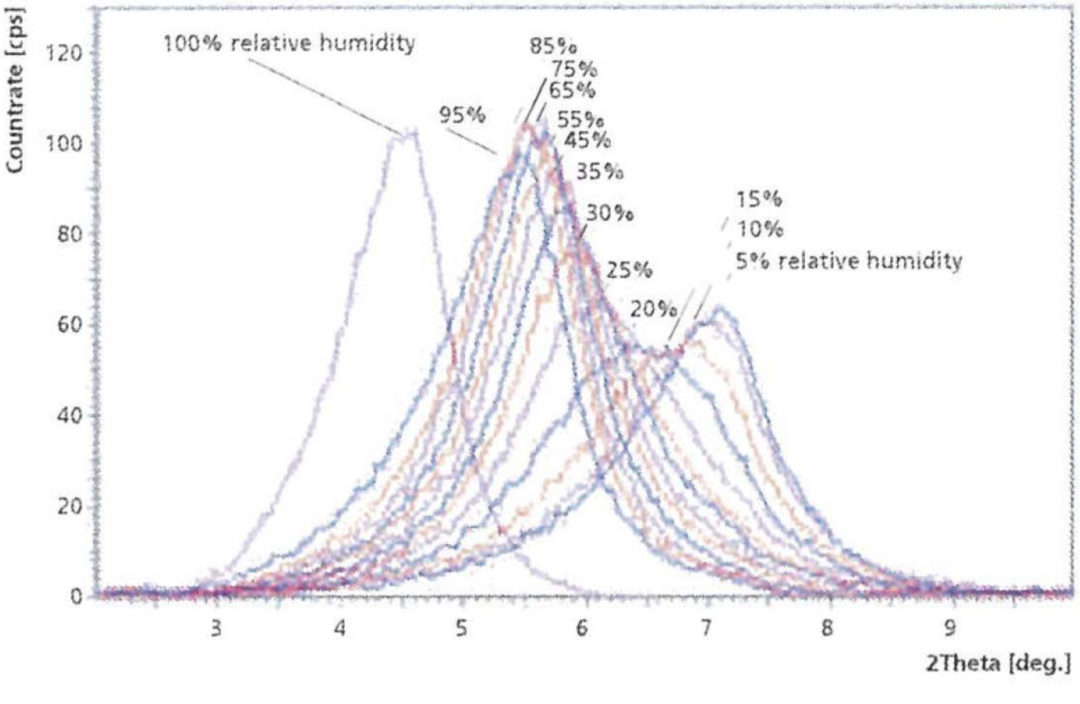
Several classes of materials exhibit considerable changes in crystal structure as a result of a change in temperature or humidity. The structure of clay minerals strongly depends on the number of water molecules incorporated. An unexpected phase transition at elevated temperature and at a high humidity level can change the properties of clays minerals. X-ray diffraction is a technique to determine rearrangements in the crystal structure upon changes in environmental conditions.

A Ca-Wyoming montmorillonite clay minerals has been measured at different relative humidities varying between 5 and 100%. A set of scans with background subtracted is displayed in the figure below. A continuous reversible shift of the (001) reflection from 7.1 degrees to 4.4 degrees (2 theta) due to the increase in relative humidity is observed. This shift reflects the incorporation and the re-organization of water molecules in the interlayer, which results in an increased interlayer separation and an elongation of the c-axis.



Shift of the (001) reflection of Ca-Wyoming montmorillonite as a function of relative humidity

Finite element model constrained by self-diffusion and selectivity coefficients to predict the dynamic exchange of cations in the interlayer of swelling clay minerals

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Diffusion is the main transport process occurring in shales and engineered barriers considered for the storage of nuclear wastes. Due to the high compaction of these environments, cations mainly diffuse in the interlayer spaces of the swelling clay minerals present in these systems. To our knowledge, the literature does not report on any finite element model, constrained by intrinsic properties of the particles (i.e., self-diffusion coefficients obtained by molecular dynamics and selectivity coefficient associated with interlayer), able to predict the dynamic exchange of two cations between the interlayer of swelling clay minerals and external aqueous reservoir.

This study aims at proposing a finite element model predicting the dynamic exchange of cations (Ca^{2+} by Na^{+} and Ca^{2+} by Sr^{2+}), from the interlayer spaces of millimeter disks of vermiculite and external aqueous reservoirs. Vermiculite was chosen as a model swelling clay because this mineral does not show any osmotic swelling in water saturated conditions, as compared to low-charge montmorillonite generally considered in the literature. Dynamic exchange experiments were performed by immersing disks of Ca-saturated vermiculite in aqueous reservoirs characterized by different NaCl and $SrCl_2$ salinities. Experimental data were obtained by the analysis of aqueous concentrations of cations released in the solution, while the finite element model considering the possible limitations at the clay/water interface was proposed to interpret the data. In order to propose a predictive model, (i) self-diffusion coefficients of interlayer cations calculated by molecular dynamics simulations, and (ii) previously evaluated selectivity coefficients associated with the interlayer, were employed as input parameters of the model.

A close agreement was observed between experimental results and simulations irrespective of the couple of cation and salinity of the aqueous reservoir considered. The results highlighted (i) the role played by the ionic flux existing at the clay/water interface, and that can limit the global diffusion process in the case of a low salinity reservoir, and (ii) demonstrated that it is possible to use intrinsic properties of swelling clay particles, especially self-diffusion coefficients stemming from molecular dynamics, to correctly predict the dynamic exchange of cations between the interlayer of swelling clays and the aqueous reservoir. These findings should contribute to the improvement of reactive diffusion models used to predict the migration of cations/pollutants in compacted swelling clay minerals.

Anion exchange properties of monoclinic lithium-aluminum layered double hydroxides synthesized by simplified method with bayerite

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The Cl^- ion and Br^- ion intercalated Li-Al layered double hydroxides (LDHs) were obtained by the imbibition of Li salt into bayerite ($Al(OH)_3$). The Li-Al-Cl LDH and Li-Al-Br LDH were crystallized in the monoclinic crystal system by using monoclinic bayerite as a precursor. The formation of Li-Al LDHs was prepared by soaking 0.5 g of bayerite in LiCl or LiBr solution followed by heat treatment in a beaker at 150 ˚C for about 1 h. The sample was centrifuged, washed and dried at 60 ˚C. The chemical compounds of Li-Al-Cl LDH and Li-Al-Br LDH were calculated by analyzing their metal ion, anion and water contents (Table 1). X ray diffraction patterns of Li-Al LDHs show Fig.1. The structure of monoclinic Li-Al LDHs, with a basal spacing of 0.76 nm, obtained by simplified method.

Distribution coefficient (K_d) of F^-, Cl^-, Br^-, NO_3^-, HPO_4^{2-} and SO_4^{2-} were determined batch-wise using a mixed solution of NaF, NaCl, KBr, $NaNO_3$, Na_2HPO_4 and Na_2SO_4. Anion uptake were calculated by the decrease of each anion concentration relative to its initial concentration. The K_d values were calculated using the following equation; K_d (mL g^{-1}) = anion uptake (mg g^{-1}) / equilibrium concentration (mg mL^{-1}). The sequence of calculated K_d values are $HPO_4^{2-} > SO_4^{2-} > F^- > Br^- > NO_3^-$ for Li-Al-Cl LDH and $HPO_4^{2-} > SO_4^{2-} > Cl^- > NO_3^-$ for Li-Al-Br LDH (Table 1). Furthermore, we studied the F^- exchange properties of Li-Al LDHs. The F^- exchange capacities are 4.2, 4.3 mmol g^{-1} for Li-Al-Cl LDH, Li-Al-Br LDH, respectively. The uptake of F^- rapid and equilibrium is achieved within 30 min.. The pH dependence of F^- uptake by Li-Al-Br LDH was examined by changing the pH of NaF solution with a HCl or a NaOH solution. The pH dependence of F^- uptake in almost constant (3.3 mmol g^{-1}) in the pH range of 4-11.

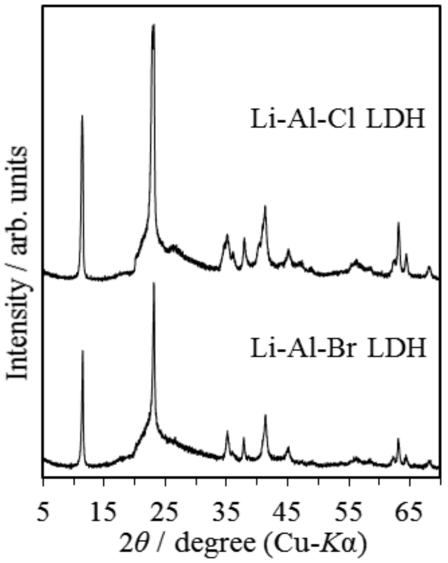

Fig.1. XRD patterns of Li-Al LDHs.

Table 1. Chemical formula and Distribution coefficient (K_d) .

Sample	Chemical formula	Distribution coefficient (K_d) /mL g^{-1}					
		F^-	Cl^-	Br^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}
Li-Al-Cl LDH	$Li_{0.52}Al(OH)_3Cl_{0.54}·0.62H_2O$	1400	-	90	10	> 10^4	8480
Li-Al-Br LDH	$Li_{0.56}Al(OH)_3Cl_{0.56}·0.39H_2O$	1030	350	-	< 10	> 10^4	7250

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For a global mapping of customary uses of alumina silicates in primary health care

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From China to Sardinia, from the Amazon to Romania, in various ways alumina silicates are or have been used to treat internal conditions (cholera, gastritis, GERD, poisoning, parasitosis including bilharzia, sexually transmitted diseases, etc.) and external conditions (infected wounds, burns, ulcerations, fractures, skin problems, rheumatisms, etc). They were also eaten during famine times (they potentiate nutrient assimilation, as used nowadays for breeding animals in our countries).

We propose to carry out a survey, country by country and continent by continent, of customary uses of alumina silicates (clays, minerals) for primary health care. The purpose of this research is to contribute to providing an immediately accessible medical tool everywhere (clay is 15% of the external core of our planet). The use of clay is an effective medicine, insufficiently exploited as an emergency medicine for populations lacking access to health care systems and pharmaceuticals. People in forced migratory movements, climatic, political and economic crises, are among those that could greatly benefit from it. Two aspects to this research, which will be complementary for the valuating of its results :

A main axis aimed at the mapping of traditional uses, continent by continent, and country by country. The teams of researchers will bring together geologist, doctor, health professional, and anthropologist. They will establish the methodology and will make the cartographic synthesis of the results of the inquiries.

And a pharmacological research on the medical uses of the clays :
- the reliability and efficiency of the practices, and their place in the panoply of caring practices.
- the indications
- the methods of access to the minerals, and selection criteria
- the preparation
- the modes of use and protocols including that (priority) of the possible heating of the product.

The results of this research should be offered to public and humanitarian health authorities to promote training for health professionals and managers, particularly for those in charge of migratory emergencies.

Acknowledgements: This research project was endowed with a first scientific council: Michel Rautureau State Doctor of Physical Sciences, French specialist of clays, Dr. Arnaud Halloy, anthrologist, University of Nice. Antoine Lazarus, Honorary Professor of Public Health and Social Medicine.

Mössbauer study of bentonites from Croatia and neighbouring countries

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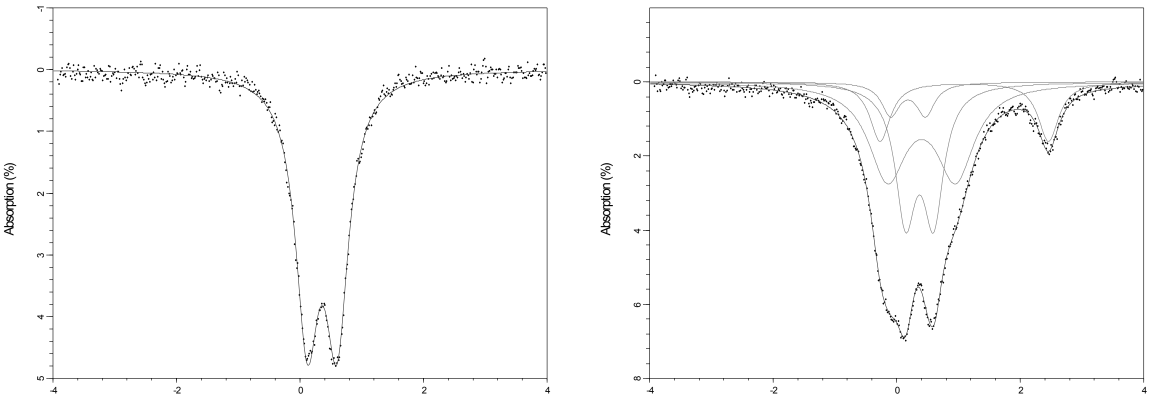
There are several known deposits of bentonites in Croatia. With the advancement of analytical methods and new findings about smectite characterisation in recent years, a demand for a full characterisation of known bentonite deposits occurred. Recently, thirteen samples of bentonites were studied by X-ray diffraction, FTIR spectroscopy, thermal (DTA and TG/DTG) and chemical methods (ICP/AES and ICP/MS). Most of the samples are from Croatia (Poljanska Luka, Šaša – Bednja, Draga – Gornja Jelenska, Lončarski Vis, Sjeničak, Paripovac, Divoselo and Bunarić – Maovice), but for comparison, samples from Bosnia and Herzegovina (Sokolac and Greda – Šipovo), Slovenia (Zaloška Gorica), and Serbia (Vranjska Banja) were also analysed.

One of the criteria for smectite classification (Emmerich et al., 2009) is their Fe-content. Therefore, in order to fully characterise investigated materials, Mössbauer spectra of < 2µm fractions were recorded. According to the chemical analyses most of the analysed bentonites are Fe-poor (they contain < 0.30 mol Fe/f.u.). Samples Divoselo 1 and Šipovo - Sokolac contain 0.30 mol Fe/f.u., while the sample from Bednja is ferrian (0.38 mol Fe/f.u.).

Mössbauer spectra recorded at room temperature differ significantly (Figure 1). Some of them, including the one of Bunarić sample with the lowest Fe content can be fitted with single or dominant doublet characteristic for Fe(III) in octahedral coordination. Others, like the one of Bednja sample with the highest Fe content have to be fitted with up to four doublets: two for Fe(III) in octahedral coordination, one attributed to Fe(II) in octahedral coordination and one for Fe(III) in tetrahedral coordination. There is no clear evidence of the presence of magnetically ordered phase, which indicates that most of the Fe present in the fine fraction of investigated smectites is incorporated in smectite structure.



a b

Figure 1: Mössbauer spectra of Bunarić (a) and Bednja bentonite (b) recorded at room temperature

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Synthesis of layered double hydroxides through a colloidal route: a comparative study of the behavior of Cu^{2+}/Al^{3+} and Mg^{2+}/Al^{3+} systems

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Elaborating stable LDH nanoparticles of controlled size and highly dispersed in water is a main prerequisite to extend their use in several application fields. A direct preparation route in water of stable and poorly aggregated colloidal M^{2+}/Al^{3+} LDH nanoparticles has been developed in our laboratory using PAm-b-PAA DHBC containing an ionizable complexing block poly(acrylic acid) (PAA) and a stabilizing neutral block poly(acrylamide) (PAm) [1]. This approach includes 2 steps: i) complexing M^{2+} and Al^{3+} cations by the DHBC anionic block leading to hybrid polyion complex (HPIC) micelles; ii) co-hydroxylation of the cations with an alkaline solution [2]. The mechanism of formation of LDH at increasing pH without DHBC that is generally accepted goes through the precipitation of $M^{III}(OH)_3$, the M^{II} cations remaining in solution, followed by dissolution of $M^{III}(OH)_3$ and co-precipitation of the M^{II}/M^{III} LDH occurring at a pH intermediate of $M^{II}(OH)_2$ and $M^{III}(OH)_3$ precipitation. In the present study we have compared the mechanism of formation of M^{2+}/Al^{3+} LDHs in the presence of DHBC with $M^{2+} = Mg^{2+}$ and Cu^{2+} cations whose solubilities as a function of pH are very different, making the precipitation pH of Cu^{2+} very close to that of Al^{3+} (~ pH 4) but on the contrary higher of about 6 pH units for Mg^{2+} (~ pH 10). Analysis by light scattering of the colloids shows that the critical ratio of acrylate function per metal cation above which colloidal stability is reached increases from 0.13 to 0.43 when replacing Mg^{2+} for Cu^{2+}. The three-fold amount of DHBC necessary in the latter case accounts for the concurrent stabilization of both Cu^{2+} and Al^{3+} hydroxides, contrary to stabilization of hydrolyzed species of Al^{3+} alone in the case of the Mg^{2+}/Al^{3+} system. The molar fractions of M^{2+} in the colloids as a function of pH, as determined by ICP-MS, in the two systems are similar but the increase started at a pH of 4 and 6 for Cu^{2+} and Mg^{2+}, respectively. These results show that incorporation of Mg^{2+} in the HPIC micelle core starts when Al^{3+} precipitation is complete while Cu^{2+} and Al^{3+} precipitate concurrently in the colloids. This led us to suggest a different nature of the precursor colloids in the two types of LDH, i. e. DHBC/($Cu(OH)_2$/$Al(OH)_3$) for Cu/Al LDH and DHBC/$Al(OH)_3$ for Mg/Al LDH.

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Zn_2Al- and Mg_2Al-layered double hydroxides as nanoreactors in the photoinduced interlayer isomerization of *E*-cinnamate

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Nowadays, the importance of the environmental conscious work became of utmost importance in the industrial as well as laboratory scale chemical syntheses. For keeping the rules of green chemistry (*e.g.*, developing selective reactions with environmentally friendly solvents or even without solvent) many possibilities exist [1]. Among other materials, layered double hydroxides (LDHs) may serve this goal well, since the reactant may be fixed in the interlayer space with anion exchange, and the sterically constrained environment may increase selectivity [2,3].

Cinnamic acid is a very important intermediate in the shikimic acid metabolic pathway of plants, and it is also very popular as an ingredient in various types of cosmetics. The acid has two stereoisomers *E* and *Z*. Unfortunately, only the *E* isomer is easily accessible. A way of obtaining the *Z* isomer is the isomerization of the *E* compound, which can be done *e.g.*, photochemically. However, photoinduced topotactic [2+2] dimerization may compete with the isomerization, therefore, optimization of the intercalation and the reaction conditions is a must. In the present contribution, results of our experimental work geared to the application of Mg_2Al-, and Zn_2Al-LDHs as a nanoreactors in the interlayer isomerization of cinnamate are described. The first step was the synthesis of the intercalated system by the co-precipitation method. The interlayer isomerization was performed with the intercalated compounds in solution. The suspensions were irradiated using a mercury light source working in 312 nm wavelength for 0 to 92 minutes. The characterization of the samples was performed by X-ray diffractometry (XRD) and infrared spectroscopy. The isomerization was followed by UV-VIS spectrometry. XRD measurements verified the successful introduction of *E*-cinnamate into the interlayer space of the LDHs. On irradiating the samples, shifts in the absorption maxima in the UV-VIS spectra showed that *E-Z* isomerization occurred, indeed.

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A Prediction of Uranium(VI) Diffusion in Montmorillonite at Various Chemical Solution Conditions

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Most nuclear waste disposal options include compacted bentonite, predominately consisting of montmorillonite clay, as part of a barrier system to minimize contaminant mobility. Uranium (U) is the primary element in spent nuclear fuel, and a potential contaminant of water resources. Uranium sorption onto clay and its slow diffusive transport away from waste canisters are expected to limit U(VI) mobility, and possibly also control nuclear fuel degradation rates based on mass action considerations.

A prediction of U(VI) diffusion in these systems is complicated by two main factors: (1) the complex mineralogical structure of montmorillonite clay, leading to two types of clay porosities and surface sites, and (2) the dependence of U(VI) sorption on U(VI) solution speciation and the specific chemical system conditions. For instance, depending on pH and ionic strength, U(VI) may sorb onto montmorillonite due to weak ion exchange reactions or the formation of stable surface complexes. Furthermore, in contrast to conventional porous media, U(VI) diffusion in montmorillonite is not only limited by contaminant sorption, but also by a (potential) lack of access to the full clay porosity for some U(VI) solution species. For instance, at the high degrees of clay compaction expected in future barrier systems, the partial or full exclusion of U(VI) from negatively-charged clay interlayer spaces may substantially decrease U(VI) fluxes.

In this modeling study, we specifically investigated how the charge of U(VI) solution species affects U(VI) sorption and diffusion behavior. For this purpose, we first simplified complex *chemical* solution speciation diagrams to *charge* speciation diagrams. Then, we coupled an existing U(VI) surface complexation model (Tournassat et al., *Geochim. Cosmochim. Acta*, 2018) with an analytical solution of the diffusion equation to simulate U(VI) mobility in lab-scale through-diffusion experiments for various chemical conditions. Our results suggest that there are two important parameters that govern U(VI) diffusion in these systems. First, U(VI) surface complexation on clay edge surfaces leads to contaminant retardation. On the field scale, this will determine how early a plume may cross site boundaries and pose risks to drinking water resources. Second, the degree of access of U(VI) solution species to diffuse layers in clay interlayer spaces largely controls U(VI) diffusive fluxes. In the field, this parameter will govern the level of U(VI) concentrations that can be expected in contaminated waters.

Layered Double Hydroxide Nanoclusters toward Correlative Imaging in Biomedical Applications

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Modern biological research and diagnosis increasingly relies on bio-imaging as a primary source of information in unraveling the cellular and molecular mechanisms of life.[1] Especially, X-ray micro computed tomography (μ-CT) is highly demanded because it can provide detailed pictures of physical microstructure and produce 3D images of a material's internal structures, such as internal organ, bones, soft tissue and blood vessels with a high resolution.[2] Over the past decade, gold or silica nanoparticles as well as organic molecules and polymers have been examined as contrast agent for μ-CT scanning.[3] On the other hand, there still remain some critical disadvantages on using these particles, such as large particle sizes (50-100 nm), low colloidal stability, complexity of synthesis, and high cost.

We here focus on the use of layered double hydroxide (LDH) as a contrasting agent for X-ray μ-CT. LDHs take various combinations of ubiquitous metals and anionic species, and thereby, allowing one to tune their interaction with X-ray. Moreover, simultaneous achievement of bio-imaging and therapeutic treatment (nanotheranostics) would become possible by using LDH-based materials as inorganic carriers for drug delivery. However, LDHs are typically form an aggregate of crystal platelets with a size of tens nm to μm, and not homogeneously-dispersble in solvents and/or homogeneously-solidified at a level required for high-resolution X-ray μ-CT imaging.

In this study, we demonstrate the synthesis of LDH nanoclusters (NC)[4] with controllable dispersibility in media, tunable gelation, and advanced applications in bio-imaging. Special attention will be paid on the development of a novel strategy for imaging of blood vessels without a current complicated process (maceration of organs to be imaged). The results of X-ray μ-CT imaging and radiography confirmed that LDH NC can give a relatively higher contrast compared to commercialized polymer-based ones, without degrading the resolution of image.

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Pseudomorphic Replication of Nano-sized Amorphous Aluminum Hydroxide into LiAl Layered Double Hydroxide

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Layered double hydroxides (LDHs) are a family of lamellar compounds with a general formula of $[M_{1-x}^{z+}M_x^{3+}(OH)_2]^{a+}[A^{n-}]_{a/n}\cdot mH_2O$, where M^{z+} and M^{3+} are cations, and A^{n-} is a charge compensating anion. As well as the chemical tuning, structuration has been employed to optimize and enhance inherent characteristics of LDHs.[1] Among the strategies for the structuration, topochemical conversion of lamellar host materials into LDHs is a promising approach to yield pure LDHs with well-defined morphologies.[2,3] To this end, a key issue is the preparation of crystalline aluminum hydroxide with a controllable morphology. On the other hand, crystalline aluminum hydroxide with a predesigned structure is hard to prepare especially when its size is in nanometer size scale. Developing a pathway to prepare nano precursory hydroxides and transcribe them into LDH via a pseudomorphic manner is highly demanded.

We here demonstrate the fabrication of hierarchically porous pure Li-Al LDH though a pseudomorphic replication from a hierarchically porous monolith composed of amorphous aluminum hydroxide nanoparticles. The highly soluble amorphous nanoparticles reacted with LiOH aq with a diffusion limited manner, allowing the pseudomorphic replication into Li/Al LDH. As well as the hierarchically porous monolith, aqueous suspension of Li/Al LDH nanocrystals was successfully obtained through the same replication strategy from corresponding suspension of aluminium hydroxide. These replicated Li/Al LDHs exhibited catalytic activity toward a transesterification of soybean oil, confirming considerable surface basicity derived from high specific surface area and intrinsic LDH nature. The discussion will be mainly dedicated to the mechanism of LDH crystallization thorough the replication process.

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Layered Double Hydroxides for energy applications

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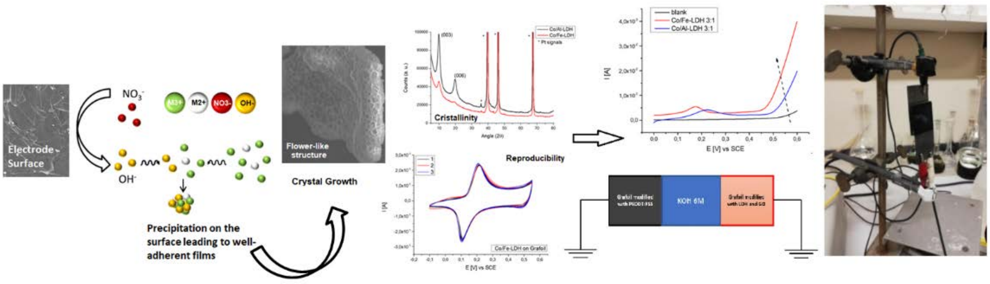
Layered double hydroxides (LDHs) containing redox active transition metals are attracting much interest in the area of electrochemistry for applications such as batteries, supercapacitors, sensors, fuel cells and as efficient electrocatalysts for oxygen evolution reaction (OER). For all these applications a fundamental property is that the active material must be well adherent to the conductive support, thus guarantying the formation of a mechanically stable coating. LDHs containing Ni or Co as bivalent and Al or Fe as trivalent cations have been electrosynthesized by a recently proposed electrosynthetic protocol that allows the deposition of thin films of on different supports. The approach is based on a potentiodynamic cathodic reduction which ensures an optimal reproducibility and mechanical stability of the coating [1]. All the LDHs films have been characterized by a comprehensive combination of techniques and some of them were evaluated for the OER and others as pseudocapacitors. Cobalt based LDHs catalysts with iron and aluminum in different molar ratios ranging from 1:1 until 4:1 were tested for the oxygen evolution reaction on GC rotating disk electrodes. In all cases studied, an optimal Fe and Al content was highlighted. Moreover, the performances as electrocatalysts were also evaluated on an unconventional stationary system based on a graphite sheet. The system resulted highly reproducible and displayed a very good performance in the stability tests performed in a cell with a potential of approximately 0.5 V vs SCE, at 10 mA cm^{-2} in 1M NaOH for at least 24 h. Nickel based LDHs have been electrosynthesized in the presence of graphene oxide to increase the double-layer capacitance with the aim to produce a material with good pseudocapacitive characteristics to be used as positive electrode of an asymmetric supercapacitor. A PEDOT:PSS was chosen as negative electrode. The performances of the first developed devices can be considered interesting.



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Assessment of reduced environmental impact of novel clay-based herbicide formulations through saturated and unsaturated column tests and volatilization quantification

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This abstract has to be considered confidential before publication of the book of abstracts (a patent application is currently being prepared on the reported content)

Dicamba is a moderately volatile and highly soluble herbicide. The high volatility causes active ingredient losses and possible damage on neighboring crops to those treated. In water, the high mobility can lead to a wide herbicide spread both in surface water bodies and in groundwater. To overcome these issues, a novel herbicide formulation was developed to minimize the potential environmental impacts of Dicamba, based on the use of natural and low components (namely, clays and biodegradable biopolymers). Dicamba was adsorbed on montmorillonite K10 with different procedures, without any chemical pre-modification of the clay surface. Some formulations were coated with biodegradable carboxymethylcellulose CMC to increase suspension stability and reduce active substance release. In this study the environmental impact of these formulations was investigated through both unsaturated and saturated column tests. Column tests were performed injection the novel formulations in sand-packed columns, mimicking the herbicide transport in the subsoil (unsaturated columns are representative of top soil and unsaturated zone, saturated columns are representative of aquifer systems, thus of the long-term behavior of the herbicide). The experimental protocol included pre-flushing with NaCl solution (e.g. 30 mM), particles injection at the same ionic strength, and a final flushing with particle-free solution. In selected unsaturated transport tests, flushing due to repent flooding (eg. extreme rain events or crop watering) was also applied. Ionic strength has been selected similar to that of water used during the herbicide application on crops. Moreover, the maximum value of ionic strength was chosen respecting Na^+ and Cl^- ions tolerance limits of treated cultures.

The results obtained in saturated conditions were modelled with MNMs software (https://areeweb.polito.it/ricerca/groundwater/software/mnms/) and those in unsaturated conditions with Hydrus 1D, in order to better elucidate and quantify the main phenomena controlling colloidal transport in porous media (attachment, detachment, straining, ripening etc..).

All the tests with the novel herbicide formulations were compared to same protocol tests with both the pure active substance and a commercial Dicamba-based product to assess the effective reduction on mobility in environmental matrix.

Modeling diffusion processes in the presence of a diffuse layer at charged mineral surfaces. A benchmark exercise.

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The electrostatic properties of clay mineral surfaces play a large role in their diffusion properties. The negative electrostatic potential field at the clay mineral surfaces results in the presence of a diffuse layer whose charge balances the mineral surface charge. The diffusion properties of the porosity fraction that is affected by this phenomenon are different from the diffusion properties of electroneutral bulk water. These properties have attracted growing interest from diverse communities in the past years, especially in the field of study of radioactive waste disposal. The influence of the diffuse layer can be described at the continuum scale by a set of equations that are formulated in terms of the Nernst-Planck equation. The number of codes that can handle the coupling between transport properties in clay affected by the presence of a diffuse layer in the porosity and chemical reactions is very limited, and no benchmark exercises have been published yet that makes it possible to validate the numerical implementation of these equations in reactive transport codes. The present study proposes a set of benchmark exercises of increasing complexity that highlight caveats related to the finite difference (volume) treatment of the Nernst-Planck equation in the presence of a diffuse layer in heterogeneous systems. Once these problems are identified and solved, the codes PHREEQC, CrunchClay, and Fortran routines written for this study gave results in very good agreement for most of the benchmark exercises. When present, the differences in results were directly traceable to the differences in averaging methods at grid cell boundaries, and to the consideration or not of the activity gradient term in the Nernst-Planck equation.

RNA-exchanged montmorillonite complexes in prebiotic chemistry

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Prebiotic chemistry is focused on the molecules that are interesting to explain the emergence of life on the primitive Earth [1]. The RNA molecule has a key role for contemporary biology, mainly with regard to the most fundamental and highly conserved cellular processes. RNA is useful of conducting all of the reactions of protein enzymes synthesis and DNA replication [2]. The interaction of nucleic acid molecules with the clay minerals can help to understand the biochemical mechanisms of these molecules in the soil ecosystem and their role in prebiotic chemistry.

The montmorillonite is a particularly good mineral to activate some chemical reaction and to preserve molecules has DNA and RNA. A key question is to understand the nature of the interaction of RNA with clay minerals [3]. This study investigated the nature of the interactions at molecular level between a ribonucleic acid and the surface of exchanged montmorillonites. Sodium montmorillonite reacted firstly with metallic salts aqueous solution ($MgCl_2.6H_2O$), ($Ca(C_2H_3O_2)_2$) and to obtain the divalent cations exchanged forms. After, samples reacted with RNA (1 mg mL^{-1}) in aqueous solution for 16 h under stirring in controlled pH. Results showed that the formation of the RNA-clay complex was totally pH dependent. The RNA molecules were highly intercalated in the interlayer spacing possibly by electrostatic interactions and hydrogen bonds. Furthermore, the binding mechanism depended of the structure of the organic molecule, solubility and its pKa value [4]. The presence of different cations such as Na^+, Ca^{2+} and Mg^{2+} strongly influences the amount of organic molecules adsorbed. The results indicated that metallic cations took part directly in the formation of bridges between the negative charges on the mineral surface and the phosphate groups of the biopolymer.

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Iridiscent Cellulose-Clay Nano Structures

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Solid films prepared from cellulose nano crystals (CNCs) present iridescence and selective reflection of left circularly polarized (LCP) light [1,2], while nano clay particles organize as lamellar structures in the solid state. It is well known that aqueous suspensions of sodium fluorohectorite (NaFh) clay biaxial platelets can form a nematic uniaxial liquid crystalline phase [3].

In this work we dissolved different quantities of cellulose nanorods in the clay nematic liquid crystalline suspensions (cellulose-NaFh nanocrystals (CNC/NaFh)). In order to preserve the photonic characteristics of the clay/nano rods suspensions solid films were prepared. We demonstrate that not only iridescent films can be produced but also their selective reflection of LCP light channel induced.

For lower concentration of CNCs the films became slightly iridescent with no selective reflection on the left circularly polarized light channel. The colors reflected by the films can vary from blue to red depending on the amount of CNCs added to the system.

The precursor suspensions and the solid films were investigated by using different techniques as scanning electron microscopy (SEM), atomic force microscopy (AFM) and polarizing optical microscopy (POM).

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Modification of bentonite with mixed cationic-nonionic surfactants

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In the present study, we investigated the influence of the cationic-nonionic surfactant co-adsorption onto properties of bentonite. Modification of clay minerals with cationic surfactants is well-known and widely described, however, information concerning the behaviors of cationic-nonionic surfactant mixtures on bentonite is limited. Nonionic surfactants are less toxic and more environmental-friendly, thus their application in sorbents preparation should be evaluated.

Two surfactants were used for modification of bentonite: Triton X100 (TX100) and hexadecyltrimethylammonium bromide (HDTMA). Bentonite was modified in two stages. The first stage includes HDTMA modification in the amount equal of a 1.0 CEC of bentonite (46 mmol/100 g – 6 h; 60°C) and the second stage involves TX100 modification in different concentrations (0.25-160 mmol/100 g – 24h; 60°C). The effectiveness of modification was evaluated by UV-Vis spectrophotometry and elemental analysis. The properties of obtained materials were studied by X-ray diffraction (XRD) and differential thermal analysis (TG–DTG/DTA).

XRD results show that the main peak (001) from montmorillonite was observed to shift slightly towards higher interlayer distances. This indicates an increase in the montmorillonite interlayer spaces due to intercalation of surfactant molecules. TG–DTG/DTA results for organo-bentonite showed differences compared to the raw bentonite. The first two endothermic peaks (dehydration and elimination of weakly adsorbed surfactant molecules at temperatures below 200°C) are weaker than those in the untreated bentonite. Some water molecules were replaced by surfactants yielded the clay surface more hydrophobic. The mass loss between 200 and 450°C was caused by the combustion of organic materials. Elemental analysis results prove that it is possible to attach about 30-35 mmolof TX100 per 100 g of bentonite previously modified with HDTMA. The pre-adsorbed HDTMA molecules attached to the bentonite surface acted as anchors for the nonionic surfactant. The mixtures of different ionic types of surfactants exhibit different properties compared with the corresponding single surfactants[1]. Generally, a mixture of nonionic and ionic surfactants increases the stability of the bulk solution or the size of the mixed micelles.

In conclusion, this work demonstrates the changes in bentonite due to adsorption of the mixed surfactants. Intercalation of mixed cationic-nonionic surfactants increases the structural and thermal stability of the system. The results achieved by this study can contribute to the further exploration of the utilization of nonionic surfactants in clay and clay mineral modification.

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The relation of weathering of granitoides and soil organic matter formation in the alpine terrain depending on altitude, The High Tatras, Slovakia

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The aim of this study is to determine the development of weathering in the alpine terrain depending on altitude. The basic physical and chemical properties of soil, mineralogy of soil and clay fraction and $\delta^{13}C$ of organic matter were determined for that purpose. The study of mineral composition (XRD analysis) was also performed with the aim to track source areas for mountain lakes (tarns) sediments (Veľké Hincovo pleso, 1946 m a.s.l and Popradské pleso, 1494 m a.s.l). The contribution belongs to complex paleolimnological study of High Tatras tarns with aim to determine a timing of the glacier disappearance and amplitude of climatic and ecological changes on the glacial/interglacial boundary (http://www.geo.sav.sk/en/depovyt-apvv-15-0292/).

The samples were collected along the altitudinal gradient from 1540 to 2350 m a.s.l that includes four altitudinal zones: supramontane zone with tree line at 1550 m a.s.l (one sample), subalpine zone with dwarf pine (*Pinus mugo*; two samples); alpine zone with rocky terrain and alpine meadows without trees (one sample) and subnival zone with rocky terrain and occasional snow also during the summer months (one sample). The bedrocks of studied areas are biotite-muscovite granodiorites to granites and biotite tonalite to granodiorites and glacier sediments derived from mentioned rocks (Nemčok et al., 1993). The soils the studied profile were dominated by undeveloped leptosols (rankers) and partly by podzol (determined base on FAO, 2014). The similar soil groups were defined by Kopáček et al, (2006). The initial stages of soil development are caused by their young age, the glacier retreat are predicted about 10000 cal BP and by alpine climate.

This work was supported by the grant APVV-15-0292.

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Illite – indicator of hydrothermal alteration conditions in a shallow-dipping epithermal precious and base metal deposit Banská Hodruša, Slovakia

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The intermediate-sulphidation precious and base metal deposit Banská Hodruša at the Rozália mine is hosted by the central zone of a Miocene andesite Štiavnica stratovolcano, located in the Central Slovakia Volcanic Field on the inner side of the Carpathian arc. The major distinct feature of the deposit is a complex multi-stage vein system with a subhorizontal orientation. Based on the obtained mineral composition of altered rocks, schematically it was possible to define five major types of alteration that occur within the deposit and its vicinity: silicification, strong and weak adularisation, strong argillisation and propylitisation. The K-feldspars and illite are major alteration products at the deposit.

The significant presence of illite has been used for determination of temperature conditions and character of fluid that formed wall-rock alterations, as well as age of illite formation. XRD analyses of clay fraction were used to determine illite polytypes and illite crystallinity - the "Kubler index" (KI). Samples from different parts of the mine showed the presence of each of $1M_d$, 1M and $2M_1$ polytypes and variable ratios of all polytypes with a slight prevalence of 2M. KI was used for the calculation of crystallisation temperatures using the data from the recent geothermal area in Taupo, New Zealand (Ji & Browne, 2000). At least 50 measurements of KI were applied. From these samples three illite-rich samples were selected for a detail study. Two of them associated with subhorizontal vein system (292 °C; 275 °C) and one related to earlier base metal stockwork mineralization that occurs close to the studied deposit (246 °C). K-Ar dating of all three samples provided ages between 12.23 and 12.67±0.35 Ma. The very similar illite ages probably show partial resetting of ages by a later hydrothermal system. The shape of illite particles was also similar and their size varied from 100 to 0.2 mm based on SEM data. However, proportion of the fraction 2 - 0.2 mm showed an, increase with crystallization temperatures. Preliminary thermal analyses indicate a potential dependence of illite dehydroxylation on crystallization temperatures. Stable isotope analyses of illites (δD and $\delta^{18}O$) indicate isotopically well homogenised fluid of magmatic-meteoric source, where the mixing took place outside of the deposit during the ascent of magmatic fluids from a deep magma chamber.

This work was supported by the grant APVV-15-0083 and the company Slovenská banská, s,r.o.

Application of electrospray spreading to organo-clay hybrid film preparation by a modified Langmuir–Blodgett technique

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A clay mineral, montmorillonite, is exfoliated into discrete clay mineral layers (denoted as clay nanosheets) bearing negative charges in aqueous dispersions at low concentrations. When amphiphilic cations are spread on a surface of a clay mineral dispersion, clay nanosheets adsorb onto a floating film of the amphiphilic cations, forming a hybrid film. In conventional procedures, a solution of an amphiphilic cation (salt) is spread on a clay mineral dispersion by manual operation. In this work, we instead applied an electrospray (ES) spreading method (Figure 1).

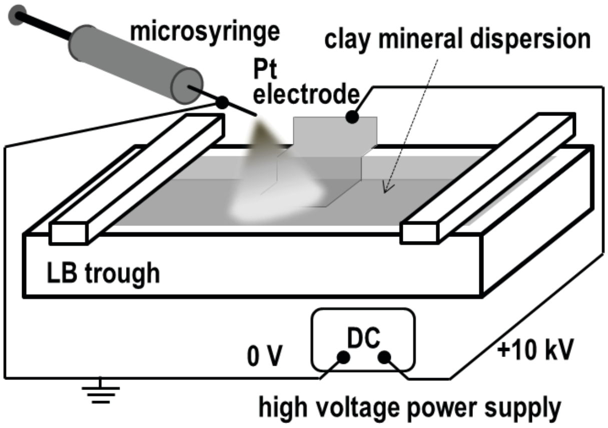

Figure 1. Experimemtal setup for electrospray spreading to a clay mineral disperison surface.

A chloroform solution of octadecylammonium chloride ($ODAH^+Cl^-$) was spread on clay mineral dispersions by ES method at different infusion rates. The surface pressure-molecular area (p-A) isotherm curves of the films exhibited unusual dependence on the infusion rates; the curves shifted to a larger molecular area side with the increase in infusion rate (from 0.5 to 2 mL min^{-1}), while they shifted back to the smaller area side with the further increase in infusion rate (from 2 to 100 mL min^{-1}). The following formation mechanism was proposed. When the $ODAH^+Cl^-$ solution was electro-sprayed, the solution drops of various sizes fell on the dispersion, depending on the infusion rate. In the case of low infusion rates, the solution drops were so fine that some evaporated before they arrived at the interface. Under these conditions, the hybrid film contained $ODAH^+Cl^-$ salt particles. In the case of high infusion rates, the large solution drops hit violently the dispersion surface, affording a hybrid film including double- and higher-layered domains.

Properties of clay-rich fine-grained sedimentary rocks from large scale molecular dynamics simulations

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Fine-grained sedimentary rocks play an important role in a wide variety of modern energy technologies: from petroleum geology; geological carbon sequestration; to radioactive waste management. Yet, despite their utility and ubiquity, many of their properties remain poorly understood. In particular, the ability to predict the permeability of such fine-grained sedimentary rocks remains one of the largest fundamental challenges in the geosciences with potentially transformative implications.

In the present work, we show how large-scale classical molecular dynamics simulations can be used to help interpret the phenomenon of nanoscale diffusion within fine-grained sedimentary material. All-atom simulations containing multiple discrete clay particles are utilized to understand the roles of dry bulk density (porosity) and pore water chemistry (charge-balancing cation and pore water salt composition) on the microstructural, mechanical and transport properties of the overlying clay matrix. Special emphasis is placed on comparing our results with the available experimental data.

Microstructural properties (pore size distribution, tortuosity, anisotropy), mechanical properties (viscosity) and transport properties (diffusion coefficients of water and ions, electrical conductivity, dielectric relaxation and hydraulic permeability) are all calculated and compared to experiment. The anion exclusion between the clay particles is calculated and compared against both experimental data and several theoretical models.

Salinity-driven wettability alterations on clay minerals surfaces:

a molecular dynamics study

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The interfacial properties of the mineral-water interface play an important role in many emerging energy related technologies. In particular, low-salinity enhanced oil recovery (EOR), a technique whereby sea water, partially desalinated, is used to push increasing amounts of crude oil from existing, and future, oil reservoirs, increasing the reservoir lifetime and overall production; is particularly susceptible to salinity-driven wettability alterations [1, 2].

In the present work, we show how a complex three-phase (oil-brine-clay) system can be understood on the basis of simpler two-phase simulations. Using Young's equation, we decouple the three-phase problem into three separate two-phase problems. We show how one can calculate and understand the phenomenon of interfacial tension through MD simulations, and we validate a variety of force-fields based upon their accuracy to reproduce experimental surface tension values. Further, we calculate contact angles between various clay minerals and brines/oils and compare simulated trends to the available experimental data [3].

The presented results highlight how we can understand wettability alteration at the molecular level, and ultimately demonstrate the roles that salinity and ionic composition play in driving wettability alterations at the molecular level.

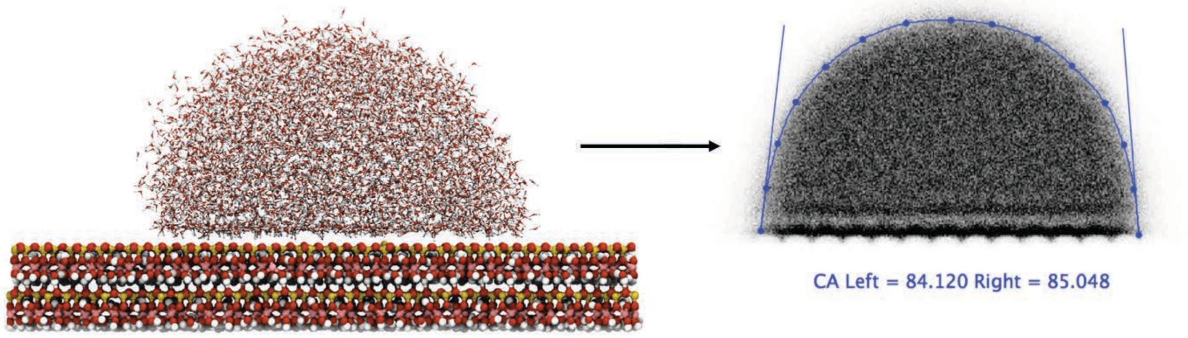

Figure 17: Snapshot of a water droplet simulation on the siloxane surface of kaolinite (left), and the post-production droplet analysis of the corresponding contact-angle (right).

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Rb–Sr dating of fault gouges

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Authigenic syn-kinematic illitic clay minerals in fault gouge offer a useful means of constraining the absolute timing of fault reactivation. Illite K–Ar and Ar–Ar dating techniques have been routinely used for this purpose, while utilisation of Rb–Sr isotopic dating is rare. This largely arises from difficulty obtaining knowledge of the initial ^{87}Sr/^{86}Sr ratio during illite crystallisation. Co-genetic illitic clay separates can precipitate in micro-scale closed systems with different initial Sr isotopic composition. In additions, clay minerals contain non-radiogenic Sr that may not be in isotopic equilibrium with illite. Thus, the ages calculated for each individual illite sample cannot represent the true crystallisation age if the initial ^{87}Sr/^{86}Sr is erroneously assumed. However, reliable Rb–Sr ages can be obtained through an internal isochron based on data from acid leachates, acid-leached and untreated aliquots of different illitic clay size fractions.

In this contribution, examples of fault gouge illite dating using the Rb–Sr technique is compared to K–Ar (Ar–Ar) methods. Fault gouge illites from major fault systems in Turkey, Australia and China mostly yield consistent Rb–Sr, K–Ar and Ar–Ar ages. However, both younger and older K–Ar and Ar–Ar ages were obtained for some tectonic settings, which can be attributed to the loss and excess of ^{40}Ar, respectively. The former can be explained by the shear deformation causing dislocations in illite crystals and hence fast-diffusion pathways impacting the Ar-retentivity even at temperatures below the closure temperature of Ar diffusion for pristine crystals of a given size (Zwingmann et al., 2019). Deformation–induced cracks and dislocations can also serve as channels to facilitate the introduction of excess ^{40}Ar into the mineral grains (Lee, 1995). Combining Rb–Sr and K–Ar (Ar–Ar) dating techniques minimises the disadvantages of each isotopic system and achieves more reliable age constraints for crustal faulting. In addition, the gain or loss of ^{40}Ar results from specific geological conditions controlling the thermal state, and the availability, transport, and chemistry of the fluid. Hence, combining K-Ar and Rb–Sr dating results adds further information to the understanding of faulting-related thermal and fluid flow history in sedimentary basins.

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Smectite-supported nano zero valent iron for efficient removal of toxic arsenic from water

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The remediation of inorganic arsenic (As) such as As^{III} (arsenite), and As^{V} (arsenate) from contaminated water has become an urgent issue as prolonged exposure of it can cause detrimental effects to human health including cancer. Consequently, for the decontamination of inorganic As, researchers exceedingly looked for high-performance and environmentally friendly adsorbents, which do not pose additional risk to the environment. Since iron-based materials have high affinities to both form of inorganic As, they are extensively used for their removal from water. In this investigation, a smectite (Western Australian bentonite)-supported nano zero valent iron (nZVI) composite has been synthesized for As^{V} adsorption. This Smec-nZVI composite material was characterized for its structural, chemical and physical properties through a number of techniques such as X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersion X-ray (EDS), Brunauer-Emmett-Teller (BET) surface area. The specific surface area of Smec-nZVI composite was found greater than only raw smectite or nZVI indicating a lower aggregation of iron nanoparticles. SEM (Figure 1) and TEM images of the composite reflect that smectite template is surrounded by "necklace" type of chain of iron beads which is quite exceptional, while EDS mapping ensured the fairly even distribution of such beads on clay. XRD results proved that elemental iron were grafted on smectite template. Furthermore, this novel composite showed a capacity of As^{V} adsorption significantly higher than that of raw smectite and nZVI with a q_m of 33.30 mg g^{-1}, which demonstrates that it can be an efficient agent to remove carcinogen As^{V} from contaminated water.

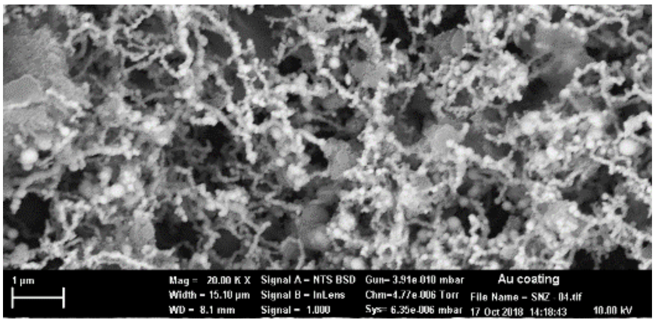

Figure 1: SEM image of chain like nZVI on smectite template

K-Ar geochronology of illite bearing clays using multicollector noble gas mass spectrometry and full major element characterization on particle size fractions generated by continuous flow centrifugation

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One of the major challenges for extracting the age of illite growth in fault gouges is resolving the frequently complex patterns of inheritance from the host rock. Of major consequence to K-Ar geochronology are K- rich phases such as muscovite and feldspar, which may be authigenic or isotopically reset in faults if these formed at high temperature (e.g. Ksienzyk et al., this conference), but more commonly appear to be inherited. An additional complication arising in fault gouges hosted in feldspar rich rocks, is that they frequently contain authigenic kaolinite, which is an obstacle to accurate XRD quantification of the different illite polytypes. It is empirically observed that these potential contaminants are depleted in particle size fractions with decreasing Stokes diameter, and the centrifugation of clay suspensions to generate particle size bins, thus fractionating illite from other minerals, is a widely adopted sample preparation procedure.

The Geological Survey of Norway has over the past few years built up a full featured laboratory and gathered expertise for the sample preparation, K-Ar geochronology and mineralogical characterization of illite and other clay minerals. The facilities include continuous flow and fixed angle rotor centrifuges, a particle size analyzer, an XRD spectrometer, a noble gas laboratory, and ICP-OES and ICP-MS instruments.

We present equations for clay centrifugation using a commercially available continuous flow centrifuge, which can be used to generate particle sizes as fine as <0.03 µm. We show that particle size data confirms the relative accuracy of the assumptions behind the equations, and that generated particle size fractions are typically clean from coarser contaminants.

Furthermore, we present K-Ar data acquired using a multicollector noble gas mass spectrometer and show that it is theoretically possible to resolve K-Ar ages down to the Holocene provided that suitable sample material can be collected. We show that concurrently with K measurement using ICP-OES, we can obtain a full range of major and several trace elements on clay aliquots <50 mg, which can be used for mass balance calculations to support XRD quantification.

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Colloidal liquid crystals of sepiolite in oil thanks to polar activators and dispersants

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Sepiolite is a natural clay mineral consisting of rod-like particles (here samples supplied by Tolsa in Spain are used). Imaging individual particles using AFM suggests they can be described as cuboidal, with a square cross section of about 25 nm and a length of around 1 μm.

Treatment with quaternary ammonium surfactants results in organoclays that are used commercially as thickeners for non-aqueous systems (here toluene is used as the solvent). Addition of organoclay produces gels, which in our work are converted to fluid dispersions by a further addition of polymeric stabilizer [1]. Alternatively, organoclays were made from unmodified clay, using benzyldodecyldimethylammonium bromide.

The stability of non-aqueous colloidal suspensions can be affected by moisture. Here however, we find that atmospheric humidity is helpful to make good dispersions; the organoclays may adsorb up to 13% by weight in water. Alternatively, a non-volatile polar activator such as propylene carbonate can be used [2].

Once well-stabilised particles were made, their liquid crystalline phase behaviour was studied. These particles spontaneously align into a nematic phase, as predicted already in the 1940s by Onsager [3]. However the polydispersity of these particles leads to a very marked broadening of the phase transition (expressed as the ratio of concentrations of coexisting isotropic and nematic phases) [4]. The ratio is 0.8 in the monodisperse case, but for our sepiolite suspensions can be as low as 0.1, in agreement with theoretical predictions for hard rod-like particles.

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Influence of Mn(II) on the sorption of Cd(II) to clay minerals

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Redox variable environments like riparian floodplain soils, wetlands, and rice paddies are important in the mobilization of trace elements from terrestrial environments into aquatic systems. Water-saturation of terrestrial environments has been shown to cause elevated dissolved concentrations of Mn^{2+} as a result of reductive dissolution of Mn(IV,III)-(oxyhydr)oxides. High concentrations of Mn^{2+} are expected to trigger a mobilization of trace elements (e.g., Zn^{2+} and Cd^{2+}) due to competition for cation adsorption to mineral surfaces.

Despite the ubiquity of Mn in terrestrial environments, only little is known about how and to what extent elevated Mn^{2+} concentrations affect trace metal mobility during periods of water-saturation, i.e., under anoxic conditions. Since clay minerals are considered major sorbent phases for cations in anoxic environments, our objective was to investigate how Mn^{2+} influences Cd^{2+} sorption onto two clay minerals, kaolinite (KGa1-b) and smectite (Syn-1).

This was investigated by performing batch experiments of Cd^{2+} and Mn^{2+} sorption to the clay minerals separately under anoxic conditions (O_2 < 0.1 ppm). A wide range of conditions with respect to pH, total metal concentration and $CaCl_2$ background electrolyte concentration was covered experimentally in order to obtain a solid dataset for modelling single metal sorption to kaolinite and smectite. In addition, acid-base titrations were conducted at different $CaCl_2$ concentrations to determine the protonation behavior of the clays. A three plane model (TPM) was used to described the experimental data quantitatively. Herein, sorbing metal cations were exclusively placed into the 1-plane at the face surfaces to form outer-sphere complexes but charge distribution between the 0-plane and 1-plane was allowed for metal cations at the edge surfaces. The competitive effect of Mn^{2+} on Cd^{2+} sorption was predicted.

Our experiments revealed that Mn^{2+} and Cd^{2+} sorption exhibited a similar sorption behavior. Sorbed amounts increased with increasing pH due to proton-metal cation competition. An increase in $CaCl_2$ concentration was observed to decrease both Mn^{2+} and Cd^{2+} sorption at pH below 7, but affected Cd^{2+} sorption more strongly. For the best description of the entire dataset, charge distribution had to be allowed for Ca^{2+} at the edge surfaces in addition to Mn^{2+} and Cd^{2+}. Based on the model parameters optimized to acid-base titration and single metal cation sorption data, strongly elevated Mn^{2+} concentrations as observed in anoxic environments were predicted to significantly decrease Cd^{2+} sorption to the clays. Experimental data on competitive systems indicated that the competitive effect of Mn^{2+} on Cd^{2+} sorption was less pronounced than predicted. The results of this study and their environmental implications will be discussed.

Redox sensitive clay minerals: implications for fines migration and enhanced oil recovery

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In oil and gas exploration and production, the chemical and physical properties of reservoir clay minerals can have an effect on drilling operations, reservoir quality and oil recovery rates. Various methods have been used to optimize the recovery of oil from reservoirs, through technologies that are more economical, easier to apply and environmentally friendly, culminating in the development of low salinity water flooding (LSWF). LSWF is a chemical method whereby the concentration of cations, especially multivalent cations, in the injected water is carefully reduced and controlled. LSWF is used in secondary and tertiary enhanced oil recovery (EOR) operations.

Though LSWF has been proven to improve oil recovery, the exact mechanisms that give rise to this increase in oil are poorly constrained. Generally, it is accepted that a either a change in wettability of the reservoir rock-oil interface occurs, or fine particles with the oil attached are destabilised and migrate. Some of the prevailing theories identified in the literature include the change in the wettability of clay minerals (Sheng JJ 2014; Myint and Firoozababi 2015; Shalabe and Segehrooni 2016), expansion of the electric double layer (EDL) (Lighthelm et al.2009), fines migration (Tang and Morrow 1999; Zeinijahroni A. et al.2015) and multicomponent ion exchange (Lager et al.2009).

In this present study, we explore a new frontier in LSWF EOR research by examining the wettability and swelling capacity of reservoir clay minerals as a function of reduction potential (Eh). We investigate how changes in Eh and salinity during a LSWF impact on the cation exchange capacity, the exchangeable cation composition and the wettability of iron rich clay minerals. In further work, we will study how this in turn impacts the swelling of the clay minerals, surface adhesion changes and, ultimately, the migration of fines.

Following the mineralogy studies, core floods will be undertaken and the changes in iron mineral and oil production in the outflow water assessed. Data gained will be fed into models, incorporating parameters of the reservoir such as confining pressure and temperature gradient. By scaling up the geochemistry data and combining them with the P, T conditions of the reservoir, we are going to create a tool for better constraining reservoir suitability for LSWF applications that could potentially set the basis for optimizing the operations.

Characterization of titania nanoparticles in mesoporous silica

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The immobilization of the titania (TiO_2) particles with clay/clay minerals and porous silicas (MPS, SBA-15) have been investigated extensively for various applications including photocatalysis. [1,2] The porous hosts play a role as a template to control the morphology (size and shape) of titania particles, whereas the morphology of the TiO_2 nanoparticle as well as their location and spatial distribution in/on MPSs are important for the performance of the resulting hybrids through the selectivity, the adsorption/diffusion of the reactants and the desorption of the products. However, these characteristics have not been precisely controlled and characterized. The ideal concept of this work is schematically shown in Figure. 1. This paper presents a novel approach in characterization of TiO_2 nanoparticles in mesoporous silica by combining different analytical techniques.

Titania nanoparticles were immobilized preferentially into the pore of a mesoporous silica, SBA-15, by the impregnation of tetraisopropyl orthotitanate.[3] The size of TiO_2 particles was controlled to be 8 and 3 nm by varying the titania loading, which was achieved by diluting tetraisopropyl orthotitanate with isopropanol. The size of TiO_2 particles was derived from XRD, and UV-Vis. absorption spectra. The distribution of the titania particles on the external surface of SBA-15 particles was confirmed by SEM and zeta potential measurement. The remaining porosity of the SBA-15-titania hybrids was characterized by N_2 adsorption/desorption isotherms and was correlated with the titania content to confirm the location of the titania in the pore. The morphology and the distribution of the TiO_2 nanoparticles in the pore were investigated by TEM.

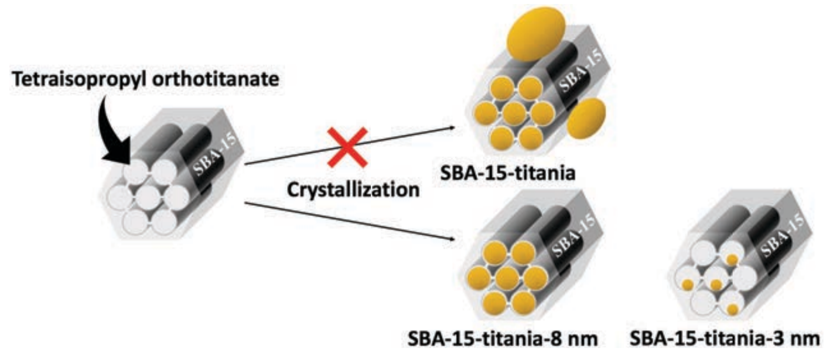

Figure 1. Schematic drawing of the morphology and the location of the titania particles in/on a mesoporous silica, SBA-15.

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Photocatalytic removal of 1,2,4-trichlorobenzene by montmorillonite-TiO_2 nanocomposites

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The use of sunlight for pollutant removal in water arouses great interest. Emerging contaminants have increased in recent years in effluents from treatment plants. In this work, new materials based on montmorillonite-TiO_2 nanocomposites are presented, comparing their photocatalytic properties in the degradation of 1,2,4-trichlorobenzene (TCB), a rather common pollutant detected in surface water.

The preparation process was carried out by adding at room temperature 2 mL of titanium isopropoxide to a dispersion of 2 g of clay in 200 mL of water, and keeping the samples under ultrasounds (sample MtTi1) or under magnetic stirring (sample MtTi2) for 24 h. The solids thus prepared were separated by centrifugation, washed with distilled water several times, dried in an oven at 70°C and calcined at 500° C. The fast formation of TiO_2 particles between the clay sheets and on its surface was expected.

Photolysis degraded up to 90% TCB after 150 min of treatment. To compare the effectiveness of the two catalysts and the natural clay, experiments have been performed in the darkness and under UV radiation. In the dark, removal by solid MtTi2 was around 10% after 90 minutes, while the solid MtTi1 immediately removed 35% of the TCB, this value remaining constant over time. In contrast, natural clay only removed 5% after 240 min. Under these conditions, it cannot be expected that the TCB will be degraded, so its removal may be due to an adsorption process (the TCB that was adsorbed on the solids disappeared from the solution and it was not detected when analyzed by UV-Vis spectroscopy). It is evident that the incorporation of Ti produces an increase in the removal activity, while the different behaviour between the two prepared solids was due to their different physicochemical properties and to the nature of the titanium species formed.

When UV radiation was applied, the removal percentage increased, reaching 40% with the natural clay after 210 min and more than 90% after 45 min when the solid MtTi1 was used, compared to approximately 80% for sample MtTi2, being higher for the sample synthesized by ultrasounds in the whole time interval considered. Logically, the process responsible for this elimination must be photodegradation.

Therefore, the catalyst prepared under ultrasounds showed a better performance than that prepared by the traditional method.

Acknowledgements: This work was funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (ERDF) through the project MAT2013-47811-C2-R.

Preparation of hydrocalumite from aluminium saline slags

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Aluminium is the second metal most used worldwide. Bauxite is the only mineral useful for its preparation, after purification by the Bayer process, and followed by molten electrolysis (Hall-Héroult process) with cryolite (Na_3AlF_6). The industrial process requires large amounts of energy, and generates high amounts of wastes. Production of aluminium from wastes and by-products is also widely developed, but it generates further wastes as saline slags. As saline slags are mainly composed of oxides, they can be used as inert filling in several fields. Aluminium oxide may be recovered from chemical treatments as a high-value-added product to be used for the preparation of other materials.[1-3]

Hydrocalumites are minerals from the LDH family, with general formula $Ca_2Al(OH)_6(anion)\bullet 2H_2O$ (particularly $Ca_2Al(OH)_6(OH,Cl)\bullet 2H_2O$). They are attractive as anion exchangers and basic Brønsted-type catalysts, among other potential uses. In this sense, we aim to recover aluminium from saline slags and to use it for the preparation of hydrocalumite.

Recovering of aluminium and preparation of hydrocalumite were approached by two methods. In the first one, both steps (extraction and formation of hydrocalumite) were carried out simultaneously by addition of various amounts of $Ca(OH)_2$ under reflux conditions for 6.5 h. Then, pH was decreased to 7.0 with HCl. In the second method, aluminium was first extracted by treatment with NaOH, under the same conditions reported before. Then, pH was decreased with HCl until turbidity was observed, and finally a calcium precursor (nitrate and chloride were tested) was added. A reference hydrocalumite was prepared using $Ca(NO_3)_2\bullet 4H_2O$ and $Al(NO_3)_3\bullet 9H_2O$.

Most of aluminium present in the saline slags was successfully extracted. Hydrocalumite was obtained in all the preparations, but it was always impurified with calcite. No other crystalline phases were observed. Nitrogen adsorption-desorption isotherms were of type II, typical from layered solids with slit-like pores. The specific surface area reached 40 m^2/g for the solid prepared by the second method, using calcium nitrate. SEM micrographs showed the loss of porosity when $CaCl_2$ was used as calcium precursor. Thus, aluminium was extracted from the saline slags and the solids obtained were all hydrocalumite-based materials, with good textural properties and potentially attractive as basic catalysts.

Acknowledgements: This work was funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (ERDF) through the project MAT2013-47811-C2-R.

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Searching for organic biosignatures on Mars: Experimental perspectives

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Upcoming exploration of Mars officially aims at identifying potential organic biosignatures in the subsurface. Despite the continuous UV irradiation of the surface, Mars subsurface has mostly acted as a giant freezer, thereby preserving potential remains of Martian life dating back from the Noachian (~4.1-3.7 Ga). Yet, volcanic events or crater-forming impacts generated hydrothermal systems, altering ancient rocks and their (possibly biogenic) organic content. It thus appears crucial to constrain the impact of hydrothermal processes on organic biogeochemical signals, especially in the presence of clay minerals which are targeted by the future rovers. Here, we submitted RNA (i.e., the most emblematic biogenic molecule) to hydrothermal conditions in the presence of Mg-smectites (i.e., a widespread clay mineral on Mars). Results show highly heterogeneous organo-mineral residues, with nano-phosphates and nano-carbonates associated to submicrometric amorphous silica particles and Mg-smectites with interlayer spaces saturated by N-rich organic compounds. Even though the chemical structure of RNA did not sustain hydrothermal conditions, the present study demonstrates that clay minerals can efficiently trap organic carbon under hydrothermal conditions typical of Martian subsurface, confirming the relevance of digging for organic carbon on Mars.

Changes in the exchangeable cation complex of montmorillonite during oedometer tests

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The effect of solution salinity on the swelling capacity of expansive materials, such as bentonite, has been known for long. It has usually been assessed by means of oedometer tests (swelling pressure, swelling capacity or consolidation tests) in which the concentration and predominant cation of the saturating solution are changed. These laboratory tests systematically show a decrease of the swelling capacity of the bentonite with the increase of salinity, which becomes less patent for high vertical loads and high bentonite densities. The extent of this decrease depends on the predominant cation in the solution and is more important for sodium than for calcium. These chemically-induced deformations are largely reversible. The explanations given to these observations usually resort to the effect of the solution salinity on the DDL thickness and to cation exchange processes. However, less attention has been paid to the latter, although the effect of the exchangeable cations on the swelling capacity is generally acknowledged.

With the aim of actually checking the changes that take place in the exchangeable cation complex in the oedometer, a series of swelling pressure and swelling capacity tests are being carried out. Two raw bentonites composed mainly of montmorillonite are being used: the FEBEX bentonite, which has predominantly divalent cations in the exchange complex (Ca^{2+} and Mg^{2+}) and the sodic MX-80 bentonite. Different concentration solutions of NaCl and $CaCl_2$ are being used to saturate the samples. The swelling pressure tests are performed at constant volume conditions, whereas the swelling capacity tests are performed under a low vertical load (0.1 MPa), which allows significant swelling of the sample. At the end of the oedometer tests the exchangeable cation complex of the samples is determined, as well as the basal spacing. Given the high salinitiy of the solutions used, care is taken to differentiate extractable from exchangeable cations. This way, the effect of cation type, solution concentration, bentonite density and deformation on the changes in the exchangeable cation complex occurred during oedometer testing can be checked.

These studies are considered to be of relevance for the assessment of the performance of the bentonite engineered barrier in nuclear waste repositories, in which the salinity of the groundwater can vary over time. However, the experimental evidence coming from dismantled large-scale tests (such as the FEBEX in situ test) indicates that, although the exchangeable cation complex is significantly modified during operation (particularly by the effect of heating), the swelling capacity of the bentonite remains macroscopically unchanged. This could indicate that the results of laboratory small-scale tests cannot be directly transferred to the real case, probably because of the boundary conditions differences.

Preparation of a Ni-Al-LDH Containing Intercalated Borate Counter Ions. Comparison of its Storage Capacity with Similar LDHs Containing other Counter Ions for Use as Cathode Materiel in Nickel Secondary Cells.

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Preparation of a nickel-aluminum layered double hydroxide containing borate charge compensating ions will be described and its electrochemical properties compared to similar LDHs containing carbonate, chloride or nitrate counter ions.

Addition of sodium tetraborate and NaOH to a mix solution of nickel and aluminum chloride gave a blue-green powder. Elemental analysis showed the powder contained an atomic ratio of boron to aluminum of 0.6, suggesting the presence of a mixture of triborate ($B_3O_3(OH)_5^{2-}$) and tetraborate ($B_4O_5(OH)_4^{2-}$) ions. The powder XRD pattern of the product showed a material with a much more ordered layered structure, with smaller d_{003} spacings, than typical found for borate intercalated LDHs (Figure 1). The basal spacing of 7.80 Å is consistent with the presence of a different triborate ions, ($B_3O_3(OH)_4^-$) lying flat in the gallery spaces.

Iodometry measurements after control potential oxidation of the LDHs showed the Ni(II) sites in the borate LDH could rapidly be oxidized to an average valence about 3.4+, compare to only about 2.5+ for the carbonate LDH. This deference is reflected in a greater storage capacity for the borate LDH when the two materials were tested as cathode materials for secondary cells. The discharge capacity of the borate LDH reached 235 mA·h/g compared less than 100 mA·h/g for the carbonate LDH (Figure 2). These values correspond to the transfer of approximately 1.2 and 0.5 electrons per nickel centers for the borate and carbonate LDHs, respectively.

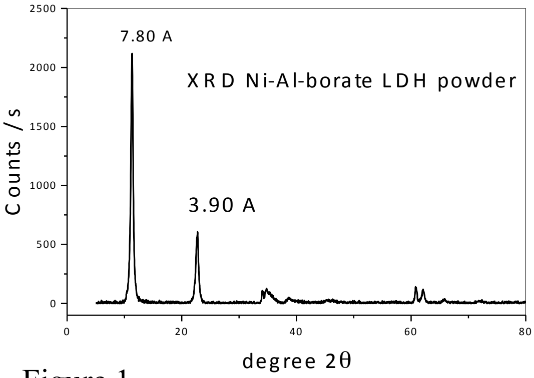

Figure 1

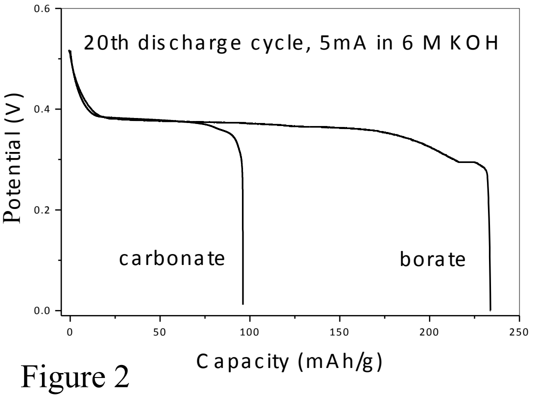

Figure 2

Influence of Layer Charge (Location and Amount) on the Hydration Properties of Synthetic Na-Saturated Smectites

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Smectite hydration controls dynamical properties of interlayer cations and thus the fate of H_2O and pollutants in surficial systems where smectite-based materials (bentonites) are often used as a major barrier component. Smectite hydration is in turn ruled by their crystal chemistry. In particular, the influence of parameters such as the amount of layer charge deficit has been described by Ferrage et al. (2010) and Dazas et al. (2015) for tetrahedrally charged trioctahedral smectites (saponites). On the other hand, the influence of the location of layer charge deficit remains incompletely documented. A set of octahedrally charged trioctahedral smectites (hectorites), with a common structural formula $^{inter}[Na_x,\ n\ H_2O]^{oct}[Mg_{6.0-x}Li_x]^{tet}[Si_{8.0}]O_{20}(OH)_4$ and a layer charge (x) varying from 0.8 to 1.6, was thus synthesized to assess the influence of layer charge position on smectite hydration and interlayer structure. Interlayer H_2O contents were measured as a function of relative humidity (RH) from H_2O vapor (de)sorption isotherms. The evolution in the proportions of mono- and bi-hydrated layers and the distribution of interlayer species were then determined from X-ray diffraction profile modeling as a function of RH. Finally, Monte Carlo simulations were performed in the grand canonical ensemble to get additional details on the distribution of H_2O molecules and charge-compensating cations within interlayers. The transitions between discrete hydration states occur at similar RH values for hectorite, independent of the amount of layer charge. When normalized to the number of interlayer cations, the number of interlayer H_2O molecules decreases with increasing layer charge, and the proportion of these H_2O molecules hydrating interlayer cations increases, as previously reported for saponites. Based on the comparison between octahedrally and tetrahedrally charged smectites (Ferrage et al., 2010; Dazas et al., 2015) with contrasting layer charge it is concluded that 1) the total amount of interlayer H_2O is about independent of layer charge amount and location; 2) the evolution of layer-to-layer distance with the amount of layer charge differs for saponite and hectorite as the result of contrasting electrostatic interactions between the 2:1 layer and interlayer cations; 3) contrary to saponite, the RH domains for the different hydrates in hectorite are not modified by the amount of layer charge.

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Ferrage E.; Lanson B.; Michot L.J.; Robert J.-L. (2010) J. Phys. Chem., C114, 4515−4526.

Hydration properties of synthetic Na-saturated stevensites

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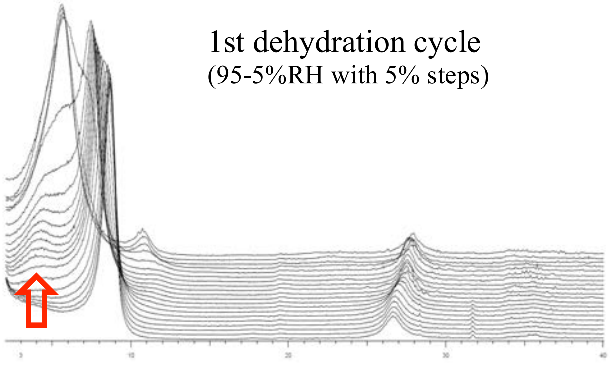
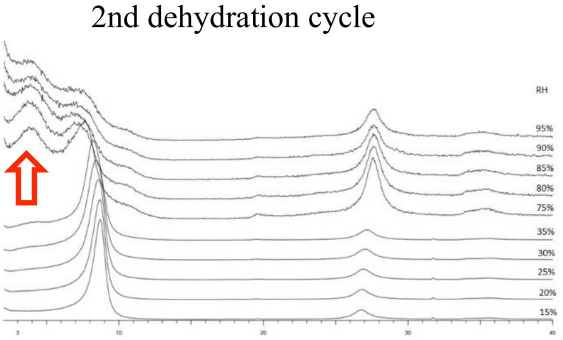
Smectites are 2:1 phyllosilicates with a layer structure consisting of an octahedral sheet sandwiched between two siliceous tetrahedral sheets. Both the occurrence of isomorphic substitutions in tetrahedral or in octahedral sheets and the presence of vacant sites in (tri)octahedral sheets induce a permanent negative layer charge, which is compensated for by the presence of exchangeable cations in smectite interlayers. Hydration properties of these interlayer cations can strongly impact dynamical properties of interlayer species and the transfer and fate of H_2O and pollutants but also smectite ability to produce a variety of nanocomposites for different applications. The influence of smectite crystal chemistry, and more especially of the amount and location of isomorphic substitutions, on smectite hydration has been largely documented over the last decade, using mostly synthetic trioctahedral smectites (saponites and hectorites – Ferrage et al., 2010; Dazas et al., 2015; Vinci et al., 2019). Hydration of stevensite, a trioctahedral smectite whose layer charge deficit arises from the presence of octahedral vacancies, has attracted much less attention although early studies reported a specific hydration behavior with the possible presence of super-reflection corresponding to the regular alternation of different hydrated states, including dehydrated layers (Brindley, 1955). The present study thus investigated the hydration behavior of two synthetic stevensites ($^{inter}[Na_{0.8}\cdot nH_2O]^{oct}[Mg_{5.2}o_{0.8}]^{tet}[Si_{8.0}]O_{20}(OH)_4$, $^{inter}[Na_{0.8}\cdot nH_2O]^{oct}[Zn_{5.2}o_{0.8}]^{tet}[Si_{8.0}]O_{20}(OH)_4$) using mainly X-ray diffraction. An environmental chamber allowing the control of relative humidity was used to determine the hydration behavior of both samples as a function of this parameter. Specific attention was paid to the possible presence and origin of previously reported super-reflections and to the possible irreversibility of stevensite layer dehydration.


1st dehydration cycle
(95-5%RH with 5% steps)


2nd dehydration cycle

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Alkali activation of gravel wash mud with KOH and NaOH

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Gravel Wash Mud (GWM) is widely available and considered suitable for geopolymer synthesis due to a high Si and Al concentration (Thapa et al., 2018). To analyze GWM as a potential geopolymer binder, it was thermally activated to form a metaclay and chemically activated by mixing with NaOH and KOH. The geopolymer cements were characterized by X-ray diffraction, scanning electron microscopy and compressive strength testing, in order to characterize the reactivity of the mostly illitic mud, the mineralogy and microstructure as well as the strength of the binder.

In general, samples calcined at 850°C reached the highest strength that increased with prolonged curing time and being the strongest after 56 days of curing. As a result of the alkali-activation process with NaOH, samples with short curing time of 14 days were moist and soft, which shows a poor alkaline dissolution and a low proportion of reactive material. In contrast the reaction with KOH was more rapid and the maximum strength was already obtained after 14 days curing time.

As 20-30% of bulk GWM was coarser than 20µm, a separation of the finer fraction (< 20µm) was done. By this the amount of quartz was distinctly reduced and clay mineral content was increased. Differences in strength between the clay-silt fraction (<20µm) and the bulk GWM were obvious. The strength of the fine GWM material was stronger by more than 3 times.

Thapa, V.B.; Waldmann, D.; Wagner, J.-F.; Lecomte, A. (**2018)** Applied Clay Science, 161, 110–118, Elsevier.

Row-indexing and its application in structural analysis for clay minerals

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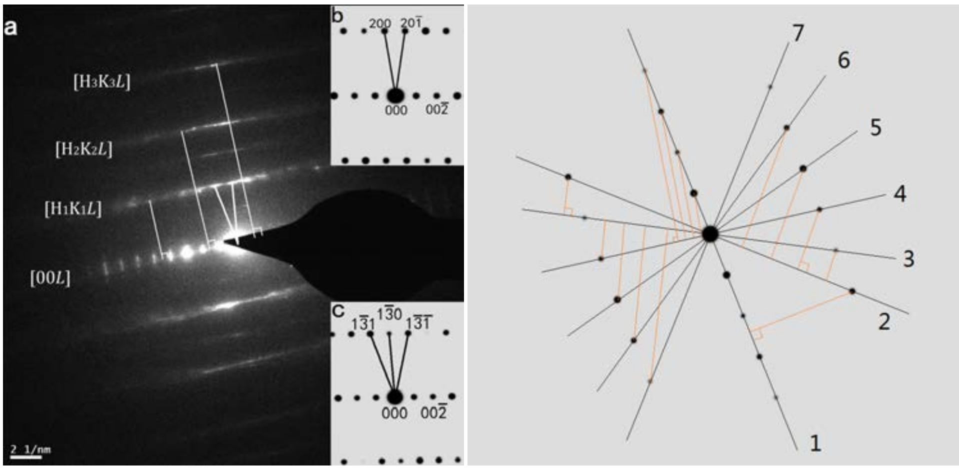
Clay minerals are very small in size (<2μm) mostly and aggregate together and are difficult to separate into single crystal. Although electron diffractometry is a powerful tool for determining clay mineral structure and microstructures, however, there are many factors that cause “defective electron diffraction patterns” which generate difficulty in clay structural studies and can even render these “patterns” useless. These factors include defects and local disorder in both crystal chemistry and structure e.g. variation in thickness of the crystal and fast amorphization by electron radiation damage. Li et al. [1] proposed a row-indexing method to overcome the difficulty in indexing those “defective electron diffraction patterns”. However, it is only available for crystal systems other than triclinic and for those electron diffraction patterns obtained along [*uv*0]. Because most clay minerals belong to the orthorhombic, trigonal, hexagonal, monoclinic and triclinic systems, the [*uv*0] row-indexing method is useless to those electron diffraction patterns with Miler index $l \neq 0$. In this work, the relationship between Miller indices *h,k,l* and row-row distance for the triclinic crystal system along any direction was proposed and extended to all other crystal systems and finally established the foundation of “row-indexing” [2]. Application in clay minerals structural analyses was exampled.



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Investigation of layer charge density of dioctahedral smectites by the Rietveld method

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The knowledge of the structural property of natural smectites such as layer charge density (LCD), is essential to optimize their technical application. The Rietveld method is assumed to be an ideal method to study clays and clay minerals. However, the turbostratically disordered structure of smectites precludes the application of the classic Rietveld method. Ufer *et al*. (2004) proposed to overcome this limitation by using a single layer model with the BGMN program. The aim of this study is to prove the validity of the refinement of LCD by the Rietveld method and provide a new method for the structural characterization of smectites.

The Rietveld refinement was carried out on the diffraction patterns of the Cu-triethylenetetramine (Cu_{trien}) exchanged dioctahedral smectites to avoid the problems of unknown cation species and complex hydration behavior in the interlayer. Meanwhile, it offered a chance to obtain the information of LCD by refining the occupation of the Cu_{trien} complex in the interlayer.

Two structural models containing different atomic coordinates of TOT layers were chosen for montmorillonite-beidellite series (iron poor) and nontronites (iron rich). The Rietveld refinement was carried on measured patterns of purified samples. For montmorillonite-beidellite series, the refinement of LCD showed led to satisfactory results for profile fitting (Figure 1), but a tendency of underestimated values in comparison with the reference (Figure 2). For nontronite samples, the refinement of LCD showed similar underestimated results. It may due to the uncertain assumption of the Debye-Waller factor (Figure 2). The present study shows that the LCD can be determined by the Rietveld method from XRD patterns of the Cu_{trien} exchanged samples.

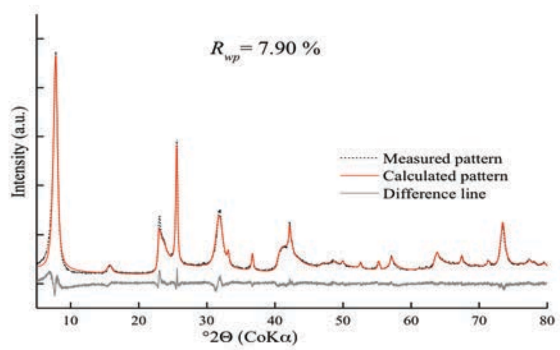

Figure 1. Refinement of purified Cu_{trien} exchanged sample XL_02

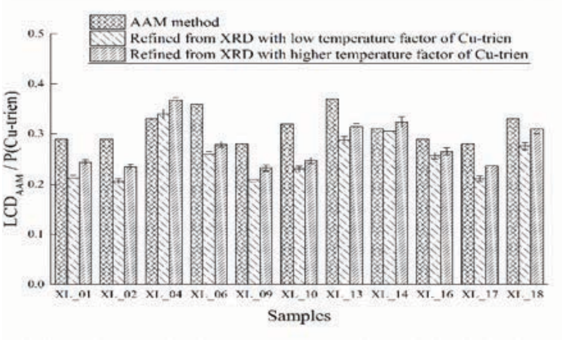

Figure 2. Rietveld refinement results of layer charge density P(Cu-trien), compared to the alkylammonium

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Very low to low-grade metamorphism of Precambrian in Fanjingshan area, Guizhou, China

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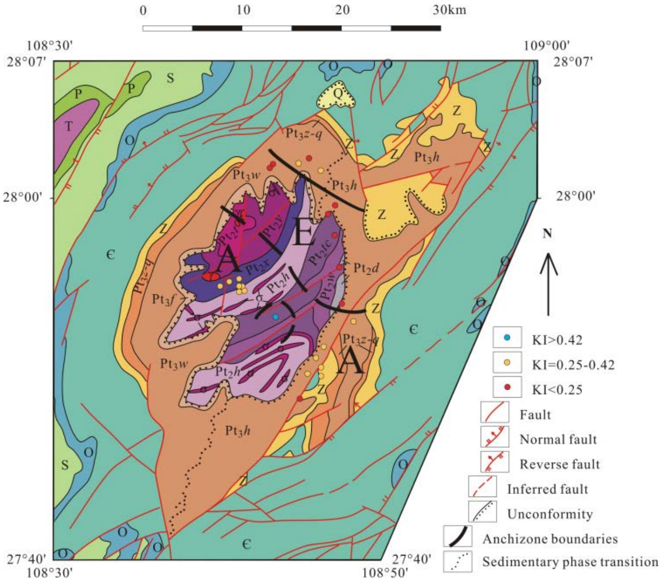
The very low to low-grade metamorphism overprinting on the Precambrian in Fanjingshan area, Guizhou, China was investigated with illite crystallinity, chlorite crystallinity, b_0 value of K-micas (illite) and geothermometry of chlorite. The results demonstrate that illite crystallinity Kübler index (KI), calibrated with Kisch IC set, ranges from 0.20 – 0.99°Δ2θ, and the Árkai index of chlorite crystallinity ranges as 0.22 – 0.63°Δ2θ, indicating the Precambrian in Fanjingshan area encountered with the geological processes from diagensis to epimetamorphism, and it remains diagenetic, anchizonal and epizonal records in rocks in the area studied. The diagenetic rock contains diagenetic index mineral illite-montmoriolite mixed-layer phase while anchizonal rock bears metamorphic index mineral paragonite. The b_0 of K-micas (illite) ranges 0.9000 – 0.9045 nm, and on average 0.9018 nm or roughly equivalent to 3.66 kbar. The cumulative frequency curve of b_0 stands in between the curves of N. New Hampshire and Otago, indicating the metamorphic pressures condition in between low-intermediate pressure and intermediate pressure facies. Peak metamorphic temperature was evaluated at 293-364°C and average 342°C. Therefore the palaeo-gradient was derived at 27°C/km. The anchizonal boundaries across strata and folding axis of the Fanjingshan anticline, clarifying the syn- to post-sedimentary or structural movement of epimetamorphism, which caused the increasing in depth and the rising of temperature and pressure in rocks at the bottom or lower part of basin due to structural burial.



Al-substitution-induced defect sites enhance adsorption of Pb^{2+} on hematite

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Al-substitution in hematite is ubiquitous in nature and strongly affects the environmental behaviors of hematite. However, the defect microstructure caused by Al-substitution and its inner relationship with the surface reactivity of hematite remain unclear. In this study, the crystal structure of Al-substituted hematite was characterized by high-resolution electron transmission microscopy (HRTEM) and high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Acid-base titration and Pb^{2+} adsorption experiments were performed to investigate the surface reactivity of Al-substituted hematite. HRTEM images revealed that the proportion of (001) facets on hematite increased from 44.0 ± 3.8% to 84.8 ± 6.5% with increasing Al-substitution. HAADF-STEM images indicated that Al-substitution resulted in more vacancies of Fe atoms on hematite (001) facets. At these Fe defect sites, additional singly ($\equiv FeOH^{-0.5}$) and triply ($\equiv Fe_3O^{-0.5}$) coordinated hydroxyl sites were formed. The weight loss due to dehydrogenation followed the order of H-10 (6.2%) > H-5 (3.3%) > H-0 (1.7%). Besides, the relative percentage of surface oxygen atoms in the surface hydroxyl sites of Al-substituted hematite was consistent with the results of thermogravimetric analysis. At pH 5, the relative charge density of H-0, H-5 and H-10 was 73, 94 and 241 mC/m^2, and their adsorption capacity for Pb^{2+} was 0.82, 1.23 and 3.51 μmol/m^2, respectively. These results indicate that the formation of more defect sites with increasing Al-substitution can significantly enhance the surface charge density and Pb^{2+} adsorption capacity of hematite.

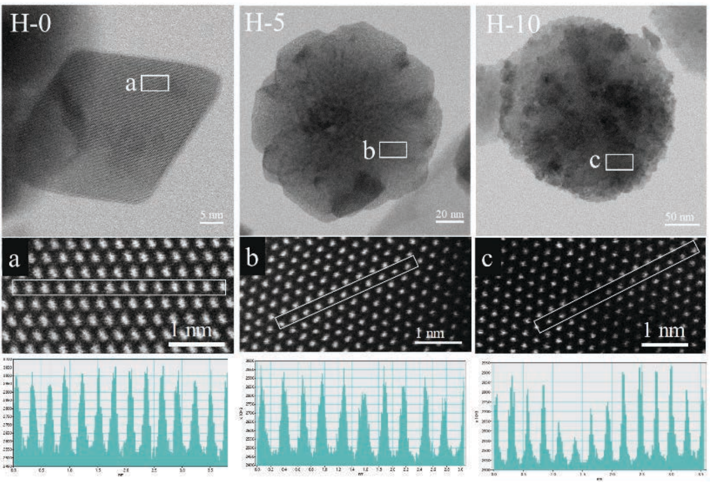

Figure 1. HAADF-STEM images of Al-substituted hematite

Swelling damage and inhibition in a Swiss clay-bearing heritage sandstone

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Many historical buildings and monuments in Switzerland, such as the Fribourg Cathedral, have been constructed from sandstones which have swelling clays in the matrix. Repeated wet-dry cycles can cause damage to the stone through the formation of strain gradients that lead to high stresses, as past work has suggested[1]. Past work has also demonstrated that a, w diaminoalkanes are effective swelling inhibitors that function by replacing the interlayer cations and reducing subsequent intracrystalline swelling[2].

In this work, samples of Villarlod molasse, a sandstone with a clay and calcareous matrix from the Swiss plateau, are subjected to wet/dry cycles with and without treatment by a diaminoalkane. Through X-ray diffraction and dilatometric studies, the diaminoalkane is shown to dehydrate the interlayers at ambient relative humidities, and significantly reduce swelling. Additionally, a possible new damage mechanism coming from extended wetting is illustrated, and the efficacy of the diaminoalkane treatment is demonstrated, as seen in Figure 1.

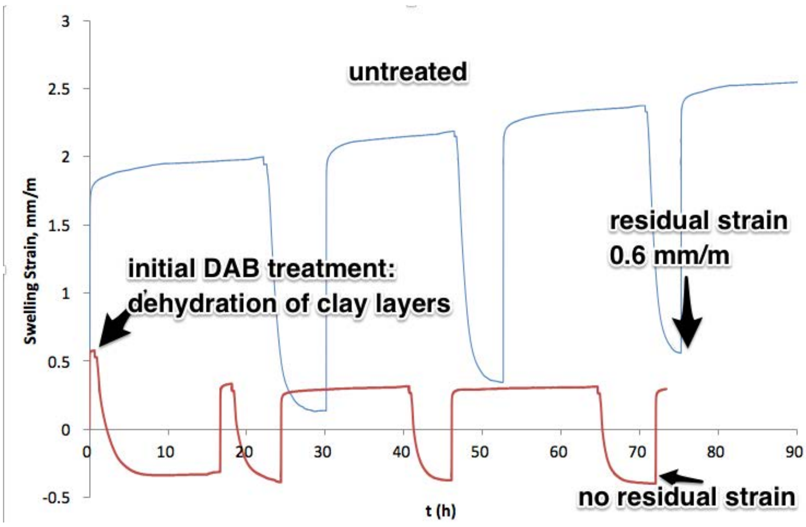

Figure 1. Swelling strain in wet-dry cycles of untreated and treated Villarlod molasse.

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The importance of clay in the faulting and fracturing of rocks

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Clays and clay minerals, in particular smectites, illites, chlorites, serpentine minerals and their mixed-layered varieties, are commonly concentrated along faults and fractures in the brittle upper parts of the continental and oceanic crust characterized by intense, low temperature (>300°C), water-rock interaction and alteration. The concentration of these mineral phases can lead to changes in the hydrodynamic behavior of a fault by modifying its frictional strength and permeability-porosity structure. This is achieved by a complex array of interacting processes related to the lack of equilibrium between the hydrous fluid and the rock, and the deformation mechanisms operating in the fault or fracture. The role of smectite at shallow crustal levels has received particular attention due to its mechanical weakness and its association with creep motion along some faults, such as along an active strand of the Californian San Andreas Fault drilled at ca. 3 km depth in the SAFOD borehole. Most discussions on the importance of these mechanically weak mineral phases revolve around the mechanisms of dissolution and pressure solution induced by crystal boundary stresses, the role of neocrystallization reactions along slip planes forming by substrate growth or as pore-filling phases and the associated changes in clay fabric related to these effects. The role of fluid pressures generated by deforming clay-rich gouges or the role of shear heating are also topics of debate in a number of fault zones. This presentation takes a look at the interaction of clay mineral-related processes at a range of geological scales and crustal depths based largely on the perspective of fault rock fabric and mineral textures. It will include a comparison of two large and active plate boundary strike-slip faults characterized by very large displacements and intense fluid-rock interaction: the San Andreas Fault of Californian and the Alpine Fault of New Zealand. Key to understanding the importance of clay minerals during brittle deformation is to resolve the relationships between the seismogenic cycle, the periodic influx of hydrous fluids, and the role played by the increasing concentration of weak hydrous minerals within a fault zone. The mechanisms of clay mineral neocrystallization and faulting will also be addressed in terms of fault rock dating by radiogenic isotopes, in particular by illite age analysis.

Biocompatible smectite-talc mineral flakes for enhancing the biodegradation of marine oil spills

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Adding natural and fertilized clay minerals to marine oil-contaminated water in laboratory experiments have been shown to significantly enhance the rate of hydrocarbon biodegradation[1-3]. Such additives may in the future represent an eco-friendly approach to biodegrade and disperse oil spills and thus remove the need to apply chemical surfactants. Clay minerals amendments can be added in the form of very thin flakes that are engineered to float on water and attach to the oil phase. The clay flakes tested so far are composed of four components: i) natural clay mineral phases (typically smectite or Fuller's Earth), ii) quaternary alkyl ammonium-modified smectite (organoclay) for enhancing attraction to the oil, iii) Na-carboxymethyl cellulose (Na-CMC) as a filming agent and iv) fertilizing compounds containing N, P and K to stimulate bacteria growth. Once added to the oil, the clay flakes provide abundant mineral surfaces as adsorption sites for cation exchange and the release of nutrients for enhancing the bacterial breakdown hydrocarbon compounds. During biodigestion, large volumes of fine-particle/biofilm aggregates are formed that detach from the oil phase and aid dispersion within the water column. Due to the relatively high expense of organoclay and Na-CMC compounds and their unknown effect on the natural environment, this contribution studies the use of talc and corn oil as an eco-friendly replacement: a product commonly known as talcum powder. Talc [$Mg_3Si_4O_{10}(OH)_2$] is an industrially available clay mineral that is neither toxic nor mutagenic and occurs as a natural alteration product of ultrabasic rocks or low-grade metamorphic siliceous dolomites. Using various concentrations of these additives, eco-clay flakes can be successfully prepared to attach to an oil spill and enhance the rate of biodegradation to a similar extent as previously documented in published experiments.

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The influence of K-bearing organic acids on the alteration of smectite: New experimental results

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Small et al. 1994[1] experimentally examined the role K-bearing organic acids on the smectite-to-illite reaction of Wyoming bentonite at 200 °C. Following Na-exchange, the reaction products were identified as R1 or R2 ordered illite-smectite (60-70% illite), however, in the absence of organic additives, no reaction with KCl was detected. In this study we report on similar experiments using 100ml of the following 4 reacting solutions: I) 0.03 M potassium chloride KCl, II) 0.06 M potassium acetate CH_3COOK, III) 0.03 M potassium oxalate $K_2C_2O_4$, and IV) 0.03 M potassium oxalate/oxalic acid $K_2C_2O_4/C_2H_2O_4$. These were reacted with 430mg of <2µm size separated bentonite from Milos at 200 °C in a rotating oven for 3 months. Afterwards the products were washed 3 times in deionized water followed by sonification and centrifugation. The mineralogical changes were analyzed mainly by X-ray diffraction (XRD) and differential thermal analysis (DTA). We first found similar hydrothermal alteration of the smectite, as described by Small et al. 1994[1], by X-ray diffraction and NEWMOD modelling. Experiment I showed only minor alteration reaction with KCl, Experiments II, III, and IV, showed R1 or R2 ordered illite-smectite (60-80% illite) duplicating Small`s results. The mineralogical results also confirmed the neoformation of K-feldspar (sanidine) and in addition calcite neoformed in experiments III and IV. Afterwards we Ca exchanged the starting material and reaction products for layer charge determination. The XRD results and NEWMOD modelling following Ca-exchange showed almost no illitic layers in samples from I. In contrast, experiments II, III and IV showed again high content but different ordering of apparent illitization (I-S 70% illite, I-S 65% illite and I/S 75% illite, respectively), R0 not R1 or R2 as in the initial reaction products. The apparent higher degree of illitization reaction occurred together with the increasing pH conditions associated with K-oxalate (pH 7.2 – 8.9) compared to the notably acidic conditions of experiments I and II (pH 5.4 – 5.7). The surface charges measure in Krakow[3] indicated some changes between the original and products with a shift of the products from 0.49 to 0.55 eq/FU in I, 0.52 in III and 0.55 eq/FU in IV, correlating with the different d(001) peak positions (16.85 to 17 Å)[2]. In contrast, no layer charge difference was detected in II. Further investigations are necessary in order to determine the precise nature of these smectite alterations.

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Constraints of sulphate in the porewater of a clay rock

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Knowledge on porewater chemistry is important for clay rocks foreseen as host rocks for geological repositories. Sulphate is an important component in many porewaters of clay rocks, such as for example the Opalinus Clay (OPA). Its control has been subject to discussions in the past[1,2,3]. To study this issue, a systematic experimental-modelling approach has been adopted. It includes microscopic analysis (SEM/EDX, EPMA) and aqueous leaching of OPA drillcore samples from the Mont Terri Rock Laboratory (CH) as well as modelling of porewaters obtained from packed-off boreholes.

Geochemical modelling indicates celestite and barite equilibrium of the porewaters. Microscopic analysis revealed the widespread, but scarce and patchy occurrence of Sr-Ba sulphate as large (mm range) and medium-sized 10-20 µm grains in carbonaceous silty zones, but also as Sr sulphate grains below 2 µm in the clay matrix in the shaly zones. Modelling suggests that porewater data are more in line with a celestite/barite mixture than with a Sr-Ba SO_4 solid solution. Furthermore, certain calcite and apatite grains revealed high sulphur contents. The amount of sulphur in these phases is roughly one magnitude higher than in the detected Sr sulphate, but the nature of this sulphur is yet unclear.

Data from borehole sampling, high-pressure squeezing and advective displacement of drillcores revealed consistent sulphate concentrations in porewaters. Aqueous leaching under anaerobic conditions, on the other hand, yielded sulphate concentrations beyond those expected when back-calculated to in-situ conditions. This is explained by dissolution of celestite and a further – so far not well constrained – sulphate source. There are experimental indications, however, that sulphate is released from the carbonate fraction in the OPA during the leaching process, which however, does not seem to affect in-situ porewater concentrations.

Overall, the combined findings underscore that sulphate concentrations in the studied clay rock are controlled by celestite equilibrium on the one hand and by diffusive exchange with the adjacent aquifers on the other.

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Determination of relevant parameters for the design of Ni-Fe layered double hydroxide based electrocatalysts for water splitting.

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In a society where the hydrogen economy appears as a sustainable opportunity in the change of energy paradigm, the research and development on alkaline electrolyser technologies is an important field to focus on. In particular, the study and design of cheap and efficient electrocatalysts is crucial. To answer these needs, transition-metal mixed oxides and hydroxides have raised interest to replace scarce elements used in current catalysts. More recently, layered double hydroxides (LDHs) were reported to be efficient catalysts, notably for the oxygen evolution reaction which is the bottle neck of the water-splitting process. Due to the arrangement of the metallic cations in this structure, these materials present interesting hydroxide sites to facilitate the reaction [1]. Also, the platelet morphology allows to obtain a high surface area favorable for catalytic applications.

In the present work, we explored some parameters of the synthesis of Ni-Fe LDHs to see their impact on the efficiency of the resulting electrocatalysts towards the oxygen evolution reaction. Samples with different metallic ratios, intercalated anions and levels of crystallinity were prepared by co-precipitation at constant pH. After characterization, the efficiency of the catalysts was evaluated in alkaline media through a benchmarked procedure. The morphological and chemical properties of the prepared LDHs were correlated with their electrochemical behavior to determine important characteristics of the material, such as its level of crystallinity, influencing their electrochemical activity and stability.

The ultimate goal of this study is to be able to correlate structural features of this class of materials with their electrocatalytic properties, interpreting them with the aid of computational models to deduce guidelines for the design of new LDH-based catalysts for oxygen evolution reaction.

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Adsorption of phthalate esters on smectite clay surfaces: a molecular dynamics simulation and experimental study

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A major process controlling the fate and transport of organic contaminants in natural environments is their tendency to partition between water and solid surfaces (e.g. soils and sediments) as adsorption can strongly hinder contaminant mobility and bacterial and photodegradation. Previous studies suggest that the clay mineral content of a given soil can play a substantial role in this partitioning, but the relevant mineral-organic interactions are not fully understood. This research focuses on the adsorption of phthalate esters by smectite clay minerals. Phthalate esters are widely used plasticizers with known or suspected endocrine disrupting properties, six of which are currently listed on the EPA priority pollutant list.

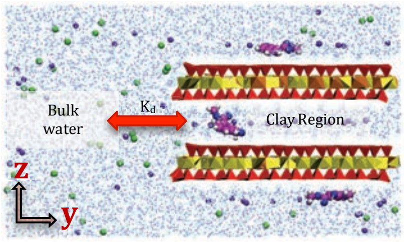

Figure 1. Simulation snapshot of two clay layers in a system containing water molecules, Ca and Cl ions, and

We developed a molecular dynamics (MD) simulation methodology to model the partitioning of phthalate molecules between a bulk aqueous reservoir and a stack of flexible Ca-smectite clay layers (Fig. 1). Our methodology uses the metadynamics technique to facilitate the exploration of the entire simulation box by phthalate molecules and reconstruct the associated free energy landscape. Simulation results are obtained for six phthalate esters that span a range of sizes and hydrophobicities and validated against newly obtained experimental batch adsorption and x-ray diffraction data. The simulation output provides atomistic-level insights that help discern mineral-organic interaction mechanisms and conformations and aid in the interpretation of experimental data. In particular, we calculate the free energy, enthalpy, and entropy of adsorption, the affinity of the phthalate esters for different clay adsorption sites (interlayer, edge, external basal surface), and examine the effects of clay charge density.

Results from our simulations highlight the strong adsorption of phthalate esters by smectite, its sensitivity to compound size and hydrophobicity, and the presence of preferential adsorption domains on the clay surface. These favorable sites were found on Ca-free patches on the clay surface, far from isomorphic substitutions. Partition coefficients calculated from our MD simulations were in good agreement with collected experimental data. A decomposition of our energetic data into enthalpic and entropic components emphasized the dominant role of entropic interactions as the underlying energetic driver of phthalate adsorption.

In this work, we were able to develop and validate a metadynamics-based methodology to gain insights into the energetics of phthalate adsorption by smectite minerals. This methodology can easily be adapted to examine different chemicals, mineral surfaces, and aqueous chemistry conditions, providing a valuable tool to further the nanoscale understanding of organic contaminant-mineral interactions.

Teaching the art of solid-state stable isotope measurements in clays: What can be learned from nanometric isotope analyses?

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Secondary ion mass spectrometry (SIMS) is an analytical tool introduced for the semi-conductor industry in the 1960's for measuring isotopic variations with depth in silicon wafers. Castaing and Slodzian at the University of Paris-Sud (Orsay) designed the modern double-focusing sector field mass spectrometers used today, and contributed to design of the NanoSIMS, capable of mapping isotopic distributions in minerals at a spatial resolution approaching 25 nm. Since the late 1970's SIMS has been used for the study of earth materials.

The ionization of elements bound in minerals is achieved using a focused beam of high energy (10 to 15 keV) primary ions (e.g., O^-, O_2^+, Cs^+) to sputter a flat mineral sample held at an accelerating voltage (5-10 keV) that creates a total ion impact energy great enough to break chemical bonds, thus generating secondary ions from the sample within the top few monolayers of the surface. The beam diameter and energy can be adjusted, and the instruments can be setup to eliminate mass/charge interferences by energy filtering or high mass resolution.

For clay science, the advantage of SIMS is that is consumes small volumes of silicates (~10^{11} atoms per μm^3), and although it is a destructive analytical technique the 5-30 µm spots are only on the order of 3 µm deep. Because this volume is greater than that of clay sized minerals (<2 µm), numerous clay particles are sampled in each analysis, generating a micron-scale bulk analysis. A special benefit is that nanometric crystal size separates (e.g., <20, 20-50, 50-100 nm) that may produce only milligrams of material, can yield dozens of analyses that average the crystal chemical composition of a particular size fraction, representing a select time period of crystal growth. If the crystallization temperature is known, changes in isotopic compositions of different clay size fractions allow determination of the paleofluid composition in equilibrium with the mineral during that period of growth. Combined with age dating (e.g., K/Ar or Ar/Ar) of each crystal size-fraction, the timing of distinct environmental events (e.g. hydrocarbon influx, toxic spills, climate change) can be evaluated.

By teaching new analytical protocols for clay mineral isotopic systematics, students are engaged in experiential learning. They make measurements that demonstrate the relationships between chemical environments and mineralogy. A large numerical dataset is produced that demonstrates the importance of statistical analysis and provides the student with a skill set for interpretation of paleo-environmental conditions recorded in the archives of clay minerals.

Identification of self-sealing mechanisms in 10–20 year old excavation damaged zones through mineralogical, petrophysical, and geochemical tests and SEM imaging

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The Opalinus Clay (OPA) formation has been chosen as host rock for Switzerland's high- and low-level nuclear wastes. Evaluating the integrity of the OPA, especially with respect to long term permeability changes in the Excavation Damaged Zones (EDZs), is critical for long term safety. Argillaceous formations such as the OPA are able to self-seal or self-heal fractures, thus decreasing induced permeability over time through a variety of processes occurring at different scales (i.e., from the tunnel- to the nm-scale). Investigations of the in-situ, self-sealing processes at selected underground galleries at the Swiss Mont Terri Underground Research Laboratory (MT URL) in St. Ursanne are in the focus of the SE-P project supported by the Swiss Federal Safety Inspectorate (ENSI), the Swiss Federal Office of Topography (swisstopo), the German Federal Institute for Geosciences and Natural Resources (BGR), and Radioactive Waste Management Limited (RWM) from the UK.

We have first focused on characterizing tunnel- and borehole-scale changes in previously well-studied EDZs of 10 and 20 years of age at the MT URL. Most of our experiments so far have focused on geophysical investigations. These have included gallery-scale (>25 m) seismic tomography and electrical resistivity tomography (ERT), which have been repeated over a time period of 10 and 18 years post-excavation, respectively, to directly image changes to the EDZ. Borehole-based (4.5–6 m) investigations have included structural analysis, interval velocity measurements (IVM), borehole ERT, and cross-hole seismics with the aim of identifying . The results of these studies have demonstrated that self-sealing has likely occurred in some, but not all, areas of the EDZs.

We are now interested in understanding the exact processes at the macro and micro-crack scales which have led to the measured changes in EDZ properties over time, as well as the most important influencing rock and rock mass properties which could drive such changes at small scales (µm-nm) (i.e, mineralogy, microstructure, micro-porosity, etc). We have drilled ten boreholes into the tunnel sidewalls of two underground galleries and taken samples of EDZ fractures, natural tectonic faults, and drilling-induced fractures for chemical, petrophysical, mineralogical, and microstructural analyses. For reference, we also have taken intact material from outside the EDZ influence.

The specific tests conducted will be X-ray diffraction powder analysis (XRD), Fourier-transform infrared spectroscopy (FTIR), total inorganic content (TIC), gravimetric water content, helium pyncometry, micro-pore size distribution, and thin section analysis. These will be complemented with scanning electron microscopy (SEM) imaging and accompanying energy dispersive spectroscopy (EDS) to identify any microstructural indicators of self-sealing processes, as well as to locate mineral precipitants not identified by XRD analysis. Laboratory tests will be compared with borehole-scale and tunnel-scale results. We will present the preliminary findings of these tests and analyses along with recommendations for future tests.

Multiple aeolian dust parageneses in loessite : mineralogical evidence for the volcanic contribution from the Early Triassic of the Central North Sea

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The mineralogy of the Smith Bank Formation (SBF) of early Triassic age was characterized in a borehole sequence from the Central North Sea. The SBF sediments in this location were buried to a relatively shallow depth (1667m) and were thought to have been deposited towards the edge of an alkaline and saline lake that had formed within the Permian Basin. The SBF sediments in this well are primarily loessitic with stratified water-laid deposits at the top and the bottom of the sequence.

The clay mineralogy of the SBF in this well contained a tosuditic mineral (regularly interstratified dioctahedral chlorite-smectite) and kaolinite, thereby contrasting with the usual chlorite-illite clay mineral assemblage characteristic of the more deeply buried sediments of the same age. Following a suggestion by Jeans (2006) that the on-shore lithostratigraphic equivalents of the SBF may have received inputs of volcanic ash, evidence for such a contribution was sought in the mineralogy of the SBF. Comparisons were made with tonsteins, which are widely accepted as being derived from volcanic ash, and it was concluded on the balance of mineralogical evidence, that volcanic ash fall had indeed contributed to the SBF sediment.

It is proposed that reactive glassy particles, probably derived from rhyo-dacitic and andesitic sources, had decomposed in pore waters of alkaline pH to yield solutions with a high Al:Si ratio from which both tosudite and kaolinite had formed during low temperature diagenesis. In general, the mineralogy of the SBF can be explained by considering the inter-related inputs from three different sources, namely terrestrial/detrital, aerial inputs including volcanic ash fall and diagenesis in its different stages.

Gone with the wind: Integrative evaluation of Austrian loess and loess loam deposits by sedimentological, mineralogical and rock chemical analyses

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Loess and weathered loess (loess loam) are important raw materials for construction that have been used in the Austrian brick industry for centuries.
Knowledge of the properties, occurrence and availability of these building materials is becoming increasingly important, in order to meet, on the one hand, the increased quality requirements in the modern brick industry and, on the other, those in new fields of use in clay construction.
Depending on their stratigraphic and geomorphological position, the geology of the source area, climatic conditions, weathering intensity and redeposition, loess and loess loam have heterogeneous properties that significantly influence their quality as raw materials for building, and thus their possible uses.

At the Geological Survey of Austria a large number of different sub-datasets exist, concerning bulk rock composition, clay mineralogy, chemistry and grain size distribution of loess and loess loam. Within the current project, these individual data sets are merged, generating a coherent database enabling henceforth the joint statistical analysis of the data. The compositional nature of the analytical data (i.e. measurement results reported in percentage units) is taken into account by applying a log-ratio approach for multivariate statistical methods.

The area studied comprises the classical Austrian loess areas in the Alpine foreland of Upper and Lower Austria and in the Vienna Basin. The results of the statistical evaluation are transferred to a geographic information system and serve as the basis for a categorization of the loess and loess loam occurrences, taking into account previously published soil-based classification approaches as well as trends and patterns derived from the analytical data.

The project objective is the designation of deposits of brick raw materials for the Austrian Interactive Raw Material Information System IRIS.

Characterization of aluminum-based drinking water treatment residuals

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Surface water carries organic compounds, suspended solids, clays, natural organic matters and other contaminants, so water needs to be properly treated before it reaches our taps. Coagulation and flocculation are the common technologies in drinking water treatment. The by-product from drinking water treatment processes is water treatment residuals (WTR). The aim of this work was to characterize mineralogical and chemical composition as well as textural parameters of WTR.

Material used in the experiments derived from water treatment station in Poland. The coagulant which was used in the process was aluminum sulfate (ALS). The chemical composition was analyzed using X-ray fluorescence spectroscopy (XRF). The mineral composition was determined using X-ray diffractometry (XRD) and fourier-transform infrared spectroscopy (FTIR). The specific surface area and porosity were determined from N_2 gas adsorption/desorption isotherms.

The chemical composition of WTR was as follows: Al_2O_3 – 36.62, SiO_2 – 7.98, CaO – 3.03, Fe_2O_3 – 0.9 wt. %. The loss of ignition was 49.49 wt. %. The WTR is amorphous and poorly ordered material, the only crystalline mineral which was found in sludge was silica. The main band in the FTIR spectra at 3450 cm^{-1} could be assigned to the stretching vibration of O-H bonds, while adsorption band at 1610 cm^{-1} represents the bending vibration of H-O-H in water molecules chemically associated with $Al(OH)_3$. The bands at 1506 and 1394 cm^{-1} was assigned to adsorbed carbonates. The bands at 1030 and 723 cm^{-1} correspond to the stretching vibrations of Si-O-Si in the quartz. Nitrogen adsorption/desorption measurements on the WTR yielded type II isotherm with a type H3 hysteresis loop. The specific surface area (BET) was 102 m^2/g. The values of total pore volume was 0.505 cm^3/g, volume of micropores, mesopores and macropores were 0.037, 0.341 and 0.127, respectively. The share of each class of pores throughout the whole pore volume was as follows: share of micropores – 7%, share of mesopores - 68% and share of macropores – 25%.

WTR is inherent element during the water treatment process. Due to the results from analysis the composition of the WTR mainly depend on the coagulant which has been used in the treatment process. In the analyzed residuals, mesopores prevail and WTR has surprisingly high specific surface area which is comparable with common sorbents, such as zeolites or bentonites.

Acknowledgments: This work was financed by the National Science Centre, Poland Grant No. 2017/27/N/ST10/00713 and PUT research project 01/13/DSPB/0891.

Transformation of Co-containing birnessite to todorokite: Effects of Co on the transformation and implications for Co mobility

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Phyllo- and tecto-manganates are ubiquitous minerals in soils, sediments, and oceanic ferromanganese nodules, and they are readily associated with many bioessential transition metals, such as Ni and Co. Interestingly, phyllomanganates, such as birnessite, can convert to tectomanganates, such as todorokite, during soil and sediment diagenesis, yet the mobility and fate of those metals during the transformation process remain largely unknown. The present work investigates the effect of Co on, and the mobility and fate of Co during the transformation of birnessite into tunnel structure minerals (tectomanganates). A range of Co-containing birnessite precursors with up to 16.9% Co/(Co+Mn) molar ratios were synthesised, and subsequently transformed via a mild reflux procedure designed to mimic the diagenesis of these layered precursors into tunnel structures. The layered precursors and reflux products were characterized using a combination of mineralogical and geochemical techniques, including powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), high resolution transmission electron microscopy (HRTEM) and extended X-ray absorption fine structure (EXAFS) spectroscopy. The results show that Co(III) is structurally incorporated into the layered precursors and reflux products, through the isomorphic substitution of Mn(III). The structural incorporation of Co(III) into the layered precursors leads to an overall reduction of Jahn-Teller distorted Mn(III) octahedra in these minerals, a key factor for their transformation to tunnel structures. As a consequence, the presence of such structural Co(III) disrupts the transformation of birnessite into todorokite, leading to the coexistence of 9.6 Å asbolane-like phyllomanganate and non-ideal 3×*n* (n up to 13), or a-disordered, todorokite-like tectomanganates in the transformation products. Overall the incomplete transformation to tectomanganates induced by the structural incorporation of non Jahn-Teller distorted cations like Co(III) into birnessite might help explain the often observed predominance of phyllomanganates over tectomanganates in soils and sediments, and the persistence of phyllomanganates in ferromanganese deposits that can be many millions of years old. The results also indicate that Co(III) initially associated with birnessite is retained in the solid phase during transformation, and thus the mobility of Co(III) is limited. EXAFS data suggest that Co is mainly located in the octahedral layers of asbolane-like phyllomanganate and at non-edge sites in non-ideal todorokite. Overall the transformation of Co-containing birnessite into non-ideal todorokite and asbolane-like layered structures maintains the strong sequestration of Co by Mn oxides.

Preparation and physicochemical characterization of Chitosan–Algerian Palygorskite composite beads as drug carriers

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Controlled drug release has demonstrated to be a key technique to control the concentration of a certain drug in the organism and therefore, to reduce both therapeutic noncompliance and side effects. In this work, we describe a method to intercalate chitosan (CS) with purified Palygorskite (Pal) to be used as drug carriers. Palygorskite/chitosan (Pal/CS) and chitosan (CS) beads cross-linked with sodium tripolyphosphate (TPP) were prepared. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning transmission electron microscopy (SEM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)) have been employed to characterize samples. Results demonstrated the effective interaction between chitosan and Palygorskite. Diclofenac sodium (DFNa), an anti-inflammatory drug was used as model drug to load into the designed beads. FTIR analysis confirmed the loading of DFNa into the clay/chitosan beads. Drug release test was carried out in Phosphate Buffer Solution (PBS, pH. 6.8). Results obtained indicate that only 33% of total drug has been released from DFNa-(Pal/CS) compared to 66% from DFNa-CS. Drug quantities released was significantly decreased with the addition of palygorskite in chitosan matrix. (Pal/CS) beads cross-linked with TPP showed positive behavior to carry diclofenac sodium and might be potential carriers for other anti-inflammatory drugs.

Angular-independent Structural Color of Liquid Crystalline Colloids of Fluorohectorite Clay Nanosheets

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Introduction Recently, two-dimensional nanostructure and nanospaces of layered clays are attracting attention as media to organize functional molecules and polymers in controlled orientation. Further, mesoscale superstructure obtained by exfoliation and dispersion of layered clay mineral is attracting colloid scientists as well as materials chemists. We recently reported that fluorohectorite (FHT) colloid show fluid liquid crystal phase over wide concentration range by entropy-driven orientation of the exfoliated nanosheets1). The liquid crystal phase possesses a lamellar-like structure with the basal spacing of several tens of nm. In this study, we clarified the effects of nanosheets concentration φ, average particle size D, and salt concentration c on the structures of the liquid crystal phase. Finally, we succeeded in preparing the liquid crystalline FHT colloids with structural colors tunable over full range of visible light by optimizing the conditions.

Experimental The FHT nanosheet colloid was prepared from the sample supplied from Topy Industries Inc., followed by removing impurity by centrifugation. The nanosheet colloids were ultrasonicated to control the average particle size. The samples were characterized by polarized microscopy (POM) and small-angle X-ray scattering (SAXS).

Results and discussion Obtained nanosheets colloids D = 1.6 µm and φ = 1.2 vol % was colorless. This sample showed reflection maximum $\lambda_{\max}$ at 205 nm in visible reflection spectrum. In the SAXS measurement, five peaks ascribed to lamellar-like structure with the basal spacing d of 68 nm were observed. According to Bragg-Snell law ($\lambda_{\max}= 2dn$), where n is the refractive index of the sample, $\lambda_{\max(SAX)}$ is calculated as 181 nm; the values from SAXS and visible spectrum are thus mostly consistent (the small difference is due to an experimental problem to be improved). Meanwhile, the sample showed blue, green, and red colors as φ increased to 0.40, 0.36, and 0.24, respectively. Accordingly, the $\lambda_{\max}$ also increased to 512, 552, and 677, respectively. Thus, it is suggested that the structural color is due to diffraction of visible light mostly formulated by Snell-Bragg's law. The structural color is also tunable by varying nanosheet size D and salt concentration c: the increase of D or decrease of c lead to increase of $\lambda_{\max.}$ Interestingly, structural color of the present nanosheet colloid have no angular dependence, different from other nanosheet systems and most of other artificial systems.

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Significantly different effects of graphene oxide and fullerol on the phase transformation of ferrihydrite

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Crystallization by particle attachment (CPA) is now recognized as a common crystallization process in both natural and synthetic systems. As the precursor particles always coexist with other substances in nature, understanding the effects of coexistent substances on the CPA process is of high importance for systematically deciphering the CPA mechanisms. One typical CPA process in nature is the transformation of poorly crystalline ferrihydrite (Fh) nanoparticles to hematite (Hem). This work, for the first time, studies the effects of coexistent carbon nanomaterials (CNMs) with different morphologies (i.e., graphene oxide (GO), fullerol (PHF)) on the transformation of Fh. The XRD, Mössbauer spectra, and TEM characterization results showed that the transformation products of Fh were mainly Hem with a small amount of goethite (Gth), regardless of the coexistent CNMs type; the transformation kinetics, the morphologies and the Hem/Gth ratio of the transformed products, however, were quite different in these systems. In particular, GO inhibited the transformation rate of Fh as compared with the control system (without CNMs). Interestingly, PHF not only accelerated the transformation rate, but also led to a larger particles size and a higher ratio of Hem/Gth for the transformed products. Above phenomena should be attributed to the different behaviors of CNMs in affecting the attachment of Fh. That is, CNMs that can enhance the aggregation (and thus the attachment) of Fh particles will accelerate the transformation process, and vice versa. This hypothesis was supported by the characterization results of the CNMs-Fh mixture before transformation, which clearly showed that the large lamellar GO dispersed Fh on its surface, reducing the aggregation and contact of Fh particles; while the nanogranular PHF formed large aggregates with Fh particles (enhancing their attachment). Moreover, the strong interactions between PHF and Fh particles helped in breaking the energy barrier during the attachment of Fh particles. As a result, PHF both kinetically and thermal dynamically benefited the CPA process in the transformation of Fh particles. This study revealed that the coexistent nanoparticles can exert significantly different effects on the CPA process of Fh particles through changing the free-energy landscapes and reaction dynamics, and it could also provide valuable information for systematically deciphering the underlying mechanisms in CPA processes.

Preparation of cellulose nanofiber/ halloysite nanotubes composite films and study on performances of the film

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In this study, cellulose nanofiber/halloysite nanotubes composite films were prepared from halloysite nanotubes (HNTs) and cellulose nanofiber (CNF) with different mass ratios. Chemical structure, crystal structure, microstructure, the thermal performance, mechanical properties and light transmission properties were characterized by using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis (TG), universal testing machine, ultraviolet-visible spectroscopy.

The results showed that the HNTs were well uniformly dispersed in the composite films. Additionally, interaction between the HNTs and the CNF formed a strong network structure and the surface of the composite films were smooth. The crystal structure of cellulose I in the HNTs/CNF composite films can be determined by analyzing the X-ray diffraction pattern, and it was shown that the HNTs were well dispersed in the CNF. In addition, with the content of HNTs increasing, the crystallinity declined, the thermal stability of the composite films went up remarkably and the light transmittance of the composite films fell down. When the composition was 3HNTs, the tensile strength of the composite films can reach 41.9 MPa and the elongation at break can reach 11.7%. As the content of HNTs in the composite film rose up, the light transmittance of the composite film went down gradually, and it also reflected that the rise of HNTs content in the composite film leaded to an growth in the haze of the composite film. Moreover, the analysis of the chemical functional groups of the composite films and the observation of its microscopic morphology proved that the HNTs were uniformly dispersed in the composite films.

Spiral growth of kaolinite nanocrystals and its constraint to the morphology of kaolinite aggregation

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The morphology of kaolinite with different geologic origin was observed through high resolution backscattered scanning electron microscopy. The units of kaolinite layers form the pseudohexagonal nanocrystals with a diameter of around 100nm and a thickness of several tens of nanometers rather than a continuous uniform plate. We observed the spiral growth of kaolinite nanocrystals originating from their screw dislocations on the (001) plane, which is parallel to the positive Burgers vector corresponding with the spiral growth mechanism[1]. Accordingly, kaolinite layers are stacked helicoidally (Fig1. a).

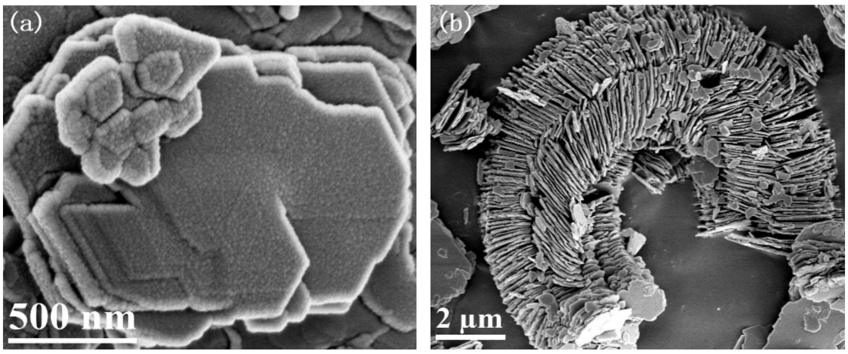

Figure1. (a) Kaolinite layers stacked helicoidally around the dislocation center; (b) Kaolinite present a worm-like aggregation.

The misfit between tetrahedral and octahedral sheets leads to spiral growth of kaolinite nanocrystals. Particularly, the lattice parameter of tetrahedron b_0 =0.927nm is slightly larger than the octahedron b_0 =0.864nm. This dimensional difference generates a twisting tendency which will result in a centripetal force. Thus, as the spiral growth proceeds, the lamellate unit stacks around a central axis caused by the centripetal force, ending with a book-like morphology instead of unrestricted morphology on the plane. This warped centripetal force furtherly forms a worm-like aggregation (Fig1. b) with the continuous stack of kaolinite layers. Simultaneously, it also generates a disordered structure in kaolinite crystal because of the spiral growth.

Keywords: Kaolinite; Nanocrystal; Spiral growth; Worm-like aggregation

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Nanoclay composites for biomedical application

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Nanoclay minerals with typically layered silicate structures, such as kaolinite, halloysite, and montmorillonite, have drawn the attention of researchers in the field of biomedical engineering owing to their nanosized structure, significant surface charge, and high adsorbability. Nanoclay-based haemostat has been externally applied for the management of massive haemorrhage due to their high absorption and biological inertness. Nanoclay minerals could interact with drugs and other biological molecules for controlled delivery, and their ability to interact with polymers to enhance the mechanical properties in the development of poly-clay nanocomposites for tissue regeneration.

Recently, we have developed benign approach to the general production of biomedical composites from nanoclay minerals. An emerging kaolinite-based composite (α-Fe_2O_3-Kaolin) was developed for hemorrhage control. α-Fe_2O_3-Kaolin can stop bleeding in approximately 183±16 s, and exhibits high wound healing ability, which was attributed to the efficient absorption of the fluid in blood, activation of blood platelets, and induction of the coagulation cascade by kaolinite and the aggregation of red blood cells induced by α-Fe_2O_3. Additionally, kaolinite has been intercalated with various organic guest species of different chain lengths to incorporated into drug delivery system. Doxorubicin (DOC)-kaolinite and the DOC-kaolinite intercalation compounds showed dramatically faster drug release in moderate acidic solution than in neutral condition, and exhibited enhanced therapeutic effects against ten model cancer cell cultures in a dose-dependent manner. Furthermore, mesoporous silica nanotubes (SiNTs) synthesized from halloysite have developed for the treatment of cervical cancer cells. Mn_3O_4 magnetic nanoparticles were anchored on the surface of SiNTs for magnetic resonance imaging, and DOX was loaded within the mesoporous walls of SiNTs for chemo-therapy. The DOX-Mn_3O_4-SiNTs multifunctional drug delivery system exhibited enhanced therapeutic effects for the simultaneous imaging diagnosis and chemotherapeutic application. Our results indicated the great potential of nanoclay composites for biomedical application.

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Methane/carbon dioxide partitioning in clay nano- and meso-pores: molecular dynamics modeling with constant reservoir composition

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The interactions among fluid species such as H_2O, CO_2, and CH_4 confined in nano- and meso-pores in shales and other rocks is of central concern to understanding the chemical behavior and transport properties of these species in the earth's subsurface and is of special concern to geological C-sequestration and enhanced production of oil and natural gas. The behavior of CO_2, and CH_4 are less well understood than that of H_2O. We present here the results of a computational modeling study of the partitioning of CO_2 and CH_4 between bulk fluid and nano- and meso-pores bounded by the common clay mineral montmorillonite. The calculations were done at 323 K and a total fluid pressure of 124 bars using a novel approach (constant reservoir composition molecular dynamics, CRC-MD) that uses bias forces to maintain a constant composition in the fluid external to the pore. This purely MD approach overcomes the difficulties in making stochastic particle insertion-deletion moves in dense fluids encountered in grand canonical Monte Carlo and related hybrid approaches. The results show that both the basal siloxane surfaces and protonated broken edge surfaces of montmorillonite prefer CO_2 relative to CH_4 suggesting that methods of enhanced oil and gas production using CO_2 will readily displace CH_4 from such pores. This preference for CO_2 is due to its preferred interaction with the surfaces and extends to approximately 20 Å from them.

Tuning the hydrophobicity of layer-structure silicates to promote adsorption of non-aqueous fluids: Effects of F^- for OH^- substitution on CO_2 partitioning into smectite interlayers

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The intercalation of non-aqueous fluids in the nanopores of organic and inorganic materials is of significant interest, particularly in the energy science community. Recently, XRD and computational modeling results have shown that structural F^- for OH^- substitution in layered silicates makes them more hydrophobic. Here, we use Grand Canonical Molecular Dynamics (GCMD) calculations to investigate how increasing the $F^-/(F^-+OH^-)$ ratio of a prototypical layered silicate (the smectite Na-hectorite) impacts the intercalation behavior of CO_2 and H_2O at elevated temperature and pressure. At the conditions of this study (T = 323 K, P = 90 bar, water-saturated CO_2), increasing F^- for OH^- substitution causes decreasing total CO_2+H_2O intercalation, increasing $CO_2/(CO_2+H_2O)$ ratios in the interlayer galleries, and an increasing energy barrier to CO_2 and H_2O intercalation. CO_2 intercalation is greatest at monolayer basal spacings, and the results support the idea that with Na^+ as the exchangeable cation the interlayers must be propped open by some H_2O molecules to allow CO_2 to enter the interlayer pores. The computed immersion energies suggest that the bilayer or a more expanded structure is the stable state under these conditions, in agreement with experimental results, and that the basal spacings of the minimum energy 2L structures increase with increasing F^- for OH^- substitution. The increase in the basal spacings for the minimum energy configuration is correlated to the decreasing H_2O and increasing CO_2 content which is most likely due to H-bonding disruption among H_2O molecules and higher probability for the formation of CO_2 clusters. These results are consistent with a wide range of experimental data for smectites at ambient conditions and elevated pressures and temperatures and suggest that F^- for OH^- substitution in conjunction with reduced structural charge and exchange with large, low charge cations may increase the ability of smectite minerals to incorporate hydrophobic species such as CH_4, CO_2, H_2, and other organic compounds.

Sepiolite as nucleating agent of extruded polystyrene composite foams

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Polymeric foams are porous materials formed by the inclusion of a gas in a dense polymer matrix. This type of material has been widely used in different industries due to an interesting combination of technical properties together with its low density (Bureiko et al., 2015). Extruded polystyrene (XPS) foam is obtained by combining the action of a nucleating agent and a foaming agent at high temperatures and pressures, each nucleus forming a cell in the foam. The number and morphology of cells determine to a large extent the technical properties of the material.

The nucleating agents reduce the nucleation-free energy, which produces a higher density of cells, but of smaller size. In this work we have evaluated the use of sepiolite (TOLSA, S.A.) as nucleating agent (1 wt.%) in the manufacture of XPS composite foams (Sep/XPS). The results have been compared with those of foams manufactured with talc (Granic 2281, GRC GROUP) (Talc/XPS). Foam containers were thermoformed from the sheets obtained by extrusion, whose mechanical properties have been determined in a digital dynamometer MTC – 100/500 (L). The morphology of the cells has been studied by optical microscopy (LEICA DMRM microscope) and scanning electron microscopy (Phenom™ G2 pro SEM 5 Kv, Eindhoven, The Netherlands).

The results reveal that Sep/XPS samples show higher mechanical strength than Talc/XPS samples. The analysis of the open cell percentage (OC) shows that there is no significant difference in this parameter. According to the OC parameter, the optical and electronic microscopy analyses confirm that the size ranges and density are similar in sepiolite and talc nucleated foams, and that there are no broken or collapsed cells. However, the Talc/XPS samples present a greater number of struts. In addition, Sep/XPS samples show a preferential growth of cells in the direction perpendicular to the extrusion, due to a preferential orientation of the cells.

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Influence of sample preparation on the microstructure of sand-clay mixtures

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This paper focuses on the influence of sample preparation on the microstructure of sand-clay mixtures, which were considered as simplified soils. Three different protocols to mix silica, kaolinite and water, corresponding to different orders of mixing, were tested in the laboratory to identify the one providing the most homogeneous microstructure. From the macroscopic to the microscopic scale, 3D X-ray tomography, 2D scanning electron microscopy (SEM), 2D environmental scanning electron microscopy (ESEM) and mercury intrusion porosimetry (MIP) were carried out on humid and dry samples. This study provides a first insight on the mechanisms of sand-clay mixing at micro scale. Preliminary results demonstrate that the microstructures of the samples show two types of clays: a thin clay layer which surrounds sandy grains, and a clay matrix. MIP results reveal a different density distribution function of porosity on the protocol of which correspond to sand then water then clay than the other two preparations.

Understanding the clay structure within these simplified soils brings microstructural features that will help to better explain the grain displacements and rotations during mechanical tests such as direct shear tests, to improve knowledge of soil’s deformation mechanisms at geotechnical interfaces.

Hierarchically porous adsorbent prepared from eco-friendly Pickering MIPEs for high-efficient adsorption of Rb^+ and Cs^+

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In this study, we prepared a novel hierarchical porous adsorbent based on surfactant-free Pickering medium internal phase emulsion (Pickering MIPEs) by using the natural palygorskite (termed as APT) and biopolymer chitosan (CTS) as synergistic stabilizer (Fig. 1). The stability of the O/W Pickering MIPEs can be increased greatly by the pH-induced assembly between APT and natural polymer CTS, and their droplet size was controlled easily by adjusting the morphology of composite particles *in situ* formed during the preparation process of emulsion. The hierarchical and interconnected pore structure and the pore size of the porous adsorbent APT/CTS-P(AM-AA) can be easily tuned by changing the pH values (Fig. 1). Due to the abundant $–COO^-$ and $–NH_2$ functional groups and unique porous structure, the as-prepared APT/CTS-P(AM-AA)adsorbent showed high adsorption capacities of 178.88 and 221.56 mg/g and rapid capture rate of 10 and 15 min (equilibrium time) for Rb^+ and Cs^+ ions, respectively. Moreover, it had excellent regeneration ability and reusability.

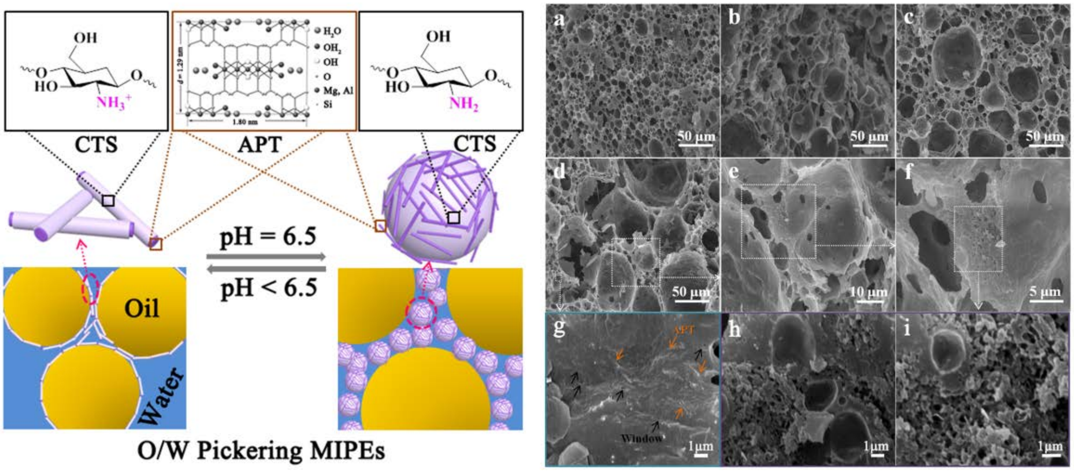

Fig. 1 Schematic representation of formation of APT/CTS composites and the stabilization mechanism of Pickering MIPEs at different pH and the SEM images of APT/CTS-P(AM-AA) prepared O/W Pickering emulsion stabilized by APT (1.0%) synergistically with CTS (1.0 wt.%) at (a) pH 3.5, (b) pH 4.5, (c) pH 5.5, (d-i) pH 6.5, respectively;

Investigation of layer charge density of dioctahedral smectites by the Rietveld method

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The knowledge of the structural property of natural smectites such as layer charge density (LCD), is essential to optimize their technical application. The Rietveld method is assumed to be an ideal method to study clays and clay minerals. However, the turbostratically disordered structure of smectites precludes the application of the classic Rietveld method. Ufer *et al*. (2004) proposed to overcome this limitation by using a single layer model with the BGMN program. The aim of this study is to prove the validity of the refinement of LCD by the Rietveld method and provide a new method for the structural characterization of smectites.

The Rietveld refinement was carried out on the diffraction patterns of the Cu-triethylenetetramine (Cu_{trien}) exchanged dioctahedral smectites to avoid the problems of unknown cation species and complex hydration behavior in the interlayer. Meanwhile, it offered a chance to obtain the information of LCD by refining the occupation of the Cu_{trien} complex in the interlayer.

Two structural models containing different atomic coordinates of TOT layers were chosen for montmorillonite-beidellite series (iron poor) and nontronites (iron rich). The Rietveld refinement was carried on measured patterns of purified samples. For montmorillonite-beidellite series, the refinement of LCD showed led to satisfactory results for profile fitting (Figure 1), but a tendency of underestimated values in comparison with the reference (Figure 2). For nontronite samples, the refinement of LCD showed similar underestimated results. It may due to the uncertain assumption of the Debye-Waller factor (Figure 2). The present study shows that the LCD can be determined by the Rietveld method from XRD patterns of the Cu_{trien} exchanged samples.

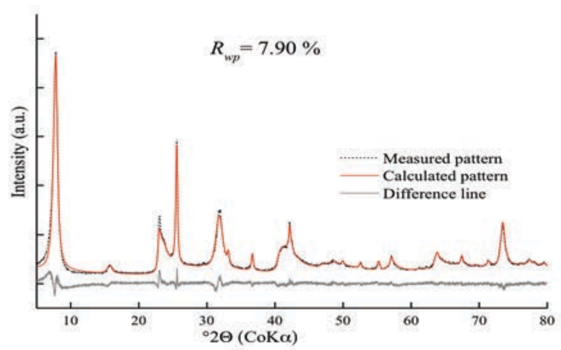

Figure 1. Refinement of purified Cu_{trien} exchanged sample XI_02

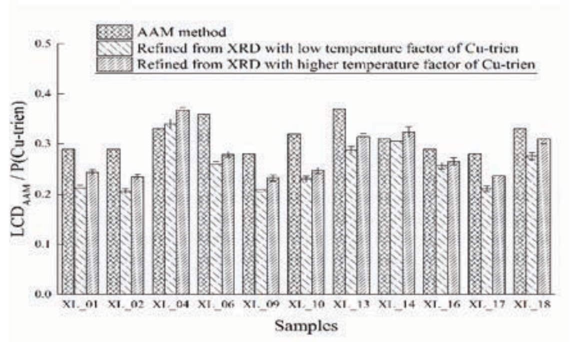

Figure 2. Rietveld refinement results of layer charge density P(Cu-trien), compared to the alkylammonium

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Localized Surface Plasmon Resonance of Noble Metals Supporting onto Titanate Nanosheets

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Liquid-phase synthesized titanate nanosheets (TNS) are rhomboidal and monolayered sheets. We can easily obtain the dispersion including uniform-shaped TNS from titanium alkoxide and tetraalkylammonium. Noble metals can be supported onto the surface of TNS by photodeposition method, because TNS have a photocatalytic property.

We suspended Au_2O_3 to TNS dispersion, and UV-irradiated in order for Au to be supported onto TNS surface. The dispersion of Au supporting onto TNS (Au/TNS) was colored red. In the same way, we obtained the yellow dispersion of Ag/TNS from Ag_2O and TNS. Maximum peaks of Au/TNS and Ag/TNS were laid about 525 and 430 nm, respectively in those absorption spectra (Figure 1.). Maximal wavelengths of Au/TNS and Ag/TNS were consisted with those of Au nanoparticles (NP) and Ag NP. The peaks of Au NP and Ag NP at 525 and 430 nm are assigned to absorption by localized surface plasmon resonance (LSPR). Therefore, these results suggest that Au/TNS and Ag/TNS have the characters of LSPR.

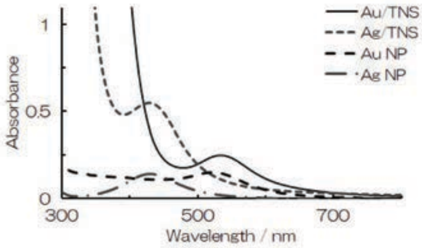

Figure 1. Absorption spectra of Au/ TNS, Ag/TNS, Au NP and Ag NP

Transmission electron microscope (TEM) images of TNS, Au/TNS and Ag/TNS are shown in Figure 2. Shapes of all TNSs were rhombus (long axis: 30 nm, short axis: 20 nm). We could find some black points on corners of Au/TNS and Ag/TNS, but couldn't on that of TNS. We speculated that these spots were Au and Ag supported onto TNS surface. In addition, the diameter of the black points on Au/TNS were about 6 nm. The diameter of Au spots was obviously smaller than 25 nm which was the estimated diameter from the maximum wavelength in the Au/TNS absorption spectrum. On the other hand, the estimated diameter mostly matched the size of TNS. We concluded that the LSPR of Au/TNS was due to collective electron oscillation which occurred not only on the surfaces of Au particles, but also on those of whole sheets.

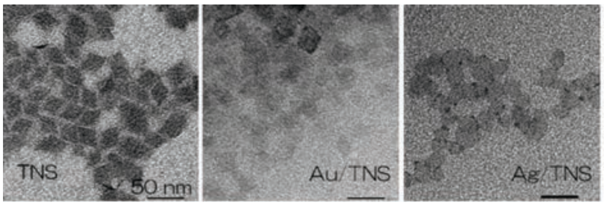

Figure 2. TEM images of TNS, Au/TNS and Ag/TNS.

Thermochromic response of smectite-organic dye hybrid materials

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Switching of spectroscopic character is important for development of sensor, electronic materials or smart materials. Interlayer space of smectite is known to be tuneable nanospace. Therefore, spectroscopic property of dyes in the interlayer space of clay can be controlled by tuning interlayer nanospace[1]. In this study, we focused on hydration and dehydration of clay. There are two types of water in interlayer space of smectite. One is bulk water which is main actor of interlayer water and other is protic water which is neighbouring to exchangeable cation or layer surface. Since protic water strongly blinded to cation or layer surface. Remove of the bulk water is occurred to obtain protic character of interlayer nano-space at the first stage of dehydration [2]. This enables protonation of intercalated dyes. Therefore, by employing pH responsive dyes of which color is changed at acidic condition, clay based thermochromic materials should be obtained.

As pH responsive dyes, crystal violet (CV), malachite green (MG), thymol blue (TB), methyl orange (MO) were employed. Smecton SA (saponite synthesized by Kunimine Industries) was used as a smectite. These chemicals are hybridized by ion-exchange reaction at the loading of typically 5%CEC.

Dehydration of hybrid caused by heating was confirmed by powder X-ray diffraction measurements and thermogravimetric analysis. All of the hybrids exhibited color change by heating indicating that the neutral form of dyes was change to protonated form. As a example, temperature dependence of absorption spectra of MG were shown in figure 1. At the 30 ^{o}C, strongest absorption band was observed at around 630 nm. This absorption spectrum is corresponding to that of neutral form of MG. On the other hand, at the 120 ^{o}C, strongest absorption band was observed at around 490 nm, which is corresponding to that of protonated form of MG. Also, this thermochromic response was found to occur gradual manner to the change of temperature. Absorption spectrum of hybrid at 120 ^{o}C was found to recovered to that at 30 ^{o}C under room temperature and normal humidity. Much slower recovery was also observed under dry condition such as in desicator. These behaviors were indicating color change was occurred by increasing and decreasing of protic/bulk water ratio due to dehydration and hydration.

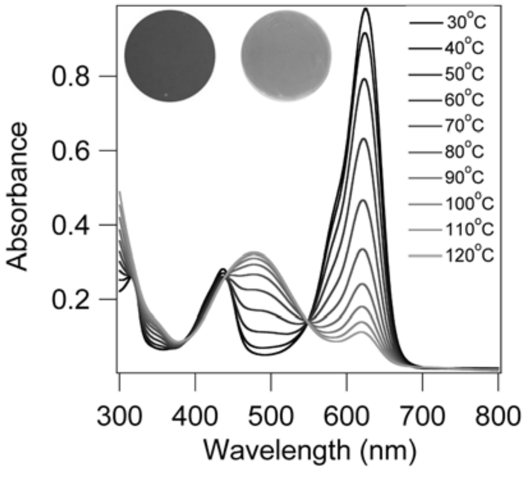

Figure 1 Absorption spectra of MG under various temperature with a range of 30 ^{o}C to 120 ^{o}C.

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Activation of Halloysite and Kaolinite by Introducing Lanthanum Oxycarbonate Nanoparticles via Co-calcination for Efficient Phosphate Removal

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Introducing reactive nanoparticles to support is a common strategy for adsorption. However, the poor reactivity of the support and its high cost of preparation constitute big disadvantages that limit its practical applications, such as for water purification. Here we show a synergistic host–guest coupling between halloysite/kaolinite clay and lanthanum oxycarbonate (LO) nanoparticles for efficient removal of phosphate from aqueous solutions. For the coupling, co-calcination of the nanoparticle precursor and the clay leads to disordering the clay unit layer to form Al_2O_3 nanoparticles, which act as the activated sites for phosphate adsorption; meanwhile, the architecture and properties of the clays enable the LO nanoparticles to anchor homogenously on the clay surfaces, thoroughly utilizing their adsorption ability. The activated halloysite/kaolinite-based nanohybrid exhibits an excellent phosphate adsorption capacity. The synergetic actions and multiple capture mechanisms are investigated by spectroscopic methods. The established strategy is applicable to a wide range of functional nanomaterials, acting as a generic platform for a range of water treatment applications.

Transformations of clay minerals in soils under the influence of chemical changes induced by long-term fertilizing experiments

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The problem of mutual relations between the physicochemical properties of the soil environment and soil mineral substrate is a fundamental issue in soil science, agricultural chemistry and agronomy. The most important are clay minerals that comprise the smallest soil fractions. Studies have shown that under conditions of prolonged excess of an ingredient or its deficiency, significant transformations of soil clay minerals can occur. Long-term fertilizer experiments are particularly useful for identifying these phenomena.

The studies were carried out at the Warsaw University of Life Sciences (SGGW) Experimental Station in Skierniewice town (central Poland) where long-term (100 years) fertilization treatments have been carried out. The research objects were soils to which various types of chemical components have been added in the following combinations: (1) N and P, (2) N, P, and K, (3) Ca, N, and P, and (4) Ca, N, P, and K. The soil samples were taken from the A horizon of sandy-loamy Planosols (WRB) developed from the glacial sediments. The main method applied was XRD, with the use of Bruker AXS D5005 diffractometer. Clay fraction (< 2 mm) was obtained without pre-treatment.

In general, the soil samples consist of quartz, feldspars and clay minerals. Diffraction patterns of clay fractions show the presence of 10Å peak (illite) as well as 12Å and 14Å peaks of the minerals, which content and origin are thought to be dependent on the nutrition combination. Beside the aluminosilicate minerals, lepidocrocite also occurs in clay fraction. Extension of the 14 Å peak at the expense of 10Å peak reduction is well visible on the diffraction patterns of the samples from K-deficit soil (NP nutrition). This can be assigned to formation of new soil clay minerals of intermediate type, most likely hydroxy-interlayered minerals (HIMs). On the other hand, in the samples from K-excess soil (NPK nutrition), distinct depletion in 14Å minerals is noted. In case of CaNP and CaNPK nutrition combinations, clay minerals structure stabilization is being observed. This is thought to be connected with the presence of Ca, which causes neutral soil reaction. Similar phenomenon of structure stabilization occurs also by manure fertilization.

We speculate that changes of clay mineral properties observed in our research are caused by applying different kind of fertilizer. In case of K-deficit, unstable illite structure undergoes destruction with the release of Al (mainly), which (in form of polymer hydroxy-Al cation) can be adsorbed in the interlayer space of 2:1 layer type clay minerals. By the K-excess, described phenomenon can be stopped and can even lead to incorporation of K into the illite structure.

The presented transformations of clay minerals can occur both in soils covered by intensive cultivation systems with a high level of fertilization as well as in soils used for a long time in agriculture and low agrotechnical culture. The consequence of mineralogical transformations are changes in such important soil properties as: sorption capacity, content and mobility of some components (mainly potassium), pH value, etc.

Removal of chromate from wastewater using modified montmorillonite obtained by intercalation with Iron and Aluminum

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Chromium is a heavy metal which can be found in the environment predominately at two of its most stable states, Cr(VI) and Cr(III), characterized by different toxicity, chemical behavior and mobility[1]. The application of bentonite clay and modified bentonite clay as adsorbent for removal of Co (II) Pb (II), Cu (II), Cr (III), Cr (VI), Ni (II), Hg (II), Cd (II), and Zn (II) metal ions from water have been considered immensely in last ten years. The different reaction conditions for adsorption including initial concentration of metal ion, interaction time, adsorbent quantity, pH of the solution etc. are critical for the adsorption studies [2]. Therefore its removal from waste water is considered to be very important. This study presents the results of chromate adsorption upon modified montmorillonite obtained by intercalation with Iron and Aluminum. The intercalation of this clay by mixed Aluminum-iron pillars allowed us to obtain d001 distances of 19 Å, the thermal treatment led to the formation of a microporous solid. Natural and pillared montmorillonite were characterized by X-ray diffraction, thermal gravimetry, Fourier transform infrared spectrometry and Mössbauer spectroscopy of iron-57 which proved this intercalation. The Mössbauer spectra of iron-57 for the different samples showed the existence of two Fe^{3+} species occupying two different sites. The species with the small quadrupol splitting are attributed to the iron incorporated into the aluminosilicate structure of the clay. While the other species represents the exchanged iron. In most cases the thermal treatment of the clay causes a decrease in the isomer shift, which shows that the bonds of the atom with its environment become more covalent. The heat treatment also causes an increase in quadrupol splitting reflecting a distortion of the environment of the iron atom.

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Removal of Malachite Green Dye onto Natural Clays: Equilibrium Isotherms and Kinetics Studies

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The adsorption of malachite green (MG) on two natural clays from Kenadsa in Bechar region (south of Algeria) has been studied in order to test the useful of this abundant material to remove basic dyes from wastewaters. Different experimental parameters such as time of adsorption, dye concentration, pH and temperature were carried out to calculate the adsorption capacity.

The samples clays of Kenadsa region are mainly composed from SiO_2 (>55%) and Al_2O_3 (>18%) followed by Fe_2O_3 , K_2O and MgO. The adsorption results indicate that basic pH solution favored the uptake of malachite green dye and at $pH<3$ the amount of adsorbed dye strongly decreases. Thermodynamic studies show that MG adsorption on studied clays is endothermic and spontaneous in nature. The kinetic data obey the pseudo second order kinetic model and equilibrium isotherms are well fitted by Langmuir isotherm.The maximum adsorption capacity of MG calculated from Langmuir isotherm model are 160.2 and 107.5 mg/g for CKV and CKB, respectively.
Finally, the results indicate that the natural clays could be employed as low-cost alternative adsorbent for removal of cationic dye from industrial wastewater.

The influence of acid modification on the sorption of radioactive and stable isotopes of Cs and Sr on bentonites

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Bentonites have a variety of application in different industries. Due to the high sorption capacity they are used for the protection of the environment from toxic and radioactive waste. Bentonites and bentonite-based materials may be used for the landscape and water remediation and also for the hazardous waste storage. One of the important demands nowadays is the radioactive waste management. However, in worst scenarios bentonites could be subjected to the rather aggressive environment. It could sufficiently change their properties so it is very important to know the stability of bentonite structure, properties and integrity of the bentonite buffer material. The best option to examine stability of the bentonite properties is to conduct experiments similar to the operational or critical conditions which, though, could be rather costly in terms of resources and time. Acid treatment at high temperatures is extremely aggressive for montmorillonites as the main component of bentonite and is quite accessible under laboratory conditions. Thus, it was decided to assess the stability of the adsorption properties of bentonites by treatment with the nitric acid.

Five bentonites with different structural features and genesis from industrial deposits in Russia and the near abroad, which are promising for use to isolate radioactive waste were selected. Thus, the industrial samples of bentonites from the Taganskoe, Dashkovskoe, 10th Khutor, Zyryanskoe, Dash-Salakhlinskoye deposits served as objects for the study. Acid treatment was carried out in 13M HNO_3 solutions at 90 °C for 1 and 5 hours at a solid-to-liquid ratio 1:100 on the magnetic stirrer under reflux. Solids were then separated with centrifuge and washed with deionized water until the neutral pH was achieved.

Mineral composition of bentonites and the structural features of montmorillonites were investigated with X-ray diffraction analysis and FT-IR spectroscopy. Dehydration and dehydroxylation behavior were studied with the thermal gravimetric analysis. Adsorption properties of natural and acid treated samples were evaluated by cation exchange capacity determination and adsorption of stable and radioactive isotopes of Cs and Sr from water solutions.

In the result of this research several factors that have the strongest influence on the stability of montmorillonite structure and properties were revealed: Fe_{oct} content, organic matter, *cis-/trans*-vacancies arrangement. This work was supported by the Russian Science Foundation project #16-17-10270-P

Microstructure and micromechanical properties of EDZ, tectonic, and drilling-induced fractures in the Opalinus Clay shale

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The Opalinus Clay shale (OPA) has been chosen as a potential host rock for Switzerland's high- and low-level nuclear waste. As such, a comprehensive characterization of the OPA at different spatial scales and through time is required to assess its long-term behaviour with respect to repository safety and integrity. Self-sealing processes are considered important for safe, long-term storage and are in the focus of the SE-P (Self-sealing Processes) project supported by the Swiss Federal Safety Inspectorate (ENSI), the Swiss Federal Office of Topography (swisstopo), the German Federal Institute for Geosciences and Natural Resources (BGR), and Radioactive Waste Management Limited (RWM) from the UK.

We have conducted in-situ experiments in selected underground galleries at the Swiss Mont Terri Underground Research Laboratory (MT URL) in St. Ursanne that aimed at investigating the evolution of the Excavation Damaged Zone (EDZ) at tunnel (27–35 m) and borehole (4.5–6.5 m) scales over 10 and 20 years. We have taken samples of rock fractures (EDZ, tectonic, and drilling-induced fractures) from boreholes drilled into two EDZs of 10 and 20 years age at the MT URL to identify what sealing processes have occurred since gallery excavation (compare with Williams et al. EuroClay2019). This study's focus is on the microstructural and micromechanical properties of selected fracture samples.

Fracture samples were scanned with an ATOS Core 300 3D scanner in order to conduct fracture roughness and morphology analyses prior to structural and mechanical testing. We aim at presenting a comparison of fracture microstructural results obtained by scanning electron microscopy (SEM) image analyses with fracture stiffness properties inferred from micro-indentation tests for different types of fractures and for intact Opalinus Clay shale specimen from inside and outside the EDZ.

Crystal growth of illite in Pennsylvanian shale of the American Mid-Continent region – inferences from clay mineralogy and K-Ar ages

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Paleozoic successions of Anadarko Basin in the central United States are largely composed of shale intervals and have historically been known as major hydrocarbon sources. Lately their importance arises from the perspective of unconventional reservoir exploitation. Clay mineral evolution in these sediments and, in particular, the processes related to illite growth have, however, remained relatively under-researched.

K-Ar data on illite has been proven to be very useful for the understanding of illitization processes in shale. Still, dating of mudstone by the K-Ar method may reveal a range of ages that are older, younger or coincide with stratigraphic ages. Illite particle nucleation-growth process acts as a major control on K-Ar ages that occasionally may be significantly different than expected.

This research examines Paleozoic shale of the Anadarko Basin cored at depths from 2980 to 3160 m. Based on comparative mineralogical data, X-ray diffraction (XRD) and electron microscopy (SEM-EDS) performed on three illite fractions (<2 µm, <1 µm, and <0.2 µm), and K-Ar age investigation, in this contribution we report on the mechanism of crystal growth of illite. Our preliminary results showed that the finest illite fraction yields about 20 Ma younger K-Ar ages than coarser particles. Furthermore, XRD and SEM-EDS data showed a dominance of smectite component in <0.2 µm fraction, while the <2 µm fraction has abundant illite.

It is generally accepted that K-Ar ages younger than the sedimentation age may result from (1) the diffusional loss of radiogenic ^{40}Ar, (2) loss of ^{40}Ar derived from the K initially found in expandable layers of mixed-layer phases, and (3) addition of K induced by burial diagenesis that in turn increases the K-Ar ratio and lowers measured ages. Detrital illite and feldspar are considered as feedstock of K needed for the illitization to proceed.

Taking into account our mineralogical and isotopic data we hypothesize that the illitization of the illite-smectite mixed layers of progressively buried shale was essentially controlled by solid-state transformation processes followed by the fast precipitation and crystal ripening of illite particles.

Genesis of palygorskite from Baiyanghe Formation of Neogene in Yangtaiwatan basin, north Gansu province, China

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Baiyanghe Formation of Neogene in Yangtaiwatan basin, north Gansu province overlain by Quaternary sand bed with thickness of 0 to 2m is represented by the continental sedimentary cycle of piedmont-pluvial face, fluvial face and lacustrine face, which is mainly composed of pebbly sandstone, sandstone, pelitic siltstone and silty mudstone. In the upper Baiyanghe Formation, the interbedding of pelitic siltstone, silty mudstone and thin gypsum bed were deposited. A series samples in two profiles under quaternary sand bed showing transitional lithofacies, namely pelitic siltstone and silty mudstone, were collected and analyzed using mineralogical methods. The mineral composition of pelitic siltstone are dominated by quartz (30% ~ 40%), feldspars (10% ~ 15%), dolomite (10% ~ 20%), and clay minerals (30% ~ 48%). The minerals in silty mudstone are more complicated and dominated by quartz (2% ~ 10%), feldspars (3% ~ 7%), calcite (2% ~ 10%), dolomite or ferrodolomite (0 ~ 15%), analcite (0 ~ 10%), and clay minerals (50% ~ 80%). Interestingly, the dominant clay minerals in pelitic siltstone are palygorskite (50% ~ 85%) followed by illite (10% ~ 20%), interstratified illite-smectite (0 ~ 10%), and chlorite (5% ~ 10%). While for the silty mudstone, no palygorskite is observed, and the dominant clay minerals are interstratified illite-smectite (60% ~ 75%) followed by illite (20% ~ 40%) and rare chlorite (0 ~ 5%).

The palygorskite only occurs in pelitic siltstone formed under the shore shallow lake environment. Towards deeper lake environment, the clay minerals are dominated by the interstratified illite-smectite in sediments. The scanning electron microscope (SEM) (Fig. 1) of separated clay minerals from pelitic siltstone displays that palygorskite mixes irregularly with other associated clay minerals, indicating the palygorskite in pelitic siltstone was not transformed directly from other clay minerals. The results show that palygorskite in present study is more favorably coexist with quartz and dolomite. It is reasonable to conclude that the palygorskite in pelitic siltstone is authigenic under specific conditions such as high Mg and Si activities and alkaline pH.

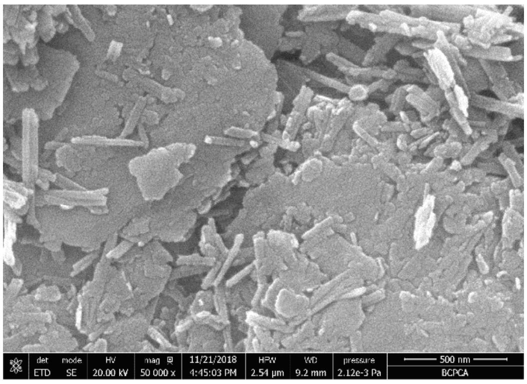

Fig. 1. SEM of separated clay minerals from pelitic siltstone, where the tubular mineral is palygorskite, the lamellar mineral is illite or interstratified illite-smectite.

The crystal growth of smectite: A study based on crystal-chemistry and morphology

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Smectites are 2:1 type swelling clay minerals widely distributed in the Earth's crust. The unique structures and properties endow them with various applications in many fields. However, little is known about the crystal growth process of these clay minerals. In this study, we tried to explain and understand this growth process and pattern from the perspective of crystal-chemistry and morphology. Smectites were synthesized by mixing 2 precursors with defined chemical compositions under diverse conditions, and their crystal-chemistry and particles size were investigated. A series of Ni and Mg-smectite precursors were hydrothermally synthesized under different temperatures (150, 220 °C). Mg and Ni-smectite precursors obtained in same temperatures were mixed with identical molar weight, and reacted at 220 °C under autogenous pressure for a certain period. All the precursors, as well as further synthesized samples are identified as smectite by X-ray diffraction analysis (XRD), and Fourier-transform infrared (FTIR) spectroscopy. The crystal-chemistry (distribution of octahedral cations) from *v*OH and the morphology (particle size) obtained by argon adsorption reflect the growth occurring during the hydrothermal treatment. For the precursors synthesized at lower temperatures (150°C), after hydrothermally treated at 220 °C, $v\mathrm{Mg_2NiOH}$ and $v\mathrm{Ni_2MgOH}$ bands occur when hydrothermal periods prolonged. Argon adsorption results indicate that particle size increases with the intensities of $v\mathrm{Mg_2NiOH}$ and $v\mathrm{Ni_2MgOH}$ increase. These are indicative of the neo-formed Mg-Ni mixed smectites from the rearrangement of Mg and Ni smectite precursors. The basal and edge surface areas of the nontronite particles and their mean diameter and thickness increase with hydrothermal period extension. These results indicate that the coarsening of smectite particles occurs via dissolution/recrystallization and epitaxial growth. Whereas for the Ni and Mg precursors hydrothermally synthesized at higher temperature (220°C), only $v\mathrm{Mg_3OH}$ and $v\mathrm{Ni_3OH}$ bands were observed, and no growth of the precursors could be evidenced from argon adsorption, even for the experiment up to one month long. It is a sensible and effective method to investigate the growth of smectite based on crystal-chemistry and morphology. This growth pattern obtained by crystal-chemistry and particles size is of eminent importance for better understanding of the growth process of smectite, as well as other clay minerals.

Keywords: Smectite, Crystal Growth, Crystal-chemistry, Argon Adsorption, FTIR

Effect of CO_2 on stress-strain cycling behaviour of smectites under geological storage conditions

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The swelling-shrinkage behavior of smectites induced by interlayer uptake or sorption of CO_2 and H_2O has been investigated with increasing interest recent years, for its potential impact on sealing efficiency of clay-bearing caprocks overlying CO_2 storage reservoirs. To get a better a better understanding of the stress-strain-sorption coupling in smectite exposed to supercritical CO_2, we performed multiple stepwise axial loading and unloading, oedometer-type experiments on ~1mm thick discs of pre-pressed Na-SWy-1 and of Ca-SAz-1 montmorillonite. Initially air-dry (AD) samples were first tested in the presence of wet CO_2 (20% RH) at 10 MPa pressure, and in the vacuum-dry (VD) state in the presence of pure (dry) CO_2 at 10MPa. The samples were incrementally loaded and unloaded at 40°C, employing effective stresses ranging from 0.5–44MPa. Control tests using wet and dry He or Ar instead of CO_2, were performed to distinguish strains due to loading related CO_2 sorption/desorption from purely poroelastic effects. All samples saturated with CO_2 exhibited 30-65% lower apparent stiffness moduli than when saturated with He or Ar, showing that CO_2 adsorption altered the mechanical response of pre-pressed smectites. Relative to the He and Ar tests, swelling strains of a few % (corrected for poro-elastic effects) were measured for AD Na-SWy-1 smectite exposed to wet CO_2, decreasing from 4.9% to 3.8% with increasing effective axial stresses in the range 1.6 –36.2 MPa. AD SAz-1 material exhibited similar tends. VD samples tested with dry CO_2 showed much smaller relative swelling strains (0.5–1.5%), which also decreased with increasing applied effective stresses. The experimental data on relative swelling strain versus effective are well fitted by a recent thermodynamic model for stress-strain-sorption behaviour in coal, though further refinements of this model are needed for broader application to the smectite-CO_2-H_2O system.

Structural characterization of chlorine Layered Double Hydroxides

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The detailed structural characterization of Layered Double Hydroxides (LDH) still remain a challenge that arises from the rarity of crystals suitable for single-crystal X-ray diffraction (XRD). However, natural samples can help to pass this challenge.

Recently we have studied two chlorine LDH minerals: chlormagaluminite, $Mg_4Al_2(OH)_{12}Cl_2(H_2O)_2$ and iowaite $Mg_6Fe^{3+}{}_2(OH)_{16}Cl_2(H_2O)_4$ by different methods including single-crystal XRD. Chlormagaluminite was found in 2*H* polytype with ordered localization of Mg and Al according to $\sqrt{3} \times \sqrt{3}$ superstructure within the metal-hydroxide layers. The interlayer space can be considered as consisting of trigonal prisms formed by H atoms of the metal-hydroxide layers (Bookin and Drits, 1993) that host Cl atoms at their centers and water molecules in the vertical edge middle points. The general architecture of the interlayer arrangement of chlormagaluminite is principally different from that of carbonate LDHs. Iowaite was found in 3*R* polytype with disordered localization of Mg and Fe^{3+} within metal-hydroxide layer, i.e. there is one *M* site occupied by $Mg_{0.75}Fe_{0.25}$. The interlayer arrangement is similar to that of chlormagaluminite with more pronounced disorder of interlayer water molecules.

The characteristic subcell parameters are $a`$ = 3.04, $d$ = 7.65 Å for chlormagaluminite and $a`$ = 3.11, $d \approx 8.0$ Å for iowaite. The difference in $a`$ is due to cation seize of M^{2+} and M^{3+}, while the difference in *d*-value reflects the strengths of interaction between metal-hydroxide layers and interlayers, i.e. *d*-value is a function of M^{2+}:M^{3+} ratio (because only M^{3+} cations contributes to the charge of metal-hydroxide layers). Therefore *d*-values of 7.65 and 7.80 Å can be used as reference points for chlorine LDHs having M^{2+}:M^{3+} = 2:1 and 3:1, respectively. The M^{2+}:M^{3+} ratio can be determined from *d*-value or *vice versa* using a linear correlation between these two components similar to that of carbonate LDHs (Zhitova et al., 2016). The characteristic *d*-values and tilt angle of linear function between *d*-value and M^{2+}:M^{3+} cation ratio differ for chlorine and carbonate LDH due to difference in the bond strengths shared between anion and metal-hydroxide layers.

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Co-existence of Clay Minerals and Nano-sized Cerium Mineral in Bachi Rare Earth Deposit, in Guangdong Province, China

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Weathered crust rare earth deposit (i.e., ion-adsorption clays) is one of the most significant rare earth deposits, where rare earth elements (REE) generally exist as ions or hydrated ions adsorbed on clay minerals in weathered crusts. Among REE, cerium (Ce) is the only element that can be oxidized from trivalent to tetravalent form (typically exist as insoluble cerianite, i.e., CeO_2) under natural oxidation environment. Generally, the formation of cerianite is closely related to the adsorption and oxidation of Mn oxides in weathered crusts. Meanwhile, previous studies also pointed out that the occurrence of cerianite is associated with clay minerals, e.g., halloysite. However, the relationship between cerianite and clay minerals is still ambiguous due to the small size and low content of cerianite in weathered crusts.

In this study, we collected samples from a tuff-weathered profile in Bachi REE deposit, a typical weathered crust rare earth deposit in Guangdong, China. Fine particles (diameter < 2 μm) were separated from bulk samples by sedimentation method and analyzed using inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The chondrite-normalized (N) REE patterns reveal that Ce anomaly in fine particles was different from that in bulk samples. Besides, the chemical analysis results show that the concentrations of Ce and the values of δCe ($\delta\mathrm{Ce} = \mathrm{Ce_N}/\sqrt{\mathrm{La_N}\times\mathrm{Pr_N}}$) were clearly higher in the fine particles that mainly composed of halloysite and kaolinite with abundant structure defects. These results indicate that Ce behaved differently as compared to other REE in the profile during weathering of tuff. Meanwhile, the nano-sized cerianite with poor crystallinity was observed on surfaces and edges of clay minerals. Moreover, Mn oxides were not co-exist with cerianite and no evidence for the correlation between Ce and Mn in these samples was found by chemical analysis. Thus, the formation of these nano-sized cerianite in the profile of Bachi deposit is mainly associated with clay minerals rather than Mn oxides, through adsorption of Ce ions by clay minerals and the subsequent oxidation from trivalent to tetravalent by oxygen. These findings are of great importance for understanding the migration, fractionation, and aggregation of Ce during the weathering process of bedrock, in particular, for the formation of cerianite, in these REE deposits.

Layered double hydroxides-based catalysts for electrochemical water splitting

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Hydrogen, as an eco-friendly energy resource with the highest energy density, has attracted lots of attention due to the current environmental and energy crisis, while its efficient production has been the bottle neck of the application of hydrogen. Electrochemical water splitting can potentially be the answer for industrialized hydrogen production. The electrode design and fabrication are always the key to lower the reaction overpotential and increase the energy efficiency. Our group has developed and advanced constructing unique cations moiety[1], doping[2-3], intercalating, introducing defects and strain[4] in layered double hydroxides-based materials for oxygen evolution and water splitting. Furthermore, constructing nanoarray structure (superaerophobic for gas evolution reaction) would also be beneficial for boosting catalytic efficiency by exposing more edge/unsaturated active sites and managing the bubbles behavior.[5-6] Our strategies based on layered double hydroxides-based materials involve both investigating microcosmic structure-activity relationship and macroscopic bubbles behavior, and shall open a new door for the development of water-splitting technologies and energy conversion.

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Multiscale Modelling of Clay Aggregate Behaviour

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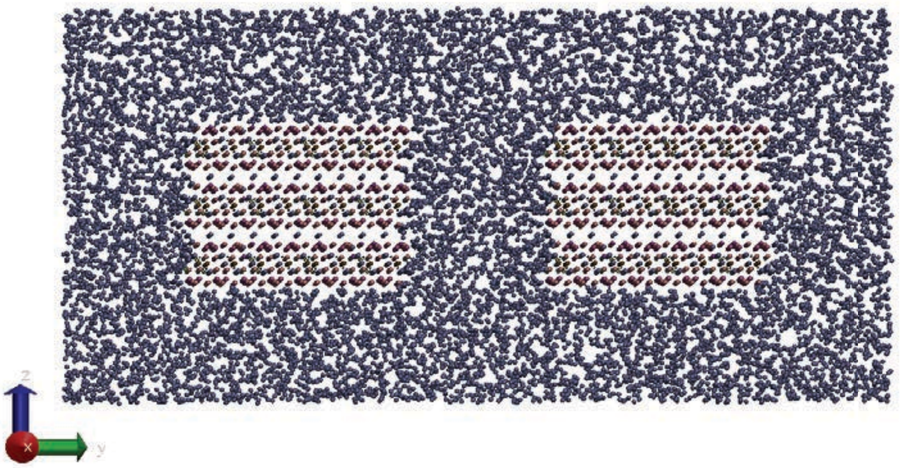
Clay is one of the most important industrial material with wide applications in civil, environmental, and medical engineering. Understanding the aggregation of clay particles is crucial to a better understanding of clay properties at different length scales. In this presentation, a multiscale approach will be presented. In this approach, inter-particle interaction will be studied at nano-scale through molecular dynamic simulation, from which the potential of mean force (PMF) will be used in meso-scale simulation through coarse-graining technique. Nanoscale and mesoscale simulation results of two types of clays, of which imogolite has tubular primary particles and illite platy particles, will be presented. Imogolite-like materials are potentially useful in medical and material sciences due to its strong monodispersity and controllable diameter. Researchers have studied the chemical composition, atomistic structure, and methods to control the diameter and thermomechanical properties of a single tube. Illite is commonly encountered in geotechnical engineering projects due to its abundance in the earth crust. This study will provide good guidance for both industries. The methodology in general can find its application in many other fields.



Inspiration from Maya blue: a new durable pigment with super-hydrophobicity based on nanotubular halloysite

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Inorganic-organic hybrid pigments based on Halloysite and indigo were prepared and then covered via chemical interactions with polyorganosilane (POS) to avoid any fading or chemical fragility in acidic, basic and organic medium (see Fig. 1).

The hybrid pigments were prepared by grinding method, and then covered with POS. X-ray diffraction and transmission electron microscopy results indicated that loading of dyes and covering with POS did not influence the crystal structure and morphology of Hal. Two conclusions can be drawn from the solid state nuclear magnetic resonance (NMR) results: (i) indigo interacts with Hal surface via hydrogen bonds; (ii) POS covered on the surface of Hal by grafting. Reflection spectra and CIE 1976 color space system were used to evaluate the color of pigments. Thermal stability, chemical resistance to ethanol, HCl and NaOH, and light fastness to visible lights (equals to 28 years in a common museum) were tested. Compared with the hybrid pigment without covering, hybrid pigments with POS showed similar color, but better resistance to high temperature, chemicals and visible light, due to the hydrophobic surface which can prevent indigo molecules from oxidation and other chemical reaction. A new route was proposed to prepare durable organic-inorganic hybrid pigments, ignoring the interaction between dye molecules and substrates.

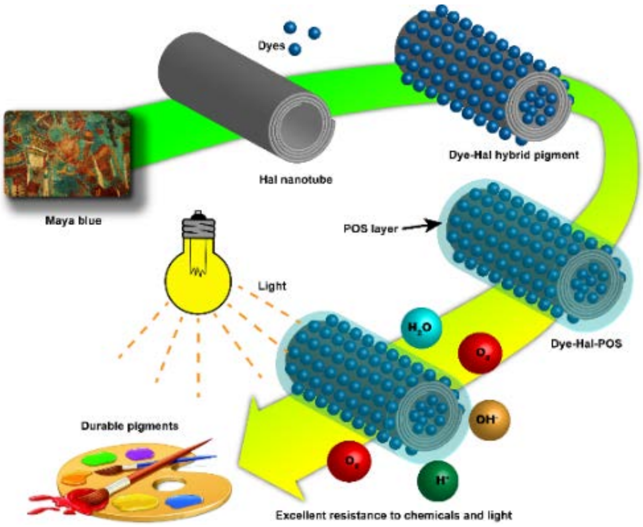

Fig. 1 Schematically interpretive diagram for the preparation and stability of hybrid pigments.

High-pressure adsorption of methane on clay minerals – texture versus structure

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Methane (CH_4) adsorbed under high pressure in clay-rich sedimentary rocks is one of the key components of gas production and storage. Along with organic matter, clay minerals provide significant volume of microporosity and specific surface area for CH_4 adsorption. However, the position of adsorption sites of CH_4 in clays is still unclear: whether the interlayer in expandable clay minerals is accessible for CH_4, or the adsorption takes place only on the external features of the crystallites. If the latter is correct, what is the influence of the clay crystallites' texture?

In the present study, two types of expandable clay minerals (SAz-1 "Cheto" montmorillonite; Mtm, and SBId-1 beidellite; Bld) and two species of illitic material (Le PUY lacustrine illite of <0.02 µm fraction, and bulk sample of hydrothermal Zempleni illite) were selected. Transmission electron microscopy (TEM) method allowed determination of the average planar diameter of the crystallites: 35 nm for Le PUY illite, 145 nm for Mtm, 320 nm for Bld, and 395 nm for Zempleni Illite. The smectites' interlayer cations were exchanged for selected cations of very different hydration properties and atomic radii. Prior to high-pressure CH_4 adsorption analysis, portions of strongly clay-bound water were subsequently removed during monitored *in situ* drying steps (60 - 210 °C under vacuum). Based on the very high CH_4 adsorption on Tetramethylammonium-exchanged (TMA) Mtm, the evolution of the interlayer distance tested during in-situ drying in X-ray diffraction (XRD) experiments, and series of Gibbs Ensemble Monte Carlo (MC) simulations, CH_4 entered the interlayer of TMA-exchanged Mtm. CH_4 adsorption on divalent-cation exchanged Mtm and Bld (Mg^{2+}, Ca^{2+}) decreased significantly after water removal, whereas Cs- and Li-exchanged Mtm's isotherms were insensitive to drying temperature. Additionally, divalent cationic forms of smectites showed hysteresis after the drying at 60 °C. Strong correlation of the maximum adsorption with the inversed planar surface of the crystallites (from TEM), and correlation between specific surface area from subcritical nitrogen adsorption and maximum adsorption of CH_4 were observed. In addition, disorientation and strong orientation of Na-exchanged Mtm sample resulted in a significant change in CH_4 adsorption, counterintuitively increasing CH_4 adsorption on the highly oriented sample. The shapes of the adsorption isotherms on both illite samples, where CH_4 intercalation could not occur, were the same, but differed from that of TMA-exchanged Mtm sample.

We conclude that CH_4 can enter the interlayer of the expandable clay minerals when it is pillared by large organic molecules. In inorganic cation exchanged smectites, CH_4 may enter the interlayer only when it is wide enough and stabilized by cations surrounded by strongly-bound water molecules. However, in smectites saturated with inorganic cations, the external adsorption sites are predominant, and adsorption in the interlayer is minor, resulting in observed hysteresis as kinetic effect of slow diffusion in ultra-narrow pores.

Acknowledgments:

The study was financed by National Science Centre, Poland; grant no.
2017/25/N/ST10/02034

Quantification of minority minerals present in clays related to acid emissions in tiles manufacturing by Evolved Gas Analysis methodology

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Mineralogical characterisation of red-firing and white-firing clays used in the manufacturing of traditional ceramic products is critical for controlling the industrial production process and therefore to determine the properties of the end-product. The control of the industrial process goes beyond the need to guarantee the quality of the final product, but also for assessing the environmental impact of the industrial process in terms of atmospheric emissions.

In fact, the presence of impurities even in low level concentration can have a big impact. That is because it is very important to carry out an accurate mineral quantification of those minerals which are related to carbon dioxide and acid emissions (hydrogen fluoride, hydrogen chloride, sulphur oxide or nitrogen oxide).

Evolved gas analysis consists on thermal analysis equipment coupled to mass spectrometry and Fourier-transform infrared spectroscopy (Figure 1). The development of hyphenated techniques provides more valuable information and lower limit quantification than other primary techniques as X-ray diffraction or infrared spectroscopy.

The main objective of this work is to develop an analytical procedure using evolved gas analysis to identify and quantify minerals such as chlorides, sulphides, carbonaceous materials. In addition to this, the study includes the analysis of acid emissions during the ceramic firing treatment even if they are present at low quantitative levels. This methodology was validated with reference materials so that it allows the identification and quantification of sulphides, chlorides compounds in concentrations lower than 0.2%. Nevertheless, this methodology reveals some limitations in the quantification of minerals related to fluoride and nitrogen emissions.

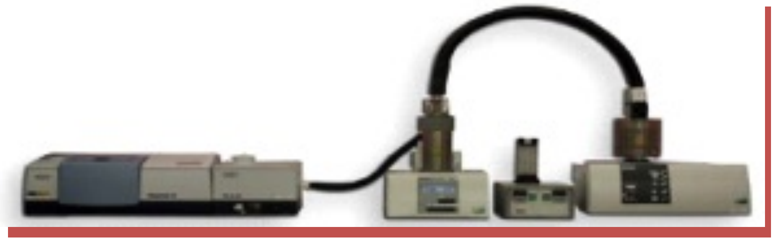

Figure 1. Evolved gas analysis Equipment

This study was co-funded by the Valencian Institute of Business Competitiveness (IVACE) and the FEDER Funds within the FEDER Operational Program of the Valencian Region 2014–2020.

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