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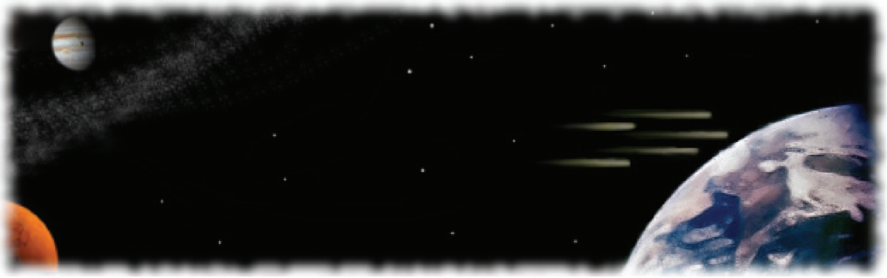
XIX^th^ Meeting of the Petrology Group of the Mineralogical Society of Poland

METEORITES: INSIGHTS INTO PLANETARY COMPOSITIONS

Abstracts and excursion guide



OBRZYCKO, OCTOBER 19-21, 2012

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XIXth Meeting of the Petrology Group of the Mineralogical Society of Poland

Meteorites: Insights into Planetary Compositions

organized by

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together with

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OBRZYCKO, OCTOBER 19-21, 2012

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GENERAL SESSION

EXCURSION GUIDE

XIX^th^ Meeting of the Petrology Group of the Mineralogical Society of Poland
Obrzycko, October 19th – 21st, 2012

Dear Colleagues,

The 19th Meeting of the Petrology Group of the Mineralogical Society of Poland is being held in the Raczyński Palace, sited among picturesque forests by the River Warta, a location kindly offered by the Adam Mickiewicz University in Poznań. The leading topic of the meeting, *Meteorites: insights into planetary composition*, is devoted to meteorites and related cosmological issues. It is no accident that this particular topic has been proposed for this meeting in Poznań, as the Poznań scientific centre has a long and widely recognized tradition in meteorite studies. This strong tradition is evidently related to the famous Morasko iron meteorite that was discovered (and is still being found) almost on the doorstep of the Institute of Geology of the UAM at the Morasko University Campus. The Poznań group of mineralogists and geologists, and a large group of passionate amateur meteorite collectors, take full advantage of the unique opportunity of investigating this well known meteorite (and many other meteoritic problems); they also do their best to promote meteoritics and cosmomineralogy (and the Earth sciences as well) in the society. The special session on meteorites provides a good opportunity to present the new results of recent studies on meteorites, discuss current problems and ideas, and define future challenges of mineralogy in cosmological studies.

The regular open session of the meeting (oral and poster) covers, as usual, various fields of mineralogy, petrology, geochemistry, environmental and related sciences. And, traditionally, this gives an overview of current trends in mineralogical sciences dealing both with basic, theoretical issues and practical, applied-science-oriented research challenges.

The closing event is the conference field excursion to the Morasko Reserve, where the latest research achievements are expected to be shown “on location”.

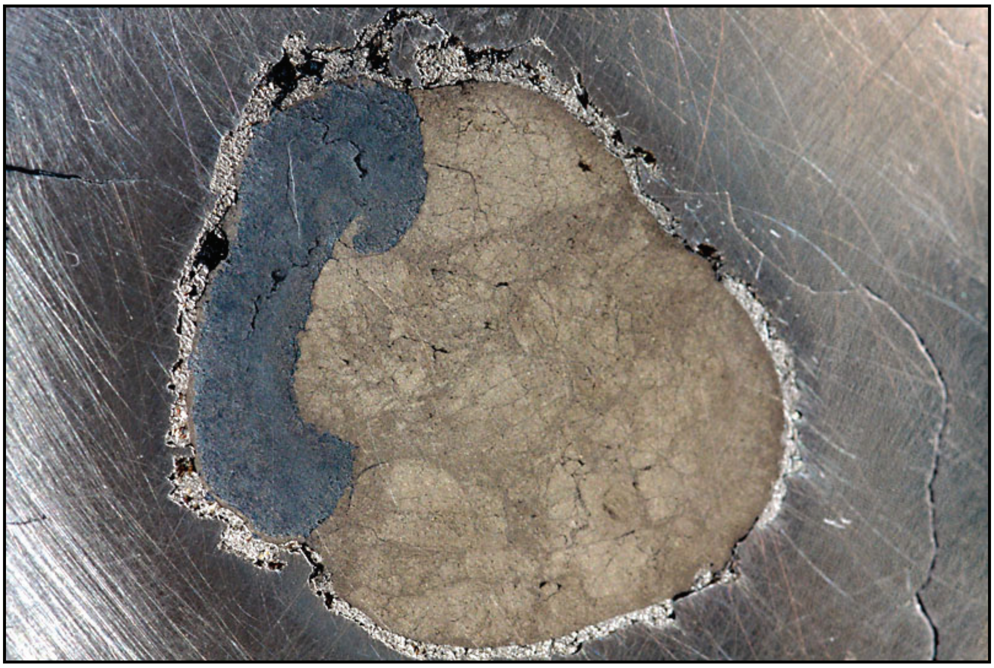
The conference host institution, the Adam Mickiewicz University, is warmly thanked for its hospitality. The supporting institutions are also thanked for their help. And last but not least, we are grateful to the Organizers, and in particular to the Poznań Group of Andrzej Muszyński, for their marvellous organizational efforts and all the arrangements they have made.

With best wishes for great scientific benefits from, and the best personal impressions of, the Obrzycko Meeting!

And see you all at the Jubilee XXth Meeting of the Petrology Group of the Mineralogical Society of Poland in 2013.

Ryszard Kryza
President of the Mineralogical Society of Poland

Polished and etched surface of the Morasko meteorite with coarse-grained intergrowths of kamacite and taenite. A rounded graphite-troilite nodule is visible in the lower part (troilite – brown, graphite – dark grey); length of the section – 13 cm



Graphite-troilite nodule in polished section (troilite – brownish, graphite – dark grey, schreibersite - silver rim around the nodule); diameter of the nodule – 2.5 cm

XIXth Meeting of the Petrology Group
of the Mineralogical Society of Poland

THEMATIC SESSION

METEORITES: INSIGHTS INTO PLANETARY COMPOSITIONS

OBRZYCKO, OCTOBER 19-21, 2012

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Micrometeorites: part of the Morasko iron meteorite shower

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Introduction

Since 1914, when in the area of the future "Morasko Meteorite Nature Reserve" a fragment of extraterrestrial matter was found, this location has aroused considerable scientific interest. Thanks to continuous studies, numerous publications concerning the geological structure and geomorphology of the area were generated (e.g. Dominik 1976; Hurnik 1976; Stankowski 2001; Stankowski et al. 2002; Stankowski 2008 – see for further literature). They have helped us to understand the mineral and chemical composition, structure and shape of different samples of the Morasko meteorite. In particular, micrometeorites (0.1-15 mm in diameter) often found as magnetic particles in the soil of the reserve, have been subjected to detailed examination. The aim of this study is to collect the available data and systematize them in a way that will allow for a comprehensive summary of knowledge on the micrometeorites from the area of the Morasko Meteorite Nature Reserve.

Methods

For 14 years, metallic pieces of possible cosmic origin have been examined by students doing Master's theses in the Faculty of Geographical and Geological Sciences at Adam Mickiewicz University in Poznań (Wysocka 1998; Piszczała 1999; Derdowski 2000; Cyz 2009; Dziurdzi 2010; Jureczko 2010; Dworzyńska 2011; Bartosz 2012). During this time, 598 samples were separated from the soil, from which 224 specimens of micrometeorites were taken for more detailed study. The selected material was subjected to XRD analysis, providing information on phase compositions. Examination under the stereoscope and scanning electron microscope (BSE imaging, EDS techniques) established the morphology and chemical composition of the micrometeorites. Additionally, in the case of the chosen micrometeorites electron microprobe studies were performed for a more precise determination of chemical composition (Cameca SX100; 15kV, 10 nA, BSE imaging, WDS techniques).

Results and interpretation

In the Morasko micrometeorites, the original iron and nickel alloys identified were kamacite α-(Fe, Ni), taenite γ-(Ni, Fe) and schreibersite $(Fe, Ni)_3P$. Stable mineral phases correspond to iron hydroxide minerals: goethite and lepidocrocite FeO(OH). Intermediate weathering mineral phases are iron oxides and hydroxides: magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and akaganeite (β-FeO(OH,Cl) (Karwowski, Gurdziel 2009). Quartz (SiO_2)

and albite ($NaAlSi_3O_8$) surrounded entire surfaces of the micrometeorite grains. Chemical analysis of partly weathered micrometeorites (conducted by EDS) showed that nickel was present in almost all analysed points of the studied thin sections. The maximum content of taenite was 43.97wt%, whilst the lowest was 3.02wt% in weathered kamacite.

The presence of kamacite, taenite and schreibersite in the weathered micrometeorites is proof that they are the part of the Morasko iron meteorite shower and have a common, extraterrestrial origin.

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Shock metamorphism and impact ejection of martian and lunar meteorites

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The rapidly increasing number of lunar and martian meteorites recovered in hot and cold deserts has revolutionized our understanding of the impact-related transfer of solid rock fragments between planets (Melosh 1984; Warren 1994; Gladman 1997; Artemieva, Ivanov 2004; Fritz et al. 2005). The suite of available lunar and martian meteorites provides unique samples to investigate the recent impact record of these planets, because the absolute ages of the ejection events can be deduced from the cosmic ray exposure history (i.e. Nishiizumi et al. 1991; Eugster 2002).

Petrology and ejection ages (i.e. the 4π cosmic ray exposure age plus the terrestrial residence time) of the recovered lunar and martian meteorites document several different impact events during the last 20 Ma (Lorenzetti et al. 2005; Fritz et al. 2007). The size of these impact events is constrained by the temporal frequency of the documented ejection events and the known lunar crater production rates. It follows that projectiles as small as ~30 m and ~200 m can produce lunar and martian meteorites, respectively, and the resulting craters are small in size (~1 and ~3 km diameter on Moon and Mars, respectively; Artemieva, Ivanov 2004; Artemieva, Shuvalov 2008).

Martian and lunar rock fragments are accelerated beyond escape velocity by interaction of the impact-induced shock wave with the target lithologies (Melosh 1984; Artemieva, Ivanov 2004). The physical boundary conditions regarding shock-pressure, shock-temperature, and pulse length of shock compression are recorded by the shock metamorphic deformations in the meteorites (Fritz et al. 2005; Fritz, Greshake 2009).

The subjected shock pressures can be deduced by characterizing the destructive shock deformation effects in the rock-forming minerals (Stöffler et al. 1991; Stöffler, Grieve 2007). For a variety of important rock-forming minerals, such as olivine, pyroxene, plagioclase and quartz, the shock effects have been generally pressure-calibrated by shock recovery experiments, and are used in the standard classification scheme for shock metamorphism in rocks and minerals (Stöffler et al. 1991; Stöffler, Grieve 2007; Fritz et al. 2011). Quantitative shock pressure barometry relies on the diagnostic shock effects in the minerals constituting the main mass of the meteorite, because these minerals cannot: 1) mimic diagnostic shock effects without being subjected to the relevant shock pressures, and 2) escape the shock pressures imparted to the rock, and thus cannot avoid to show the relevant shock deformation effects.

In addition, localized shock-pressure and -temperature excursions can lead to the formation of small regions of shock melt; e.g. shock veins and/or melt pockets. Thermal equilibration between a few 100's µm sized silicate melt pockets and cool host rock results in quenching within a few milliseconds. These melt pockets serve as a natural laboratory in which high-pressure phases are formed and preserved. In the martian meteorite Chassigny, the shock-induced melt pockets are completely transformed into a set of high-pressure mineral phases including ferropericlase, amorphous (Mg,Fe)SiO_3-perovskite, ringwoodite, wadsleyite, high-pressure phosphate γ-$Ca_3(PO4)_2$ and $CaTi_2O_4$-structured chromite, the mineral phases considered to be major constituents of the Earth's mantle (Fritz, Greshake 2009).

Impact experiments with microorganisms sandwiched between rock disks show that to some degree bacterial spores and lichens can survive the same shock pressure and temperature conditions that are recorded in martian meteorites. In theory, meteorites impact-ejected from Mars-like planets could, therefore, also serve as agents for the exchange of viable organisms between different planets in a given solar system (Meyer et al. 2011).

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Meteorites and cosmic dust: learning from the debris from planetary system formation

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Meteorites and cosmic dust provide important constraints on the formation of our Solar System. This paper will review the current state of knowledge on planetary system formation.

The earliest stages of the formation of planetary systems are relatively well understood. Planetary systems form as the by-product of star formation by the gravitational collapse and fragmentation of molecular gas clouds to form clusters of hundreds to thousands of stars. During collapse the angular momentum of cloud fragments results in the formation of accretion disks around forming stars (e.g. Lissauer, 1993). It is within these nebulae that planets and the parent asteroids and comets of meteorites and cosmic dust form.

A key to the nature of the materials formed in protoplanetary accretionary disks is the thermal behaviour of the disk. Heliocentric temperature gradients in a nebula occur due to the adiabatic heating of inward migrating gas and heating by solar irradiation. Viscous heating mechanisms also are thought to have operated, whilst short-term energetic outbursts (e.g. FU Orionis events) and shockwaves potentially could result in dramatic changes in the thermal environment on a range of scales (Boss 1998). In contrast cooling depends mainly on disk opacity and thus the degree of dispersion of thermally opaque dust by settling to the mid-plane.

The thermal environment of protoplanetary disks influences the solid to gas partitioning of elements depending on volatility. Heliocentric temperature gradients would be expected to result in compositional variations with distance from the young star and are likely to be crucial in determining the overall architecture of planetary systems due to the generation of a snow-line at which increases in solid spatial density allow the rapid accretion of giant planets (D'Angelo et al. 2010). Simple radial compositional differences, however, are complicated by a variety of mixing mechanisms within disks.

The components of chondritic meteorites testify to the complexity of the thermal environment of our Solar System's protoplanetary disk, the solar nebula. The highest temperature components preserved in chondrites are calcium-aluminium-rich inclusions (CAIs) and have mineralogies largely consistent with high temperature condensates from nebula gas. The textures and mineralogies of CAIs, however, indicate transient, repeated heating events with relatively rapid cooling difficult to reconcile with nebula-wide heating (Macpherson et al. 2005). Chondrules, rounded silicate-dominated particles in chondrites, derived by crystallisation of liquid droplets, likewise testify to transient repeated heating, albeit at lower temperatures. A wide variety of mechanisms have been proposed for the formation of these objects, with gas-drag heating within nebula shockwaves being the most successful in explaining their diverse properties, although other processes such as electric discharges, impact melting and even volcanism may have generated at least some chondrules. Chondrules and CAIs both testify to energetic disturbances within the solar nebula (Ciesla, Hood 2002).

Radial mixing of solids in the solar nebula is an unavoidable consequence of disk dynamics. The solar nebula transfers materials inwards to accrete to the early Sun, whilst transferring angular momentum outwards. Gas drag on solids within the solar nebula causes their inwards migration. The overall nature of chondrites, however, suggests mixing occurred both inwards and outwards. CAIs predate chondrules by as much as 1 Ma and would not be present in the accretion zones of the parent bodies of meteorites had outwards mixing not occurred. The abundance of ^{26}Al within CAIs is perhaps most consistent with the formation of these objects within a high temperature inner disk and their scattering over the disk by a magnetic X-wind (Shu et al. 2001). Furthermore, astronomical observations confirm that X-winds occur within many, but not all, young T-Tauri stars. Late stage mixing, due to tidal interactions with the giant planets also strongly influenced the final compositions of planetary bodies (Bottke et al. 2001).

The timing of events within the solar nebula is also important. Many igneous meteorites testify to significant melting and differentiation of some asteroids. These meteorites have early formation ages comparable to or older than chondrites. Such differentiated bodies are thought to have formed rapidly in the terrestrial planet region and accreted sufficient ^{26}Al to melt. Subsequent gravitational perturbation scattered some of these bodies to the asteroid belt where they are preserved today (Bottke et al. 2001).

There remain numerous outstanding questions on the formation of our solar system. How is CAI and chondrule formation reconciled with the survival of primitive matrix? How are the differences between meteorites explained in the context of radial mixing? Were any exceptional events, such as FU Orionis or triggering supernovae involved in the formation of our Solar System? Did the discrete sources of presolar grains influence |the final nature of our planetary system? The answers may still await in meteorites and cosmic dust.

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A new eucrite from the Oman desert: a mineralogical and petrological study

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During the last twelve years, private and university teams have collected numerous meteorites in the Oman desert (Hofmann et al. 2006). Finds from this area represent almost all known types of meteorites. Recently, our studies were focused on a single stone (168 g), found during the Russian expedition in 2004. The greenish-brown stone lacking any fusion crust was found on the desert plain in the Dhofar region. The shock stage of the meteorite is high and the weathering grade is low.

One doubly polished petrographic thin section was produced and studied using optical microscopy and scanning electron microscopy. Mineral chemistry was determined by electron microprobe analysis.

The meteorite dominantly consists of large Ca-rich feldspar (maskylenite) and Ca-poor pyroxenes which often show exsolution lamellae. Minor phases include chromite and an SiO_2 phase. Mineral chemistry is the following: Ca-rich pyroxene $Fs_{22.4-26.1}Wo_{41.1-45.1}$, FeO/MnO = 31; Ca-poor pyroxene $Fs_{54.7-57.8}Wo_{1.8-3.4}$, FeO/MnO = 32; plagioclase $An_{82.9-91.2.}$ Small clasts with basaltic textures and others with more recrystallized textures were also encountered.

The meteorite is heavily fragmented and the constituent minerals display strong shock effects. The plagioclase is almost completely converted into maskelynite, and the pyroxenes show undulatory extinction and intense twinning. Strong shock is also indicated by recrystallized shock melt distributed throughout the meteorite.

In summary, the meteorite is a highly shocked polymict eucrite with unusually high amount of maskylenite. It is believed that the parent body of eucrites is Vesta 4, based on the recent Dawn mission (Mayne et al. 2010).

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SEM images of selected mineral constituents of the Orgueil CI1 chondrite – implications for the IDPs history of its parent body

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Based on SEM imaging and EDS spectra analysis of fresh surfaces of the Orgueil CI1 chondrite, we have described five different dust-related mineral components embedded within the carbonaceous matrix. The results allow us to distinguish: 1) pristine (silicate?) fibers and whiskers, 2) barrel- and disc-shaped iron oxide microspherules, 3) isometric sulphide forms, 4) spherulitic iron sulphide blebs, 5) irregular low-density silicate aggregates. A subdivision of the dust-related particles into: 1) presolar and 2) secondary assemblages, which have formed during cometary history of the Orgueil parent body, is proposed.

Interplanetary dust particles (IDPs) within carbonaceous meteorites originated from comets, due to collisions of asteroids, moons and planets or may represent pre-solar nebular crystallites. Many particles are composites, low-density agglomerates and condensates, but they often include also pre-solar crystallites. The most widespread are siliceous “fibers” (tubular) and “whiskers” (finer ones) (Miyake et al. 2010) or carbonaceous tubules containing magnetite crystals with an unusual, barrel-shaped and discoidal appearance (Jedwab 1971; Hua, Busseck 1998). In addition, an hypothesis that the Orgueil meteorite may have originated from a Jupiter-family or Halley-type comet has also been proposed (Gounelle et al. 2006). In the paper, new results of SEM and EDS studies of Orgueil meteorite inclusions are present.

Two, very small, fragments (app. weight of 0.1 g) of Orgueil meteorite from the collection of Mineralogical Museum, University of Wrocław (specimen marked as MM UWr.-1-32) have been examined. All measurements were carried out on a Hitachi S-3400N Scanning Electron Microscope equipped with a tungsten electron emitter with SE and BSE detectors at the Faculty of Chemistry, University of Wrocław. EDS spectra were recorded with a Thermo Scientific Ultra Dry detector (resolution 129 eV) and analyzed by Noran System 7. Selected samples were coated with a thin gold layer, using a Cressington 108A sputter coater, but some freshly fractured, interior surfaces of the meteorite were left uncoated to gather better Z contrast.

The SEM studies revealed the presence of several types of interstellar dust fragments. Firstly, single long, occasionally flattened needles with a length of 11.6-44.5 μm and 2.2-5.2 μm in diameter have been observed. Occasionally, narrowed or curved varieties can be distinguished. Locally, the very fine needles (whiskers) are clustered in sheave aggregates similar in length. In terms of chemical composition, they are ferroan epsomites and/or epsomites with unspecified iron sulphate intergrowths. Secondly, single plate hexagonal crystals occur on their rough surfaces. Their size ranges from 17.0 μm to 54.2 μm in diameter, up to 5.1 μm in height and up to 32.8 μm in single edge length. Regarding phase and chemical composition, they represent pyrrhotite, previously noted by Bullock et al. (2005) and interpreted as a product of pristine troilite alteration in an aqueous environment. Thirdly, most interesting in terms of morphology are framboidal iron oxide microspheres (from below 2.7 μm up to 12.8 μm diameter), which overlie the surfaces of small cavities in the carbonaceous matrix. Most of these crystals show unusual forms – – barrel-shaped arrays of discs, ca 5.9 μm in height, with a diameter of each disc between 9.4 and 11.0 μm. Single individuals often crystallized as trapezohedrons or as combinations of trapezohedron and trisoctahedron, with well developed (113) or/and (112) and (221) walls. In terms of chemical composition, they correspond to magnetite with minor components such as Mg, Al (1-4wt.%) and traces of Ni and Cr. The magnetite is also interpreted as a product of troilite alteration in an aqueous environment (e.g. Bullock et al. 2005). Fourthly, in the studied matrix low-density irregular microaggregates occur. The longest axis of each microaggregate is up to 16.7 μm in length. They have different size and correspond chemically to epsomite and Na-Mg sulphates (similar to vanthoffite, blödite, konyaite or löweite). Fifthly, rare iron sulphides, blebs, microspherules or angular grains (up to 3.8 μm in size) are irregularly distributed and often overgrow the large low-density assemblages or condensates. EDS spectra similar to magnetite, magnesioferrite, epsomite (also ferroan), magnesite, siderite, olivine? and aggregates/intergrowths of these above phases were obtained. However, magnetite seems to be the most common constituent.

A cometary (presolar) origin of the dust remnants within the Orgueil meteorite matrix is supported by a large number of inclusions such as (primarily silicate?) fibers, the presence of iron sulphides and low-density aggregates. The iron oxides, growing on the walls of caverns, and the secondary sulphates and carbonates found in the clusters are the result of subsequent secondary alteration in a specific (hydrothermal?) microenvironment due to crystallization in a water-containing environment (e.g. from the comet) in interstellar open space (e.g. Bullock et al. 2005; Jedwab 1971; Tomeoka, Buseck 1988). According to I-Xe magnetite age determination, the pristine minerals (also sulphides) crystallized at 4.566 Ga and are postdated by aqueous alteration 2 to 7 Ma after formation (Hohenberg et al. 2000).

It should also be noted that the described forms are only replicas (pseudomorphs) of ancient remnants of interstellar dust, and their exact determination and classification are difficult. This requires further investigations using other advanced spectroscopic and isotopic methods. Such work is currently in progress.

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Magnetic investigation of chemical composition and shock-induced structural modifications in the Morasko meteorite

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The Morasko meteorite is composed of an (Fe,Ni)-alloy (about 98wt.%) and of about 2wt.% FeS nodules (Stankowski, Muszyński 2008). The composition and structure of iron-nickel-rich parts were investigated by X-ray diffraction (XRD), metallographic techniques, scanning electron microscopy (SEM), electron microprobe analysis, differential thermal analysis (DTA), magnetic measurements and transmission ^{57}Fe Mössbauer spectrometry (TMS). Microstructural analysis by SEM and optical microscopy has shown that the sample is composed of large grains of Fe-Ni alloy, in which secondary phase crystals with well developed crystal habit and size about 10 μm are distributed. DTA confirmed that the transformation from α to γ-Fe-Ni solid solution appearing as a function of temperature corresponds to about 5wt.% Ni in the Fe-Ni alloy (Idzikowski et al. 2010). A possible scenario of extraterrestrial sample solidification is related to the microstructural and magnetic behaviour.

Shock-induced metamorphism resulting from hypervelocity impacts strongly depends on the shock conditions (especially pressure and temperature). Some dislocations and twins (evidence of plastic deformation) were found in different pieces of the Morasko meteorite. Shocked and impact-unchanged parts of the iron-nickel alloy smithereens were separated from this cosmic material by optical metallographic techniques. Differences in the shape of magnetization versus temperature lines for those two samples are clearly related to structural modifications introduced during the impact. The influence of laboratory furnace temperature-induced shocks, applied to the impact-unchanged parts of the meteorite by short annealing at 1200ºC, on microstructure and magnetic behaviour of this heat-treated material is discussed in comparison to the properties of other Fe-Ni systems (e.g. Valderruten et al. 2008, 2010).

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What have meteorites to do with coal fires? A case of Upper and Lower Silesian Basins

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Natural coal fires, that are known to occur, i.a. at coal-mining waste dumps, can trigger a number of geological processes that lead to crystallization of new mineral species. Depending on local conditions, mainly temperature and Eh potential (i.e. oxygen and CO content), various transformation zones are formed, usually built of multi-mineral complex rocks and mixtures.

Burnt rocks form layered complexes of alternating rocks representing oxic (clinkers, buchites and some paralavas and metacarbonate rocks) or anoxic (metapelites called *black blocks*, other paralavas and metacarbonate rocks) transformations. Most rock types contain polymorphs of $Mg_2Al_4AlSi_5O_{18}$ (Fe-bearing indialite, cordierite-sekaninaite), hematite and magnesioferrite Fe_2MgO_4. The second group, usually less common, tends to concentrate minerals that are typically of extraterrestrial origin.

The mineral associations of a metacarbonate post-concretion rock from Siemianowice Śląskie were first described by Kruszewski (2006). The most important constituent of the rock, representing highly reduced formation conditions, is natural calcium sulphide, oldhamite – a galena-group mineral almost exclusively found in meteorites (e.g. enstatite chondrites, Crozaz, Lundberg 1995; Zakłodzie enstatite achondrite, Grossman 2000). Its other terrestrial occurrences include burning dumps of the Chelyabinsk Coal Basin (Sokol et al. 2005), and similar environments in Germany (Witzke, Rüger 1998) and France (Eytier et al. 2004). The Silesian oldhamite forms octahedra up to 20 μm, often highly hydrolyzed to form massive portlandite. Occasionally it concentrates Mg, Fe (up to 0.35wt.%) and Mn (up to 0.18wt.%), but is often enriched in Cl (up to 0.21wt.%) and may contain up to 0.36wt.% F. Oldhamite, together with pyrrhotite (troilite?), is also found as a minor constituent of hydrothermal-like thin veins cutting the pyrometamorphic complex of a dump in Przygórze near Nowa Ruda (Lower Silesian Coal Basin). The veins contain calcite, aragonite, fluorite, diopside, andradite, periclase, perovskite, magnesioferrite and a series of Ca silicates, mostly anorthite, melilite, tobermorite and cuspidine. Oldhamite is closely associated with an accessory FeS-ZnS-MnS solid solution phase of clear hexagonal habit. The composition of the Fe-rich end-member, $Fe_{0.51}Zn_{0.40}Ca_{0.05}Mg_{0.03}Mn_{0.02}S$, resembles that of buseckite – a new member of the wurtzite group, found intergrown with troilite in the Zakłodzie meteorite (Ma 2011), but electron diffraction data will be needed to distinguish between buseckite and troilite. Troilite was primarily identified as a product of the pyrometamorphic decomposition of siderite, coexisting with magnesioferrite and maghemite, in samples from Czerwionka and Radlin. A troilite-like species is also present in some non-clinker metapelites from Czerwionka.

Diopside rich in the kushiroite member was found in a paragenesis with forsteritic olivine ($Fo_{89}Fa_{8}Co_{3}$, with "Co" for calcio-olivine), magnesioferrite ($Mf_{87}Sp_{12}Qan_{1}Jc_{1}$, with "Qan" for qandilite Mg_2TiO_4) and Fe-bearing anorthite ($An_{88}Ab_{11}Kfs_{1}$, containing up to 2.09wt.% FeO). This paragenesis forms a single zone within cordieritic buchite, close to its contact with glassy red clinker. The clinopyroxene forms prismatic crystals up to 25 x 20 µm. Its mean end-member composition is $Di_{34}Ku_{37}Hd_{16}$, corresponding to $Ca_{0.99}(Mg_{0.61}Fe^{2+}{}_{0.23}Al_{0.17}Ti_{0.03})_{\Sigma 1.02}(Si_{1.72}Al_{0.28})_{\Sigma 2.00}O_6$. Occasionally, the kushiroite member is dominant. Kushiroite (Ku), previously known as Tschermak's component (CaTs), was originally described by Kimura et al. (2009) from ALH 85085 chondrite. Diopside-esseneite present in a metacarbonate slag from Rydułtowy is slightly enriched in kushiroite component, with mean end-member components being $Di_{41}Es_{28}Hd_{18}Ku_{10}$.

Iron phosphides, mainly an FeP phase of empirical formula $Fe_{1.00}(P_{1.01}As_{0.01}S_{0.01})_{\Sigma 2.00}$, are very common in a *black block* (black metamudstone) fragments from Czerwionka. It is not specific to meteorites unlike barringerite $(Fe,Ni)_2P$, found here in minor quantities only. A single crystal in the Fe-Ti-P system, probably florenskyite (known exclusively from Kaidun meteorite – Ivanov et al. 2000), was identified. The presence of cohenite $(Fe,Ni,Co)_3C$ has not yet been confirmed. The parent rock forms compact zones, up to tens of centimeters wide, within violet to red metapelite alternating with paralava. The paralava itself contains an accessory celsian and whitlockite-like phase of the formula being $(Ca_{17.97}Na_{0.02})(Mg_{1.20}Fe_{0.81}Mn_{0.01})_{\Sigma 2.02}(PO_4)_{12}[(P_{1,29}S_{0,32}Si_{0,24})O_3(OH)_{1.70}F_{0,05}Cl_{0,01}](H_2O)_{1.29}$. Whitlockite-group minerals, though primarily often identified in meteorites, were shown to be merrillite (Dowty 1977), which is a Na-rich representative of the group.

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Yarkovsky-driven origin of near-earth asteroids and meteoroids of the Flora family

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Dynamical resonances in the asteroid main belt are the gateway to the production of near-earth asteroids (NEAs) (Greenberg, Nolan 1999). Spreading of asteroid families and reaching resonance orbits (Bottke et al 2000; Bottke et al. 2001; Bottke et al .2002) was recently proposed to be due to the Yarkovsky effect (Vokrouhlicky 1998; Vokrouhlicky 1999; Spitale, Greenberg 2001; Morbidelli, Vokrouhlicky 2003). Very effective secular resonance with Saturn v6, which lies at the inner edge of the asteroid belt, can be reached due to the Yarkovsky effect only by retrograde objects. Resonance orbits with Jupiter (like 3:1, 2:1 and others), which reside in the main belt, can be reached by both prograde and retrograde asteroids. For this reason, the theoretical (Bottke et al. 2001, Bottke et al. 2002) and observed (La Spina et al. 2004) ratio between NEAs with retrograde/prograde spins is 2 ± 0.2.

If the above considerations are true, the influence of the Yarkovsky effect should be observable among the objects in asteroid families. The results of a 10-year-long observation campaign of the Flora family objects (Kryszczyńska et al. 2012) show the Yarkovsky splitting between prograde and retrograde objects. The observed ratio between prograde and retrograde asteroids is 2.6. The location of the Flora family close to the v6 resonance explains the lack of retrograde objects and confirms the excess of retrograde rotators among NEAs and their origin from the v6. The same evolutionary path is expected for meteoroids, which are even more sensitive to nongravitational effects because of their smaller size.

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The Zakłodzie and alike achondrites: mineral chemistry (preliminary data)

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Introduction

The Zakłodzie achondrite was proposed, based on its distinctive mineralogical, geochemical and textural characteristics, to be a "precursor" for a possible new classificatory group of the "primitive enstatite achondrites" (Pilski 2004; Pilski et al. 2011; Przylibski et al. 2005, 2012), and a special research project, aimed at verifying this proposal, was carried out in 2009-2012. Here, we present the preliminary results of EMPA investigations of a set of samples, candidates for the new meteorite group:

1. Zakłodzie Z09
2. Happy Canyon
3. Itqiy
4. NWA 2965
5. NWA 4301
6. NWA 4799
7. SAU 402

Methods

Mineralogical investigations have been performed on the samples selected, using optical microscopy (transmitted and reflected light) and electron microprobe analysis (EMPA; BSE imaging, WDS and EDS techniques). The EMPA data were obtained in the Institute für Geologie, Mineralogie & Geophysik, RUB, Bochum, Germany (Cameca SX50; 15kV, 10 nA, beam ~5-8 µm) in 2009 and 2011, and in the Department of Mineralogy and Petrology, University of Wrocław (Cambridge Microscan M9 donated by the Free University Amsterdam, 15 kV, 50 nA, beam ~3-8 µm) in 2009. For reference, earlier reported data from Zakłodzie and unpublished new analyses provided by Łukasz Karwowski were used.

Preliminary results and interpretation

The mineral species detected in the seven samples are shown in Table 1. In the new specimen of Zakłodzie Z09 being a kind of reference for comparison with the other meteorites, we have selected 277 analyses of pyroxene (66 analytical points), feldspars (20), silica phase (1), kamacite (100), troilite (35), keilite (8), oldhamite (2), schreibersite (4), sinoite (38), and FeOx (secondary Fe-rich phases) (3).

Pyroxene in Zakłodzie Z09 has a very constant composition, with the enstatite end-member strongly dominating: Wo 0.009, En 0.987 and Fs 0.004 mol. fraction (average of n 66). Feldspars in sample Z09 are represented by plagioclase, though the compositions vary over quite a broad range: Or 0.01-0.07, Ab 0.61-0.89, and An 0.04-0.37 mol. fraction. This compositional range is similar to that reported earlier by Przylibski et al. 2005, and by Łukasz Karwowski (unpublished data). An SiO_2 phase (quartz, cristobalite?) in Z09 shows SiO_2 90.84wt.%, and significant amount of Al_2O_3 Na_2O, and K_2O, all indicating the probable admixture of feldspar.

Table 1. Mineral composition of the Zakłodzie and similar achondrites (FeOx – secondary Fe-rich phases).

Meteorite	Silicates				Opaques									
	Pyroxene (En/CEn)	Olivine	Feldspar	SiO2	Kamacite	Taenite	Troilite	Keilite	Daubreelite	Oldhamite	Schreibersite	Sinoite SiNO	Graphite	FeOx
Zakłodzie Z09	x	x	x	x	x	x	x	x		x	x	x	x	x
Happy Canyon	x		x	x	x		x							x
Itqiy	x				x			x						x
NWA 2965	x		x	x					x					x
NWA 4301	x		x		x		x				x			x
NWA 4799	x		x	x	x		x		x					
SAU 402	x		x		x		x							x

Kamacite is the most widespread opaque in the Zakłodzie. One hundred points measured in sample Z09 on metal indicate a constant composition, with an average of: Fe 90.69 wt.%, Ni 5.99, Si 1.55, Co 0.45 and P 0.24 wt.%. The remaining mineral components measured in sample Z09 yielded the following mean compositions (in wt.%): troilite (average of n = 35 points): Fe 55.28, S 37.24, with admixtures of Cr 4.86, Mn 1.35, Ti 0.90 and Ni 0.16; keilite (n 8): Fe 29.94, Mn 23.23, Mg 5.05, Ca 0.82 and S 39.11; oldhamite (n 2): Ca 54.74 and S 42.47, with traces of Mn, Fe, Mg and P; schreibersite (n 4): Fe 71.22, Ni 12.86 and P 13.95, with minor Si and Co; sinoite (n 38): Si 55.44, with calculated N 28.2 and O 15.4, and minor admixtures are Na, Al, K and Fe; secondary iron-rich phases (FeOx) measured in several spots, show: Fe 72.37, Ni 2.60 and Si 1.59, as well as traces of Mg, Ca, Mn and Co.

Summary observations from the other achondrites studied

1. Pyroxene has been found in all samples measured. Its composition is constant, rich in En (ca 97-99mol.%).
2. Feldspars represented by plagioclase are found in all but one (Itgiy) meteorites; their compositions fall within the range established for Zakłodzie: Or 0.01-0.07, Ab 0.60-0.90,

and An 0.02-0.39 mol. fraction. Locally, the feldspars are richer in potassium – up to Or 0.14 mol. fraction.

3. Metal is represented by kamacite (not measured only in NWA 2965) containing 5.85 to 6.76wt.% of Ni.
4. Sulphides are common and are represented by troilite, keilite, daubreelite and oldhamite.
5. Other mineral phases, found occasionally in some of the samples (especially in Zakłodzie), are schreibersite, sinoite and graphite.
6. Secondary Fe-rich phases display variable compositions (but with rather constant mean values); characteristically, they contain significant admixture of Ni.

Summing up, the new data extend our knowledge of the mineral composition of enstatite meteorites that cannot be included into any present group of meteorites and are usually classified as anomalous. The observed similarities in mineral contents and in mineral chemistry (in particular in Zakłodzie, Happy Canyon, NWA 4301, NWA 4799 and NWA 2965) support the idea of defining a new group of meteorites, i.e. the primitive enstatite achondrites ("Zaklodzieites"), as earlier suggested (Pilski 2004; Pilski et al. 2011; Przylibski et al. 2005). We assume that they have formed as a result of short and incomplete melting of the protolith which was the source rock of the enstatite chondrites (Przylibski et al. 2012).

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Brecciation of the Pułtusk meteorite and its deformational history

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Introduction

The Pułtusk meteorite fell on January 30th 1868 in Poland. It is classified as an H4-5 (Binns 1968; Manecki 1972) regolith breccia (Ganapathy, Anders 1973). Its shock stage was defined as S3 (Stöffler et al. 1991) based on observations of olivine crystals. In spite of high equilibration and a medium shock index, the chondrite shows some evidence of strong deformational events and the presence of fragments out of equilibrium occurring in cataclastic zones.

Samples

The analyzed samples of the Pułtusk meteorite were generously provided by the Museum of the Earth, Polish Academy of Sciences in Warsaw; the Mineralogical Museum of the University of Wroclaw; the Thugutt Mineralogical Museum of the Faculty of Geology, University of Warsaw; the Mineralogical Museum of Jagiellonian University in Kraków and the Geological Museum at the Institute of Geological Sciences PAS in Kraków.

Brecciation

Samples are mainly composed of the H4 lithology, cut by cataclastic, darkened zones. These zones embed, in turn, more equilibrated, recrystallized, sigmoidal clasts with H5 and H6 texture. Impact melt clasts are also present.

Clasts H5 and H6 contain twinned plagioclase crystals with the composition of 82% molar content of Ab and 6mol% Or. Minerals inside the clasts are well equilibrated with each other, the best visible for olivine, pyroxene, chromite and ilmenite. Olivine and pyroxene show very narrow ranges of composition, with sharp peaks at 18-19mol% Fa and 16.5-17mol% Fs, respectively. Cataclastic zones, overprinted on the petrological brecciation, are composed of crushed chondrules and fractured, isolated grains of the same, well equilibrated composition as the clasts and host. However, some chondrules, isolated grains and lithic inclusions with CM mineral and chemical composition occur in the cataclastic parts. Zonal picotite crystals are also present in the H4 host. Impact melt clasts are mainly composed of olivine, low-Ca pyroxene with major element composition the same as in the unmelted parts. However, phosphates are absent from the impact melt clasts.

Deformational structures

The investigated samples display undulatory extinction of light and irregular, rarely planar fractures in silicates. However, traces of stronger deformation may locally be detected in chromite-plagioclase assemblages (Rubin 2003), native copper flanks (Rubin 1994), and plessite intergrowths. All of the spinels (chromium- and aluminium-rich) may be found in the chromite-plagioclase assemblages and merrilite grains and potassium feldspar glasses are associated with them.

The Pułtusk meteorite displays very distinct features of strong high strain-rate deformation. There are prominent shear zones and microfaults cutting through chondrules, silicate and phosphate but also kamacite grains as well as foreign inclusions. Slip surfaces are well-defined and show displacements of ~0.1 mm or more. Slickensides and frictional melt veins/offshoots of impact melt are located at the boundaries of the darkened, cataclastic and light parts.

The meteorite also shows a strong anisotropy of magnetic susceptibility, with the development of preferential, yet uniform at the sample scale, orientation of the metal grains as determined by magnetic methods and computer-aided high resolution tomographic scanning. In the analyzed cataclastic and impact-melted samples, metal nodules and veins occur abundantly but the modal content of metal does not differ significantly (Krzesińska 2011).

Discussion

The deformational features show that Pułtusk was at first equilibrated in its parent body and later deformed in a high strain rate – low shock pressure event. Numerical and experimental work (Pierazzo, Melosh 2000; van der Bogert et al. 2003) has demonstrated that high strain-rate but low pressure conditions may have occurred during oblique collision of the parent body with another asteroid body. The shock wave generated by the impact weakens with decreasing impact angle and, instead, high strain-rate processes start to dominate. It is important that ultra-high shear stresses that develop during hypervelocity collision allow for only short-lived, microscopic displacements/microfaulting, but are sufficient for frictional melting to occur (Spray 1995). In Pułtusk, the very high strain-rate character of the deformation is especially recorded in kamacite grains which were deformed in a brittle regime. The strain rate was responsible for the formation of shear zones and veins filled with frictional/impact offshoot melt, remobilization of metal and formation of nodules, veins and preferential orientation of metal particles. The cataclastic texture of the darkened clasts is also in good agreement with high strain-rate shearing rather than shock processes. The event was also responsible for the overall brecciation, mixing the material of different degrees of recrystallization from the impact crater basement and the parent body regolith with spalled foreign material, embedding it into deformed zones.

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Limitations on information retrievable from Antarctic meteorites due to influence of terrestrial weathering

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More than 16,000 meteorites have been collected by the ANSMET program in Antarctica; among them there are Lunar, Martian and rare types of carbonaceous meteorites. All of those meteorites are finds and most of them were weathered on the surface of the Earth for considerable amounts of time (Nishiizumi 1995). Understanding terrestrial weathering of Antarctic meteorites is important since weathering processes can modify meteorite characteristics (e.g. trace-element abundances), and thereby interfere with the retrieval of information on pre-terrestrial solar system processes (e.g. Bland et al. 2006). This problem can be especially significant when dealing with rare types of meteorites, of which populations Antarctic samples may constitute a major fraction. The purposes of this paper are to identify elemental redistribution and the distribution of possible weathering features in interior and exterior thin-sections from the same meteorite EET79004.

Weathering rates in Antarctica are relatively low when compared to other terrestrial environments (Campbell, Claridge 1987), but in some cases this process can be rapid (e.g. Jull et al. 1988; Harvey, Score 1991). Weathering changes the chemical, isotopic and textural properties of meteorites (e.g. Bland et al. 2006). One of the first effects is the oxidation of iron and formation of Fe-oxides and oxyhydroxides that give a meteorite a rusty reddish color (e.g. Gooding 1986). Another result of weathering is dissolution of primary minerals such as olivine and pyroxene, and formation of clays and other phyllosilicates (e.g. Gooding 1986) as well as evaporites (e.g. Velbel et al. 1991). The bulk chemical composition of weathered meteorites can also change; major elements are mobilized (Lee, Bland 2004), and rare earth elements are redistributed (e.g. Mittlefehldt, Lindstrom 1991; Crozaz et al. 2003).

Meteorite EET79004 is a polymict eucrite and it was selected for this study because it was shown by Mittlefehldt and Lindstrom (1991) that interior and exterior parts of this meteorite have different rare earth elements (REE) patterns. They showed in their Figure 4 that, relative to the corresponding interior sample, an exterior sample of EETA79004 is enriched (by less than a factor of two) in La, Sm, and Tb (LREE); depleted (by less than a factor of two) in Ce; and has nearly identical Eu, Yb, and Lu abundances (the latter, HREE). Mittlefehldt and Lindstrom (1991) concluded that this pattern resulted from weathering. This conclusion was subsequently supported by the finding that LREE enrichment, a negative Ce anomaly and a very similar REE redistribution pattern are typical of weathering of terrestrial basalts under oxidizing conditions (Patino et al. 2003). Although studies of REE mobilization in terrestrially weathered materials are abundant, research on REE mobility in extraterrestrial materials is rare (Mittlefehldt, Lindstrom 1991; Crozaz et al. 2003). Secondary host phases of REE have been moderately well characterized in weathered terrestrial rocks (e.g. Taunton et al. 2000), but not yet for meteorites.

Optical petrography, SEM-BSE and EDS methods were used for this study. EET79004, although not indicated as evaporite-bearing in the Antarctic Meteorites Database, includes evaporite minerals (mostly Ca-sulphates) filling cracks in the outermost 3-4 mm. Vesicles are filled with large euhedral tabular Ca-S phases and small microcrystalline or amorphous K-S phases. An attempt was made to evaluate if, and to what extent, the visible weathering features are related to the previously reported REE redistribution created probably during weathering of this meteorite, and to identify secondary host phases of REE in these materials. Although some Ca-P phases with high Z-contrast have been found, it was not possible to determine if they are the REE host phases. Conclusions: 1) the outermost part of a meteorite (up to cm depth) undergoes significant weathering (even in relatively “fresh” specimens; 2) some elements (e.g. sulphur) undergo a very significant redistribution; 3) phases formed during weathering are distributed very irregularly within a meteorite such that samples of the same meteorite, taken at a similar distance from the fusion crust, can have significantly different properties (e.g. normal or disturbed REE patterns).

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Morasko meteorite – the current state of knowledge

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Introduction

Morasko IAB iron octahedrites, together with similar falls in Seeläsgen (in Polish Przełazy) and Jankowo Dolne (all in central-west Poland), have been found along a common line, and show similar geochemical characteristics. The irons studied differ from other IAB meteorites in their exceptionally low Ir and high Ge contents. These features strongly suggest a genetic relationship. The size of the Morasko strewn field (especially when extrapolated to Seeläsgen and Jankowo Dolne), as well as the large number of finds, indicate that the likely single iron shower originated from a large meteoroid. This summary overviews the following topics: history of finds; fall and craters; age of the fall; strewn field of three meteorites: Jankowo Dolne, Morasko and Seeläsgen; mineralogy and chemistry of the Morasko meteorite and micrometeorites.

History

The Morasko iron became known to science with the November 12, 1914, find during the digging of trenches near the village of Morasko, then only a few kilometers north of Poznań city. The finder wrote a letter to the director of a museum in Poznań (then Germany), that about half a meter under the surface he had found a lump of metal weighing 75 kg. The famous Seeläsgen iron was found in 1847 at the village of Seeläsgen (Przełazy), 130 km WSW of Poznań. The Jankowo Dolne iron was found as a lump of rusted iron by a farmer from the village of Jankowo Dolne near Gniezno (ca 90 km ENE of Poznań) in September 1971, but the find remained unknown to all but some local inhabitants. Only in 2004, a student, M. Szyszka, got to know about the possible find near Jankowo Dolne and during his first hunting in March 2004 he found three small fragments. In June 2004, he found a 11.5 kg lump of regmaglypted iron resting on top of an old beehive, most probably the one discovered in 1971.

Fall and craters

The great majority of finds of Morasko are confined to a relatively small area on the northern slope of a terminal moraine formed during the last glaciation. As accepted by many authors, the fall of the Morasko iron produced several craters, up to a few tens of meters across, in soft glacial sedimentary deposits (Pilski, Walton 1999). The relief of the fall site is typical of a glacitectonically deformed front moraine of the latest Vistulian stage (see details in Stankowski 2001, 2008). Stankowski (2008) summarized the current state of knowledge on the Morasko meteorite fall and gave an extended reference list.

Age of fall

The time of the fall has been defined using ^{14}C dating and palynological investigations at ca 5000 years ago (Hurnik et al. (1976); Stankowski, 2008 and references therein). For more details on the age of the fall see Stankowski, this volume.

Strewn field

Meteorite Morasko is known as the largest iron-meteorite shower in Europe (Pilski, Walton 1999). Three well known iron meteorites (IAB-MG) from central-west Poland: Morasko, Seeläsgen (Przełazy) and Jankowo Dolne, belong to the Morasko iron meteorite shower. The size of the strewn field, including Seeläsgen and Jankowo Dolne, as well as hundreds of finds, suggest together that the shower originated from a large meteoroid.

The first interpretation of the Morasko strewn field came from Pokrzywnicki (1964), who first discovered that Morasko may be an iron shower, and mapped Morasko finds. A next attempt to determine the Morasko strewn field was made by Pilski (2003), who added to the localities published by Pokrzywnicki several localities of recent finds submitted by private meteorite hunters. All new finds were situated not far from the old ones known to Pokrzywnicki, mostly on the northern slope of a terminal moraine.

Mineralogy and chemistry

The meteorites have been studied by many authors (including a few MSc students), e.g. Pokrzywnicki (1964), Dominik (1976), Hurnik et al. 1976, Classen (1978), Czegka (1996), Pilski and Walton (1999), Stankowski (2001), Muszyński et al. (2001), Karwowski (2004, 2005), Karwowski and Muszyński (2006, 2007, 2008), Karwowski et al. (2009a, 2009b), Wojnarowska at al. (2008), Jastrzębska (2009), Pilski et al. (2012) (for more references see Dworzyńska, Muszyński, this volume).

The three iron falls display many similarities in petrography, mineralogy and chemical features. All three meteorites belong to the IAB–MG group. They are composed mainly of coarse-grained kamacite and taenite, with accessory cohenite and schreibersite. A distinct feature of all three irons is the presence of characteristic nodules, usually ca 1-1.5 cm in size, composed of graphite and troilite, with minor silicates, sulphides, oxides and phosphates.

The large size of the body would explain the observed small differences in Ir contents, similar to those reported from the Canyon Diablo iron. The similar chemical compositions of the irons studied, in particular the Ir contents, indicate that the meteoroid was rather homogeneous and no important fractional crystallization processes took place in it.

Micrometeorites

Micrometeorites (0.1–15 mm in diameter) can be often found as magnetic particles in the soil of the Morasko reserve area. In the Morasko micrometeorites, the original minerals are iron and nickel alloys: kamacite, taenite and schreibersite. Goethite and lepidocrocite are the stable minerals of final weathering, whilst micrometeorites in the intermediate stage of weathering contain magnetite, maghemite and akaganeite (Karwowski, Gurdziel 2009). Chemical analysis of partly weathered micrometeorites showed that nickel was present in numerous analyzed grains (for more details see: Dworzyńska, Muszyński this volume). The studied micrometeorites have the same mineralogical composition as the Morasko iron and originated from the common meteorite shower.

Conclusion

The three iron meteorite falls, Morasko, Seeläsgen (Przełazy) and Jankowo Dolne, found along a common line in central-west Poland, represent a single meteorite shower dated at ca 5000 Ma. Their mineralogical and chemical features indicate that they originated from a large and rather homogeneous meteoroid.

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Oborniki (Wargowo) 2012 possible meteorite fall – preliminary study

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Until the year 2012, the name “Oborniki meteorite” was reserved for two samples found in the 1930's in the forests near Oborniki and lost during World War II (Pokrzywnicki 1964). In the present paper we report the first chemical data for a possible meteorite fall which occurred in this area in spring 2012.

The fall took place at midnight of 27/28th April 2012 in Wargowo village near Oborniki, about 25 km NW of Poznań (ca 15 km from the Morasko Meteorite Nature Reserve). According to a witness, the fall was associated with a loud sound. Officially, two separate pieces were found: the larger fragment is more than 3 cm in diameter, and the smaller has a diameter of ca 2 cm. However, there is some press information that additional pieces were also found. The smaller sample has been provided for research, which included microscopic observations and chemical composition estimates using the SEM-EDS method.

The studied piece is rather rounded, with a predominantly gray color, metallic luster and a weight of about 18 g. The sample is characterized by high porosity and a thin rust layer on the whole surface. Three different chemical phases were recognized.

Phase I is metallic and covers about 70% of the sample surface. It occurs either in massive form or as rhombic and cubic (max. 2 mm) crystals with a metallic to glassy luster. The crystals either show perfect cleavage with an angle of ca 90° and are significantly scratched on their external surfaces. Based on semi-quantitative analysis, the dominant elements in Phase I are chromium (Cr_2O_3 54-83wt%) and iron (Fe_2O_3 10-39wt%). Silica (SiO_2) does not exceed 5% and MgO, Al_2O_3, Na_2O, K_2O, NiO and Pt are minor phases. The presence of Cu, Zr, Pb and Mo was not detected.

Phase II is also metallic. It occurs mainly in a shallow depression on the surface of the sample and is distinguished by a golden colour. Chemically, Phase II displays some similarity to the Phase I – it also consists of chromium (Cr_2O_3 51-63wt%) and iron (Fe_2O_3 11-23wt%), while SiO_2, Al_2O_3 and CaO contents increase (up to 11, 3 and 4wt%, respectively). In contrast to Phase I, the presence of Cu_2O (max. 4wt%) was observed. Platinum (Pt) content is rather minor but in one analysis it increases to the level of 14wt%.

Phase III is similar to a silicate or glass. It forms several small (min. 0.25 mm) and two larger ‘crystals’ (max 3.5 mm in diameter). It is blue to dark blue in colour, with glassy or greasy luster and conchoidal fracture. The dominant components of phase III are SiO_2 (more than 40wt%), CaO (max. 36wt%) and MgO (max. 10wt%). The remaining major oxides: Al_2O_3, Cr_2O_3 and Fe_2O_3 reach a maximum of several wt%. The EDS spectrum shows also minor contents of Na, K, Ti, Sc, Mo, Pb and Pt (max. 3wt%). During analysis no visible effects of interactions with a beam were observed.

The analyses performed on secondary phases (rust) did not demonstrate any distinct changes in chemical composition. The rust present on Phase I displays some increase in Co, and on Phase II a small increase in V.

Based on preliminary observations, we conclude that the studied object is not natural. This is supported by the high porosity of sample, the rust presence and no typical melting crust. Such a conclusion is also supported by chemical analysis of the distinguished phases, especially the presence of such elements as platinum. On this basis, the sample studied is classified as a meteorwrong and the name "Oborniki meteorite" should be still reserved for the two samples lost during World War II.

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Tarnobrzeg – a first European candidate for martian meteorite

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Most martian meteorites have been found by Antarctic scientific expeditions and meteorite collectors in Northwest Africa and Oman. Finds in other localities have been hindered so far by difficulties in prospecting and identifying meteorites in forested and urban areas. A Tarnobrzeg sample is a candidate for the first martian meteorite in Europe. The specimen is a 2318 g cumulate found in the suburbs of Tarnobrzeg (Southern Poland), consisting mostly of clinopyroxene and magnetite. Thin section examinations and EMPA analyses have shown that its main constituents are diopside and augite (94vol.%), with magnetite as a minor phase (~5vol.%). Accessory minerals are olivine, kaersutite amphibole, fluorapatite, ilmenite and Mg-hercynite. The CaO vs. Mg/(Mg+Fe) ratio and Mg/Si vs. Al/Si weight ratio place Tarnobrzeg among the nakhlites. Also the FeO/MnO ratio in olivine is typical of martian samples. REE signatures from bulk sample and pyroxene show similar patterns to MIL 03346 nakhlite (Day et al. 2006); however, oxygen isotope analyses are required to confirm an extraterrestrial origin for the specimen. An alternative explanation is that the sample is a glacial erratic from the Mindel Glaciation, with a possible original exposure in the Mustavaara Layered Intrusion, northern Finland.

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Meteorites and the composition of the terrestrial planets

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There are differentiated and undifferentiated meteorites. *Differentiated meteorites* (e.g. iron meteorites, eucrites) are the results of melting of the parent planet. *Undifferentiated meteorites* are derived from unmelted parent bodies. They are called *chondritic meteorites*. Their chemical composition is close to the solar composition, after allowing for depletion of the volatile elements. Chondritic meteorites are characterized by a limited range of Mg/Si, from 0.7 to 0.9, and Fe/Si, from 1.2 to 1.8; the higher values are close to the ratios measured in the solar photosphere (0.91 for Mg/Si and 1.81 for Fe/Si). This indicates the absence of the two major planetary fractionation processes, namely partial melting, leading to planetary crusts with high Al/Mg and Si/Mg ratios, and metal separation, i.e. core formation.

The bulk compositions of the Earth and the other terrestrial planets seem to be within the range of chondritic meteorites. The bulk composition of the Earth is better known than that of any other planet. A detailed comparison shows that CV-chondrites match the composition of the Earth better than other types of chondritic meteorites: (A) The Earth is similarly enriched in refractory elements as CV chondrites. (B) Assuming that the Earth's core contains about 7% Si yields a bulk Earth Mg/Si within the narrow range of carbonaceous chondrites, but very different from ordinary and enstatite chondrites. (C) The Earth and carbonaceous chondrites show similar patterns of the moderately volatile elements: in particular, both are depleted in Na and Mn to the same degree. Enstatite and ordinary chondrites are also depleted in volatile elements, but their depletion patterns are very different. (D) The Earth, chondritic meteorites and other planets lie approximately on the same $^{53}Cr/^{52}Cr$ vs $^{55}Mn/^{52}Cr$ isochron, indicating that the depletion of Mn and probably of all other moderately volatile elements in the Earth and in carbonaceous chondrites occurred shortly after the first solids had formed in the solar nebula, during the life-time of the 3.7 my ^{53}Mn. There is little evidence for loss of volatile elements by later evaporation or impact heating.

However, there are also differences between the chemistry of type 3 carbonaceous chondrites and the Earth: (A) The bulk Earth has excess Fe relative to the common groups of chondritic meteorites. Silicates may have been lost during collisional growth of the Earth involving giant impacts. (B) The Earth is more depleted in volatiles than type 3 carbonaceous chondrites, although the patterns are similar. (C) The terrestrial pattern of very volatile elements (In, Bi, Cd) is different from chondritic meteorites, possibly reflecting processes during the initial differentiation of the Earth. (D) Carbonaceous chondrites have isotope anomalies in Cr, Ti, Ni, Zr, Ba, Nd and Sm that are not observed in the Earth. The stable isotopic composition of several elements in the Earth is similar to ordinary chondrites and fits well with enstatite chondrites, except for Li and Si. (E) The highly siderophile elements in the mantle of the Earth have been delivered by a late meteoritic component. Excess Pd, Ru and Rh in the terrestrial pattern makes it impossible to identify this component amongst the known types of meteorites.

In summary, the composition of the Primitive Mantle derived here shows that the Earth was assembled from material that had experienced many of the chemical fractionation processes also found in chondritic meteorites. These processes occurred at the initial stage of solar system formation, under conditions thought to be present in the solar nebula. But the stable isotope record excludes chondritic meteorites as the “building blocks” of the Earth. Meteorites formed in local environments separated from that part of the inner solar system, where much of the material forming the terrestrial planets was sourced (see Palme, O’Neill 2012).

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Mineral resources of extraterrestrial bodies of the Solar System

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In the Institute of Mining Engineering at Wrocław University of Technology research on extraterrestrial resources of the Solar System, especially metallic resources, has been carried out for several years. Special attention has been paid to minor bodies from the asteroid belt. Till now, the analyses of concentration of metallic resources in the parent bodies of ordinary chondrites (some of S and Q-type asteroids) as well as iron meteorites (some of M-type asteroids) have been made.

The research on asteroids carried out by unmanned spacecrafts indicates that those bodies are covered with regolith (www.nasa.gov 2012; http://hayabusa.sci.isas.jaxa.jp 2012). This is a loose and poorly sorted rock, typically composed of partly sorted silicate grains and minerals with higher density – Fe-Ni, sulphides, chromite, and others. Thus, the regolith can be considered as a typical loose sedimentary deposit.

The investigations of ordinary chondrites carried out by the authors proved that at shallow depths, under the regolith layer, less cohesive rocks with high porosity occur (Pilski et al. 2001; Przylibski et al. 2003). They can be also considered as deposits, which may be easily exploited. According to the onion shell model of an asteroid, under the layer, which will be first excavated, rocks of higher metamorphic grade occur. As was shown by Krzesińska (2011), a decreased content of Fe-Ni grains, as well as metal sulphides with simultaneously increasing grain size in those rock types, is profitable from a mining and economic point of view.

Taking into account also the calculated densities of asteroids (Britt, Consolmagno 2000; Birlan 2002; Britt et al. 2002) of between 0.95 ± 0.39 and 2.96 ± 1.09 g/cm^3, one may assume that the rubble-pie model of an asteroid should be also considered. Empty spaces, fissures, and cracks should then be typical features of most asteroids (Britt, Consolmagno 2001). This textural phenomenon will be very helpful when exploitation of any resources on asteroids is planned. It will reduce the costs and simplify operations of deposits dredging, mining, and crushing.

One may state that practically a whole asteroid may be considered as a deposit of metals. This statement may be supported by a comparison of metal concentrations in terrestrial deposits (Nieć 1990) versus their content in the Earth's crust (Craig et al. 2001), and in parent bodies of ordinary chondrites. Especially important are the concentrations of Al, Fe, Ni, and Cu and Au. In the parent bodies of ordinary chondrites, those metals occur in concentrations high enough to be considered as deposits according to current criteria for terrestrial deposits (Nieć 1990). In fact, the economic value of those deposits is even higher and the extraction much more profitable, as asteroids are not single-metal but polymetallic deposits.

To show how big are the resources on a single asteroid, an estimate of resources on 6 Hebe, an S-type asteroid, was carried out. The resources of Pt, Pd and other Platinum Group Metals (PGM) and their value were calculated (Łuszczek 2012).

In our team at Wrocław University of Technology, other estimates of mineral reserves and economic values of selected asteroids were also undertaken. Recent work concerns the most common asteroids – the parent bodies of carbonaceous chondrites. Similar chemical, mineralogical and petrographic research on other bodies of the Solar System is in progress. They are undifferentiated parent objects of primitive achondrites. Further investigation will include differentiated planets and some of their moons. The aim of these studies is to determine the potential resources and technology of mining of selected resources from extraterrestrial bodies in the Solar System.

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Composition and growth morphology of feldspar crystals from the Morasko meteorite: LA-ICP-MS and Raman – SEM EDS imaging study

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Alkali feldspar crystals have been recognized in some pieces of the Morasko meteorite. Their major element compositions have been determined by EMPA and LA-ICP-MS. Preliminary data, reported on the basis of EMPA investigations, demonstrated that all the feldspars have a composition either strongly enriched in potassium or in sodium. Also in all of them three end-members of the ternary solid-solution were present. In the albite crystals orthoclase and anorthite components are very low and vary, respectively, from 3.75 to 4.2 and from 0.0 to 0.05. Similarly in K-feldspar albite and anorthite components were also very low, varying, respectively, between 2.34-3.01 and 0.12-0.18. Much more extensive information was obtained through a LA-ICP-MS study. It seems that in Morasko four types of feldspar crystals are present. Their presence is also confirmed by EDS-mapping as well as high resolution chemical Raman imaging. They differ in composition in terms of major and trace elements. In addition to feldspar crystals of almost pure Na- and K- composition, oligoclase and alkali feldspar either highly enriched in the Ab end-member or of ternary composition occur. Some compatible and incompatible elements have been chosen (e.g. Ba, Sr, Rb, LREE, Pb, Ga, Cl) to track the origin of the crystals. All four types display a trace element pattern which systematically changes according to M-site heterovalent substitution, e.g. show a strong geochemical affinity to potassium, sodium or calcium. Oligoclase and alkali feldspar with balanced orthoclase and albite contents are enriched in all the above-mentioned trace elements, except chlorine. Their evolution toward the end-member composition results in drastic trace element impoverishment. Instead, chlorine and trace elements, which typically are transferred by fluids, appear. The feldspars are co-genetic. Changes in their composition are discussed in relation to the major and trace element compositions of the surrounding mineral association.

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Melt-weathering meteorite crust in the light of mineralogical and luminescence investigations – time indicator of an impact event

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The high surface temperature of a meteorite passing through the Earth's atmosphere leads to changes in mineralogical properties and to superficial luminescence resetting. It has been documented in small meteorites from NE border of the Morasko Meteorite Natural Reserve with SEM/EDS data and by a luminescence study (TL technique).

It is difficult to determine the temperature gradient inside the meteorite during its flight in the atmosphere, and to establish how deep is the zone of luminescence resetting. Directly after the fall, this zone is transformed by weathering processes – a melt-weathering meteorite crust is created. Simultaneously, the meteorite temperature influences the surrounding strata and the sinter-weathering "skin/rim" is formed.

Numerous analyses of material from the Morasko melt crusts confirmed a chemical composition typical of iron meteorites. However, a very wide diversity of chemical compositions was documented. The existence of distinct spherical silicate grains was observed. The results of the SEM/EDS studies indicated that the luminescence dating substantially refers to the external parts of meteorite, namely its melt-weathering zone.

The analyses of melt crusts were compared with data for the mineral material from the vicinity of the meteorites. Instrumental analyses were carried out for the melt-weathering crust (three samples) and the surrounding mineral material (two samples, the first from above and the second from beneath the sinter-weathering crust).

Sample	Lab. No. UG	TL age (ka)
Melt crusts of the meteorites		
70 g	6603	4.7±0.7
1201 g	6682	4.9±0.9
~60 g	6683	4.6±0.8
Material surrounding	6604	5.4±0.8
the 70 g meteorite	6605	5.5±0.8

The luminescence age indicators for melt-weathering crusts and the surrounding material differ. However, it must be noted that the basic dating results for both types of material fall within the limits of measurement errors.

It should be added that an earlier study of the sinter-weathering skin of four other meteorites (>10 kg up to 164 kg) gave the TL age results from 4.7 to 6.1 ka.

The recent and older dating results confirm that the Morasko meteorite fall event happened ~5000 years BP.

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Multimethod datings of the Morasko meteorite impact

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Group falls, so-called meteorite showers, are a natural phenomenon. The Morasko impact is one of them (Pilski, Walton 1999). This local fall led to breaking through the surface layer of Quaternary sediments of limited thickness; hence, fragments of granitic material were found within the frontal part of the falling meteorite. As a result, the meteorite plunged into the Neogene sediments of the so-called Poznań series (Karwowski et al. 2012). The 2011 discovery of a ~35 kg meteorite lump, located at a depth of ~160 cm, that pierced the glacitectonically disturbed Neogene sediments occurring almost on the land surface (Meteorite Men, episode 301 "Morasko Poland", Science Channel, 2011), is the fundamental proof of the local, *in situ* impact, disproving hypotheses treating the Morasko meteorites as being brought by an ice sheet/ice sheets, like erratics.

Many depressions of glacigenic origin are still present around the Moraska Góra (the highest point in this part of Wielkopolska, ca 154 m above sea level). Particularly distinctive, however, is a group of small, very symmetric depressions without external drainage that are situated at a distance of ca 600 m from the Moraska Góra peak, on its north-northeastern side. The origin of these depressions has been interpreted in two ways: as kettle-holes (Karczewski 1976) and as impact craters (Pokrzywnicki 1957; Hurnik (Ed.) 1976; Stankowski 2009). The oldest arguments questioning their cryogenic origin came from palynological data, which indicated that accumulation/sedimentation of organic deposits inside the depressions was restricted to about 5000 to 5500 years ago (Tobolski 1976), i.e. a minimum ca 5000 years later than the beginning of sedimentation in the kettle-holes in this part of Wielkopolska, which proceeded during the Late Glacial (Ołtuszewski 1957; Litt, Tobolski 1991; Makohonienko 1991; Tobolski 1991). In the case of the Morasko depressions, there are several explanations of their origin: a) the environmental conditions in the depressions prevented formation of organic sediments for several thousands of years, b) degradation of dead-ice blocks took place not in the Late Glacial as everywhere else in this part of Wielkopolska, but in the Middle Holocene climatic optimum (very unbelievable), c) the origin of the depressions has nothing to do with cryogenic processes (most likely).

The palynological estimates were proved by radiocarbon dating. Samples from the bottom parts of the organic sediments were dated at the Poznań Radiocarbon Laboratory, under the supervision of T. Goslar. Among others, two dated samples from approximately 3-5 cm above the mineral bottom, gave the following results: in the largest depression A – 4495 ± 35 ka (Poz-18863; 4980-5300 cal. BP), in the second in size depression B – 4760 ka (Poz-18960; 5320-5600 cal. BP), The calibrated dates agree closely with Tobolski's (1976) interpretations.

Palynological and radiocarbon analyses are not sufficient to prove the origin of the depressions (kettle-holes or impact craters) or of the time of potential impact. This was achieved by a luminescence study (using TL and OSL techniques).

The high temperature attained by the outer part of a meteor passing through the Earth's atmosphere leads to changes in luminescence both in its surface layers and, after collapse, in the mineral substrate from the immediate vicinity of an impacting body. After excavation from strata of a local fall, meteorites typically display the development of two different layers: a) an outer sinter-weathering crust, formed mainly of the material into which the meteorite plunged, with the simultaneous presence of meteoritic matter (micrometeorites and spherules), and b) an inner melt-weathering crust (usually rather thin), reflecting the properties of meteorite matter transformed by weathering processes. In both cases the earlier luminescence is zeroing. The heat of falling extraterrestrial matter leads also to zeroing of the surrounding material (full or partial). It is why the extensive luminescence study was done.

TL data of the melt–weathering crust for small meteorites are: weight 70 g – 4.7 ± 0.7 ka (kilo years ago) (UG-6603), weight 1201 g – 4.9 ± 0.9 ka (UG-6682), weight ~60 g – 4.6 ± 0.8 ka (UG-6683). The measurements have been made by St. Fedorowicz from Gdańsk University and G. Poręba from Silesian University of Technology (Stankowski et al. in press).

The TL data of sinter-weathering crusts in four large meteorites are: weight 10.5 kg – 4.7 ± 0.4 ka (UG-5943), weight 11 kg – 5.0 ± 0.7 ka (UG-5942), weight 21 kg – 6.1-0.7 ka (UG-5244), 164 kg – 5.2-0.9 ka (UG-5941). The data were determined by St. Fedorowicz from Gdańsk University; see also Stankowski et al. (2007).

The OSL research has been carried out for mineral sediments of Neogene and Quaternary age, occurring at the bottoms of the two largest craters in Morasko. All the OSL analyses were made by A. Bluszcz from the Silesian University of Technology – lab. numbers of data for the largest crater A: GdTL 1328-1332 and for the second in size crater B: GdTL 1333-1336 (Stankowski, Bluszcz 2012). At the bottom of the largest one, built of the Neogene sediments (so-call Poznań series), a considerable variation in indicators was observed. The oldest dates show a time range from ~350,000 to ~45,000 years, inconsistent with the age of the original sediments. Large numbers of indicators range from ~30,000 to ~10,000 years. Among the data obtained, there are also many with values lower than 10,000 years, with a significant proportion dated at < 5000 years. The rejuvenation, and especially the significant representation of the dates below 10,000 years, seems to justify the reset time of the deposits, and therefore the time of the Morasko Meteorite fall. At the bottom of the second largest Morasko crater, Quaternary deposits are present. There are sediments older than the last glacial period (the age of sediments ~18,000 years occurs only near the topographic surface in a very thin discontinued cover), with an age over ~130,000 years. Only occasionally they are ~45,000 years. Other indicators did not exceed 27,000 years, with a significant number of the dates < 10,000 years. This range of ages seems to confirm the suggestion that the resetting time was young. The obtained luminescence results of zeroing time reflect a relatively young high temperature and pressure event. This proves also the impact origin of the depressions/craters (Stankowski 2009; Stankowski, Bluszcz 2012).

The multimethod – palynological, radiocarbon and luminescence datings performed on the sinter-weathering crusts and melt-weathering crusts of meteorites and on the mineral material from the bottoms of circular depressions located about 600 m to NNE of Morasko Hill indicate that the impact connected with generation of the craters took place ~5000 years ago.

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Unusual magnetic properties of Fe-based structurally metastable systems

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Rapid solidification of molten alloys has proved to be a reliable route for the synthesis of advanced materials useful in technical applications. Among different technologies the melt spinning technique is most favorable because of its simplicity and flexibility. During melt spinning a thin stream of metallic liquid is ejected under pressure onto the surface of a fast rotating wheel, made usually from Cu, and cooled causing rapid solidification. This technique is used to develop materials that require extremely high cooling rates in order to form metastable amorphous (metallic glasses) or crystalline phases. The highest cooling rate achievable by melt spinning could be of the order of 10^7 K/s. In this way high quality materials can be produced with lower costs directly during solidification or by refining the amorphous structure and trapping the nucleated metastable phases in the form of nanocrystals (metallic nanocomposites). Usually rapid solidification of many compositions occurs in very short periods of time and in low volumes. It could take place also during extraterrestrial matter solidification.

A method based on the semi-empirical Miedema's and geometric models allowed us to calculate glass forming abilities (GFA) and the glass forming ranges (GFR) in a ternary system and its sub-binaries. Śniadecki et al. (2012) for the first time combined the two mentioned models to calculate the formation enthalpies of amorphous alloys and their crystalline (solid solution) counterparts, as well as differences between them for the Y-Cu-Al system. This theoretical approach could be also used for Fe-Zr-B, Ni-Zr-B and Fe-Ni-S (elements found in meteorite Morasko e.g. by Stankowski, Muszyński 2008; Idzikowski et al. 2010) to predict the glass forming ability and metastability of the phases.

Results for the nonmagnetic Y-Cu-Al system indicate that compositions close to Y-Al and Y-Cu sub-binaries exhibit the highest GFA values. In addition, from the normalized entropy change S_σ/k_B, the highest GFA was predicted for sub-binaries close to Y-Cu. In both cases, Y atoms play an important role, due to their large atomic radii and highly negative interfacial enthalpies with other constituents. The glass forming ability parameter ΔP_{HS} includes both the enthalpy and entropy changes and indicates the range with the highest GFA in the vicinity of the $Y_{40}Cu_{31}Al_{29}$ alloy composition.

Properties of Fe-based melt-spun alloys with Ni, Zr and B will be discussed to show examples of methods for developing new structurally metastable metallic systems. In particular many details of our previous experimental and theoretical investigations in the processing of nanocrystalline soft magnetic materials made from an amorphous precursor with a nominal chemical composition of $Fe_{81-x}Ni_xZr_7B_{12}$, x = 10-40 (Kopcewicz at al. 2003, Kostyrya at al. 2005; Kostyrya, Idzikowski 2006) and 64 (Idzikowski et al. 2004) will be now summarized with some further comments.

The transformation from the amorphous into the nanocrystalline state was investigated by means of structural measurements (x-ray diffraction – XRD, transmission electron microscopy – TEM) as well as by differential scanning calorimetry (DSC) and transmission and conversion electron ^{57}Fe Mössbauer spectrometry (CEMS). Additionally, magnetic (vibrating sample magnetometry – VSM) measurements were performed. The subsequent annealing favors the emergence of a fine grained fraction of a magnetically ordered metastable cubic $Fe_xNi_{23-x}B_6$ phase in an amorphous matrix. The relationship between the structures of the metastable and equilibrium phases and their transformations will be discussed. The magnetic behaviour of pure $Ni_{23}B_6$ and $Fe_{23}B_6$ phases was studied theoretically using the spin polarized tight binding linear muffin-tin orbital (TB-LMTO) method. Anomalously high magnetic moments of Fe atoms were found in some non-equivalent positions in the crystal structure. The possibilities of increasing the saturation magnetization value by applying an optimal chemical composition and a crystal structure and decreasing the coercive force of the nanocrystalline alloys utilizing intergranular exchange coupling will be shown.

In general, for nanocrystalline composites the temperature dependencies of magnetic parameters corresponding to nanosized grains deviate from those of a bulk alloy with the same composition. Two mechanisms responsible for the observed effects have been proposed by Skorvánek at al. (2000), and Idzikowski et al. (2004): (i) influence of the chemical and structural nature of the intergranular amorphous phase, and (ii) grain-intergranular phase interface contribution, both resulting from the annealing treatment. Different magnetic behaviour may be observed for low, medium, and high volumetric fractions of nanocrystallites.

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Alteration of crystalline rocks: a few comments from case studies in SW Poland to potential research of the Martian surface

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Growing interest in Martian geology, stimulated, for example, by new chemical data from the Mars surface, has inspired scientists to correlate observations from this planet with the geology of the Earth. It is well known that the dominant mineral-forming processes on the Earth's surface are hydration and oxidation of primary minerals, including those rich in iron and magnesium. The same alteration processes occur in meteorites found on Earth. It is also believed that similar processes could have happened on Mars when water was an active agent on its surface (e.g. Chevrier, Mathe 2007). This has been confirmed by spectroscopic chemical analyses (VNIR, CRISM, TES) of the Martian ground that showed the presence of elements typical of volcanic rocks of the Earth, such as basalts and andesites. Furthermore, some spectra of the Martian soil are very similar to those obtained for hydrosilicates and aluminosilicates in weathering covers on the Earth (Mustard et al. 2008). Some authors (e.g. Bishop et al. 1998) argue that the weathering conditions on Mars are similar to subaqueous alteration – palagonitization. In many publications, clay minerals are considered among the main components covering the surface of the planet. Among them, sepiolite, smectite, kaolinite and amorphous silica have been confirmed by spectrometric data (McKeown et al. 2011). Apart from these phases, iron hydroxides, sulphates and carbonates have been reported. It has been suggested that iron-rich minerals are responsible for the colour of the "red planet".

On Earth, environmental analogues for weathering of the Martian rocks can be found, e.g. as weathering covers of crystalline rocks, in particular those rich in Fe and Mg, including mafic (to a lesser extent also ultramafic) effusive and intrusive igneous rocks. Similar rocks, comprising pyroxene, plagioclase and olivine, are known from Mars (Bandfield et al. 2000). Such rocks can be the source rocks for the Martian weathering covers that contain clay minerals, amorphous silica, zeolites, and iron oxides and hydroxides.

Cenozoic basaltoids occur in the Sudetes and Fore-Sudetic Block in Lower Silesia (SW Poland), partly covered by weathering crusts, that contain mineral assemblages most likely analogous to those on the Mars surface. In altered basaltoids and their weathering products in Lower Silesia, a range of secondary minerals have been recognized, e.g. smectite-group clay minerals (montmorillonite, beidellite), kaolinite-halloysite and iron hydroxides (goethite and lepidocrocite). In associated volcanic breccias, such minerals as zeolites, amorphous silica and smectite (montmorillonite-like) have been identified (August 2003). Apart from that, in altered mantle xenoliths in the basaltoids, comprising peridotites and gabbros, secondary phases such as saponite, beidellite and goethite, poorly crystalline hydrophosphate and amorphous silica have been confirmed (August 2009).

Apart from the Cenozoic basaltoids and their xenoliths, secondary Fe-oxides and hydroxides, sepiolite, smectites and amorphous silica occur in the lateritic weathering products of ultramafic bodies, e.g. in the Szklary Massif in the Fore-Sudetic Block (Dubińska et al. 2000). Abundant secondary mineralization, comprising hydrosulphates and clay minerals, is developed in pyrite-bearing schists at Wieściszowice in the West Sudetes.

Most of these weathering covers on crystalline rocks in Lower Silesia were formed due to intense water-rock interaction under a tropical climate in the Miocene. Only the pyrite-schists at Wieściszowice still undergo intense weathering in the current mild-climate conditions.

It is likely that warm and humid conditions, similar to those during the Miocene in Lower Silesia, characterized the Mars surface when the weathering covers were formed. Future mineralogical and chemical investigations of Martian surface deposits, and their correlation with the results of studies of terrestial materials, would extend our knowledge of the composition of the Martian surface.

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Petrography, mineral chemistry and differentiation processes of Permian mafic lavas from the Czerwieńczyce graben (eastern part of the Intra-Sudetic Basin)

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The Czerwieńczyce graben, which forms the easternmost part of the Intra-Sudetic Basin in SW Poland, is filled with a Lower Permian sedimentary succession with intercalations of rhyolitic tuffs and mafic lavas (Oberc, Wójcik 1965). The succession originated in a post-orogenic, intra-continental setting in an extensional regime associated with the gravitational collapse of an orogen in the eastern part of the Variscan Belt of Europe. The mafic lavas in the Czerwieńczyce graben postdate a regionally extensive ignimbrite deposit, the Góry Suche Rhyolitic Tuffs (Awdankiewicz 1999), and belong to the youngest volcanic products in the Intra-Sudetic Basin. However, more detailed data on the Czerwieńczyce mafic lavas are so far lacking. In this contribution we (1) describe the petrographic and mineralogical characteristics of these rocks and cognate enclaves which they host, and (2) discuss possible differentiation processes of the parental magmas. This preliminary study is based on a microscopic investigation of 8 thin sections and 125 microprobe chemical analyses of minerals in one thin section.

The Czerwieńczyce mafic lavas are tentatively classified as basaltic andesites. They are porphyritic, with sparse phenocrysts (< 1.5 mm long) of plagioclase and olivine, the latter replaced by smectite(?), set in a microcrystalline, intersertal groundmass composed of plagioclase laths overgrown by alkali feldspars, subhedral to anhedral pyroxenes, opaques and apatite. There are small amounts of anhedral, interstitial quartz, but also abundant interstitial clay minerals, which probably replace former volcanic glass. Plagioclase ranges from labradorite at cores to andesine at rims (An68-32). Cores and mantles of plagioclase are relatively homogeneous, normal to oscillatory zoning is mainly found near the margins of crystals. Alkali feldspars are Na-sanidine and anorthoclase. Pyroxenes comprise enstatite rimmed by pigeonite and smaller individual crystals of pigeonite, rarely augite. The opaques are ilmenite and titanomagnetite. Chromian titanomagnetite and titanian chromite are found as inclusions in pseudomorphs after olivine phenocrysts.

The mafic lavas occasionally contain small (micro)gabbroic enclaves, up to 15 mm long. These microgabbros consist predominantly of plagioclase with much less abundant enstatite. Plagioclase forms euhedral plates up to 1.3 mm long. Enstatite crystals are smaller and anhedral. There are locally abundant interstitial clay minerals and calcite. Some of the clay minerals may also form pseudomorphs after subhedral olivines. In places there are small crystals of Fe, Cu and Zn sulphides.

Plagioclase of the gabbroic enclaves is normally zoned labradorite (An71-53), but in some crystals there are also patches of bytownite (An82). This plagioclase is strongly poikilitic and contains abundant small inclusions of titanomagnetite and pleonaste as well as oval aggregates of smectite (pseudomorphs after olivine?). Enstatite in the enclaves shows a sieve texture, with oval 'cavities' and 'channels' filled with calcic plagioclase (up to An85) which, in turn, hosts numerous inclusions of titanomagnetite, pleonaste and oval aggregates of smectite (after olivine?). Along the margins some enstatite crystals are partly overgrown by augite and fluoro-edenite.

The mafic lavas from Czerwieńczyce and the microgabbroic enclaves they host show strong similarities in terms of modal composition, which suggest a close genetic relationship. The microgabbros most likely are cognate enclaves (autholiths) and represent cumulates which formed at some depth within the magmatic system and were brought up to the surface by the basaltic andesite lavas during their eruption. Some differences in modal composition and mineral chemistry between the autholith and the host rock (in the autholith: lack of pigeonite and alkali feldspars, more calcic plagioclase, edenite rimming enstatite, accessory sulphides, enrichment in magnesium in ilmenite) may be linked to crystallization from compositionally distinctive batches of magma and/or more prolonged crystallization of the cumulates at higher pressures. At the time of entrainment in the erupting magma, these gabbroic cumulates were not yet fully crystallized and the autholiths contained some interstitial melt. It is also possible that the rising basaltic andesite magma infiltrated the gabbroic cumulates. This interstitial melt was quenched to glass upon the final emplacement and cooling, and was eventually replaced by the clay minerals and calcite.

The autholiths may provide constraints on crystallization, and related differentiation processes, in the magmatic system which the basaltic andesite magmas came from. In general, the modal composition of the microgabbros suggests fractionation of plagioclase from the magma as well as of some enstatite, olivine and accessory minerals (titanomagnetite, pleonaste). Possibly, the actual mechanism of differentiation was fractional crystallization with imperfect segregation of crystals and residual melt, as suggested by the interstitial altered glass in the microgabbroic autholith. However, the poikilitic and sieve textures in the microgabbros reflect also a more complex crystallization history of the cumulates, which probably involved reactions with interstitial melts, or partial remelting of the cumulate (e.g. incongruent partial melting of enstatite with crystallization of olivine, pleonaste and titanomagnetite, prior to crystallization of plagioclase).

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Late- and post-orogenic volcanism in a Variscan intramontane through: SHRIMP zircon ages, volume estimates and geodynamic significance of Permo-Carboniferous volcanic succession of the Intra-Sudetic Basin

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In Carboniferous and Permian times, large areas of Europe were affected by voluminous volcanism which was associated with intra-continental extension and rifting during the late- and post-orogenic stages of the Variscan Orogeny (e.g. Wilson et al. 2004). The volcanic rocks vary from dominantly mafic in the north of the Variscan Belt, e.g. in the Northern Permian Basin, to dominantly felsic and bimodal further south, in the Southern Permian Basin and coeval intramontane troughs (McCann et al. 2006). In NE Germany, ca 70-80 000 km^3 of volcanic rocks were emplaced within less than 10 Ma at the Carboniferous-Permian boundary (302-294 Ma; Breitkreuz, Kennedy 1999). Paulick and Breitkreuz (2005) consider that the Upper Palaeozoic volcanic rocks of NE Germany are part of a felsic-lava dominated large igneous province (LIP).

In this study, we discuss new data on the age and volumes of volcanic rocks erupted in the Intra-Sudetic Basin (ISB), which is representative of several tens of similar, late Palaeozoic troughs in the Central European Variscides. In the Intra-Sudetic Basin, the volcanic rocks comprise scattered outcrops in Carboniferous deposits and an extensive, 0.7 km thick complex in Permian deposits. The older, Carboniferous volcanic rocks are calc-alkaline rhyodacites, with minor rhyolites, andesites and basaltic andesites. The younger, Permian volcanics represent a mildly alkaline suite of rhyolitic tuffs, rhyolites, trachyandesites and basaltic trachyandesites. Fifteen representative samples (three mafic and twelve felsic rocks) were used for the SHRIMP zircon study. Zircons were separated using standard techniques and were analyzed at the Beijing SHRIMP Centre, Chinese Academy of Geological Sciences. Volume estimates of the volcanic rocks are based on existing geological maps (Awdankiewicz 1999 and references therein).

The new SHRIMP data negate earlier views on the Early Carboniferous phase of volcanism in the Intra-Sudetic Basin: the supposed Lower Carboniferous lavas and synsedimentary sills are, in fact, younger, i.e. Upper Carboniferous intrusives emplaced at 304-306 Ma. The volcanic and shallow-level subvolcanic activity in the ISB developed in two main phases, in the Late Carboniferous (313-304 Ma) and Early Permian (298-283 Ma), with the peak of activity at ca 290-289 Ma. The total volume of magma emplaced from volcanic centres within the basin possibly reached several hundreds of cubic kilometres (up to ca 500 km^3?; the preserved volume is ca 300 km^3, but a significant amount of volcanic rocks has been eroded). The contribution of the Carboniferous volcanic stage is rather small (ca 5% of the total volume). The majority of volcanic rocks (ca 95%)

were emplaced during the younger, Permian volcanic stage. Some volcanic associations / volcanic centres cropping out in the Carboniferous deposits were assembled in several magma batches over prolonged periods of time, during both stages of volcanism; e.g. the ages of successive intrusions and extrusions west of Wałbrzych range from 311 to 293 Ma (five samples). Other volcanic centres, related to the more voluminous Permian volcanic stage, probably developed over much shorter time spans, as near Unisław Śląski in the central part of the basin, where four samples of various volcanic units were dated at 289-290 Ma. The timing of activity at some volcanic centres still remains controversial (Carboniferous and Permian, or Permian only?), as the samples dated so far may represent only the youngest magmatic phases (e.g. the Rusinowa-Grzmiąca belt east of Wałbrzych, with two samples dated at ca 293 and 288 Ma).

The Carboniferous and Permian stages of volcanism in the ISB can be referred to as late- and post-orogenic, respectively. These successive stages can be linked to major tectonic processes in the Variscan Belt, such as the termination of orogenic activity at the turn of the Westphalian and Stephanian and the gravitational collapse of the orogen in Stephanian-Early Permian times (cf. Wilson et al. 2004). The climax of volcanism in the Intra-Sudetic Basin postdated the peak of volcanism in the central part of the Permo-Carboniferous volcanic province of Europe (NE Germany) by a few million years. The magma volumes emplaced in the Intra-Sudetic Basin alone were relatively small. However, the cumulative volume of volcanic rocks emplaced in the tens of similar basins across the Variscan Belt must have represented a major contribution to the magmatic output of the whole province.

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Experimental petrology: a new insight into deep Earth composition

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Meteorites remain the main data source for inferring deep Earth composition (McDonough 2003; Palme, O'Neill 2003) whereas seismic waves give fundamental information on the structure of our planet (Bina 2003; McDonough 2003). However, the constant development of high pressure methods in recent decades has allowed us to simulate core and mantle conditions on the surface of the Earth. As a consequence, we can examine the mineralogical composition, crystal structure and physical structure of experimental samples of a meteorite composition and compare these features to those which are expected from geophysical and computational data (Li, Fei 2003).

Two main approaches are used to reach high pressure conditions. One is maximizing the force and second is minimizing the area. The first approach is based on the multianvil press technology, and pressures up to 26 GPa can at present be achieved in a moment (Frost et al. 2004). The second approach is connected with the use of diamond anvil cells. It allows us to reach pressures greater than 365 GPa (Bassett 2009) which correspond to the pressure in the centre of the Earth. In the presented poster, an explanation of the two methods mentioned above will be followed by a review of experimental results obtained through application of these techniques in the last decade.

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Botryoidal hematite formed in burning coal waste dumps: a clue to the origin of hematite spherules on Mars?

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Hematite spherules "blueberries" are one of many intriguing features found in some abundance on the surface of Mars. Since 2004, they have been examined and photographed by the Mars Exploration Rover, notably on the equatorial Meridiani Planum. The spherules comprise grey hematite with a microcrystalline structure ranging in size from hundreds of micrometers to many centimeters. The spherules are associated with massive, subhorizontal layered deposits rich in sulphates, i.e. gypsum, jarosite, kieserite – $MgSO_4 \cdot H_2O$ and other polyhydrated sulphates. Though various explanations for the origin of the nodules have been proposed, e.g. that they are sedimentary concretions or that they are volcanic, their origin(s) remains a matter for debate.

On burning coal dumps at the Marcel Mine in Silesia, Poland, hematite spherules occur in intimate association with sulphate phases. The hematite crystallized on sulphates at a waning (fumarolic, pneumatolytic) stage in the burning of self-ignited coal waste. Sulphate minerals formed before the hematite include alunite – $KAl_3[(SO_4)_2|(OH)_6]$, anhydrite – $CaSO_4$, godovikovite – $(NH_4)Al[SO_4]_2$, iowaite – $Mg_4Fe\ (OH)_8OCl \cdot 4(H_2O)$, coctaite – $(NH_4)Ca[SO_4]_2 \cdot H_2O$, *steklite* – $K,Al(SO_4)_2$, lesukite – $Al_2Cl(OH)_5 \cdot 2H_2O$, millosevichite – $Al_2[SO_4]_3$ and natroalunite – $NaAl_3[(SO_4)_2|(OH)_6]$.

Most of the hematite formed in the coal-waste dumps is botryoidal. A small proportion is represented by spheroids similar to those seen in the Martian images. They differ only in being much smaller (ca 20-50 μm). If the nodules lying on the Meridiani Planum match what is seen in the dumps, and if they are a winnowed fraction of what was in their source, there might well be large residual fields of non-spherical botryoidal hematite closer to a source that was volcanic.

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Copper and lead accumulation in copper ore wastes and the possibility of their agricultural use

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Copper and lead minerals, i.e. malachite and cerussite, are found to be the basic oxidized components of the heavy fractions studied in this paper. They always occur on the outer edges of particles, which are the central parts of sulphides (mostly covellite or chalcocite). Cerussite develops on the outer boundaries of galena crystals and along cleavage cracks. Both galena and cerussite are very common copper minerals identified in Polish deposits (Kucha, Mayer 2007). Malachite and cerussite are the last phases of alteration of sulphides into oxide minerals. In relation to the original composition of a mineral ore (Konstantynowicz 1971), the content of carbonates in the studied sediments is very high.

Chalcocite and digenite occur mainly in the coarsest grain fractions; fine fractions are poor in opaque minerals. Chalcocite and digenite are accompanied by isolated grains of chalcopyrite, bornite and native copper, which bear marks of strong alteration along the cleavage, at the edges of cracks and on external surfaces. Malachite or hematite are formed at the expense of sulphides, whereas cuprite forms after native copper. In the finest grain-size fractions, bornite grains are almost completely altered, and the optical characteristics of chalcopyrite are often left unchanged. Bornite is much less resistant to changes in hypergene weathering conditions.

The ore minerals occur in the sediments in the form of sulphides, oxides and carbonates. Lead and copper carbonates, i.e. malachite and cerussite, result from the alteration of metal sulphides. The copper sulphides occur mainly in fractions coarser than 0.016 mm. The bulk of the fine heavy fractions consists of carbonates, malachite and cerussite replacing covellite and galena, respectively. High concentrations of copper (more than 5000 mg/kg) are a result of the presence of carbonates (which constitute up to 90% of the heavy fraction), poorly soluble and stable in an alkaline environment.

As shown in previous studies (Diatta et al. 2009), sediments from tailing ponds can be used as an acidity regulator when mixed with acidic soils. The pH of soil occurring in the immediate vicinity of the pond is slightly acidic to neutral, and usually ranges between 5.0 and 6.6 (Lis, Pasieczna 1999), so their use to control the acidity is also possible. It was reported that the copper concentration varies over a wide range, from 810 to over 5181 mg/kg. Bioavailable fractions of copper (determined by the phytotoxicity test, i.e. CH_3COONH_4 + EDTA, pH 4.65) vary within the range 217-1646 mg/kg and are not directly dependent on changes in sediment pH, which tentatively decreases with increasing sampling depth. The same regularity applies to lead. It should be emphasized that the chemical test used is characterized by the pH values occurring in most agricultural soils in Poland.

The reaction of plants and their lower or higher ability to accumulate these metals is strongly dependent on the root system (different for cereals, potatoes, vegetables) and the pH of the soil, obtained by mixing the sediment with the acidic soil. The reaction of plants to the presence of copper and lead in the environment will increase with an increase of fine fractions in the sediment, which means that more malachite and cerussite occur in the sediment. As was shown by the studies of the sediments from the other pond (Duczmal-Czernikiewicz et al. 2012), oxidation of the sediments leads to changes in both the mineral and chemical components of the wastes.

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Stable isotopic composition of carbonates and sulphates from soilsand paleosols of the Poznań Formation (Neogene, Polish Lowland)

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Introduction

Soil carbonates and sulphates form in soils in very low precipitation conditions, less than 100 cm per annum (Lee 1999). They are commonly preserved in continental sediments and paleosols, and they are a possible indicator of climatic conditions (Retallack 1997). Oxygen, carbon and sulfur isotopes may be used to elucidate paleoecology and paleoclimate (Sheldon 1999). The Mio-Pliocene Poznań Formation, Polish Lowland, contains horizons of pedogenic carbonates (Duczmal-Czernikiewicz 2011), sometimes coexisting with gypsum horizons (Wyrwicki 1974; Wichrowski 1981). The aim of this work was to determine the isotopic composition of pedogenic carbonates and sulphates which were formed in the Dymaczewo Stare old open-pit mine, near Poznań. The isotopic record may provide additional information, which enables us to reconstruct the climatic evolution during the Miocene and Pliocene in Central Europe.

Methods

Isotopic analysis was carried out using a dual inlet and triple collector mass spectrometer (modified and modernized MI1305 model). Carbonate samples were analyzed on CO_2 produced by reaction with 100% H_3PO_4 in a glass vacuum line connected to the inlet system of the mass spectrometer. The reaction proceeded at an electronically controlled temperature of 25°C ± 0.2°C to achieve $\delta^{18}O$ in the PDB scale. For normalization of both $\delta^{13}C$ and $\delta^{18}O$ values, the international standard NBS-19 was analyzed in each series of samples. The analytical uncertainty of both delta values in terms of standard deviation was better than 0.06‰. Gypsum samples were converted to $BaSO_4$, from which sulfur and oxygen were quantitatively extracted in the form of SO_2 (Halas, Szaran 2004) and CO_2 (Halas et al. 2004) gases. These gases were analyzed using the SO^+ or CO_2^+ mass-spectrum, respectively.

Results and interpretation

Calcretes from the Dymaczewo Stare open-pit mine occur at two separate levels, at depths of 0.75 m and 2.5 m below the contemporary ground surface. Their shape is elongated and they reach up to 1.5 m in diameter. The calcretes consist of calcite (sparite or micrite), with common intercalations of Fe-oxides (mainly hematite). Some nodules contain septarian crystallaria, which narrow outward from the centers of the nodules formation, in compaction processes and recrystallization of carbonates. They are filled with two distinct carbonate generations. In the outer concretion rims and/or as carbonate breccias cement, gypsum crystals have been found. They reach lengths from 1-2 mm in brecciated parts of the nodules, up to 10 cm in the outer rims of the nodules.

X-ray diffraction studies proved that the sulphate minerals are represented by gypsum crystals (up to 5 cm length) and basaluminite (white powder). Gypsum crystallaria which form rims around the concretions, could have been incorporated by organic matter.

Values of $\delta^{13}C$ in carbonates from the open pit vary from –34.71‰ (in the inner part of concretions) to –36.98‰ (in the outer part of concretions) and –40.73‰ (in the lower horizon of carbonates). Delta $\delta^{18}O$ values vary from –5.32‰ in the lower horizon to –4.65‰ in the upper horizon of carbonates.

$\delta^{34}S$ in gypsum show weak positive values, from 3.80 to 4.80‰, which agree with the isotopic signature of sulfur in basaluminite: 3.72‰. $\delta^{18}O$ values range from –3.20‰ in basaluminite through –3.20, -1.70 to –0.40‰ in the gypsum crystals. In a gypsum crystal, which incorporates clays and organic matter, $\delta^{18}O$ attains the positive value of 7.23‰.

The carbonates from the Dymaczewo Stare open-pit mine are strongly depleted in ^{13}C isotope. Their isotopic record is affected by drying and wetting cycles, which allow for the formation of slickensides through infiltration of carbon compounds into the opened cracks and slits (Retallack 1997). The isotope records may be modified by vegetation during contemporary weathering processes. The isotopic composition of sulfur in the sulphates indicates continental conditions and arid or semi-arid climatic episodes during the development of the paleosols, and also recrystallization of gypsum crystals, which contain intercalations of clay minerals and organic matter.

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Low temperature synthesis and stability of fluorpyromorphite $Pb_5(PO_4)_3F$ at pH 2–11

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The purpose of this study was the low temperature synthesis and experimental determination of solubility at different pH of the F variety of pyromorphite: $Pb_5(PO_4)_3F$ (fluorpyromorphite). To synthesise 10 g of fluorpyromorphite, we used 3.45 g of $NH_4H_2PO_4$, 17.14 g of $Pb(NO_3)$ and 0.43 g of NaF. Each chemical was diluted in 500ml of redistilled water, and the solutions were mixed using a peristaltic pump. After the addition, the product of the synthesis was allowed to age for 14 days, washed several times with water and air-dried.

The product of synthesis was identified as fluorpyromorphite $Pb_5(PO_4)_3F$ by powder XRD (Joint Committee on Powder Diffraction Standards card number 24-0348). The unit cell parameters are a = 9.743 Å, c = 7.322 Å, which are similar to a = 9.75 Å, c = 7.3 Å reported in the standard card. A different method of synthesis is a reason for the slight difference in the values obtained.

300 mg of synthetic FPY was dissolved for over 2 months in 250 mL of 0.05 sM NH_4NO_3 at temperature 25°C, open to the air. The experiments were repeated several times for pH between 2 and 11. Solutions were periodically syringe-sampled and analyzed for Pb using AAS, and for PO_4^{3-} or F^- using colorimetry. The molar ratios of the ions are essential to determine the pH range of congruent dissolution. PHREEQC computer code (with the thermodynamic database Lawrence Livermore National Laboratory) were used to calculate the activity of ions and speciation in the solution. The result will be applied in further experiments to determine the thermodynamic properties of fluorpyromorphite in comparison with other lead apatites.

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Varved clays in the catchment area of Junikowski Stream – XRD detection of clay minerals

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Introduction

In the Poznań area, varved clays occur in the middle part of the Junikowski Stream catchment area. They were deposited in a glacial channel, during the period between the Poznań and Leszno phases of the Vistulian Glaciation, and attain a maximum thickness of 10-15 m. Varved clays of ice-dammed lakes are characterized by a heterogenous vertical profile in terms of grain size.

The material described, deposited in the ice-dammed lakes of an ice-sheet foreland, came mainly from a melting glacier and was deposited by rivers. These clays are characterized by a specific structure resulting from an alternating arrangement of light (sandy-silty or silty) and dark layers (silty-clayey or clayey). Rhythmic sedimentation of varved deposits is the result of changing deposition conditions within the period of a year. An annual layer forms a varve.

The structural anisotropy simultaneously causes the variability of physical and mechanical properties of clays, which is primarily the result of differences in sediment granulometry. The mineral composition, mainly light and dark layers of the clay fraction, influences also the engineering features of the varved clays.

Methods

The first stage in the determination of the mineral composition of the clay fraction consisted of the X-ray analysis of soil samples, separately for the light layers (6 samples) and dark layers (4 samples). The X-ray Powder Diffraction (XRD) method used in the study was based on the Thermo Electron roentgenopraph (ARL X'tra model). The WinXRD software was used to obtain the diffraction patterns and to prepare the qualitative analysis. The angular range of the investigation based on the diffraction patterns was 3-30º 2θ with the step – 0.02.

In all samples, the analysed clay fraction was divided into two sub-fractions: < 0.2 µm and < 2 µm. For the needs of the X-ray analysis, 3 types of preparations were produced: in the natural state, saturated with ethylene glycol and calcined at a temperature of 550°C.

Discussion and Conclusions

On analysis of the received diffraction patterns and selected literature (Stoch 1974; Myślińska 1965; Manecki, Muszyński 2008), it can be concluded that the basic clay mineral present in the clay fraction of the investigated deposits is hydromica (illite). Kaolinite, smectite and chlorite are observed in smaller amounts.

In all investigated samples, a low-angle peak, equal to 10 Å, corresponding to hydromica (illite) can be clearly observed. At the same time, its presence can be confirmed by high-angle reflections equal to ca 4.95-5.00 Å and 3.32-3.33 Å respectively (Fig. 1).

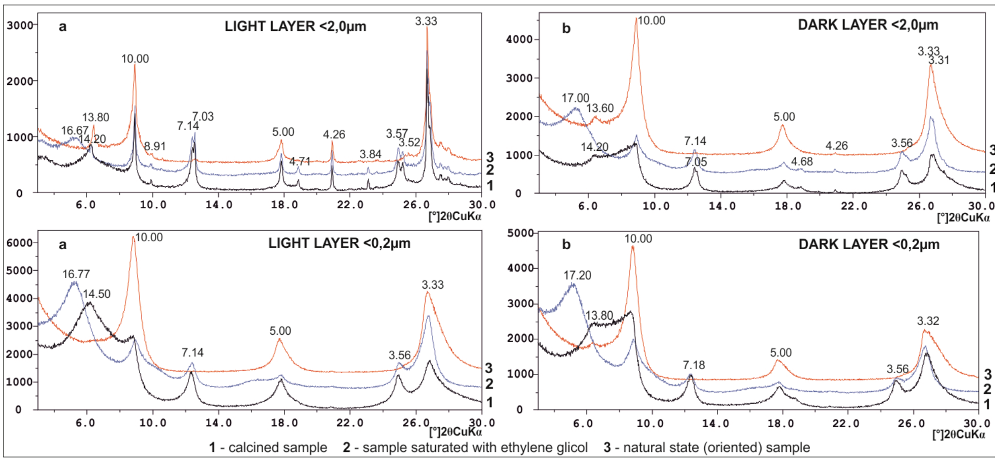

Fig. 1. X-ray diffraction patterns of the chosen samples of varved clays:
a – for the dark layer, b – for the light layer.

The first low-angle peaks of 16.67-17.20 Å present in Fig. 1. for ethylene glycol saturated samples and 13.80-14.50 Å for the natural state sample are characteristic of mixed package silicates – smectite and chlorite or swelling chlorite. The reflections of 7.10 Å and 3.55 Å can be also attributed to chlorite. The latter one confirms the presence of a chlorite-kaolinite mixture. The low-angle peaks in the diffraction patterns of ca 7.14 Å are typical of kaolinite.

The low-angle peak of 8.91 Å visible in the light layer samples implies the possibility of an admixture of sulphates. Based on the diffraction patterns generated separately for the light and the dark layers of the varved clays from the catchment area of the Junikowski Stream, it can be concluded that in the vertical profile within the clay fraction no changes in mineral composition can be observed. Nevertheless, a distinct difference in the amount of quartz is visible. The content of quartz is considerably higher in the light layers than in the dark layers (clear reflections of 4.24-4.26 Å in the light layer samples).

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Geochemical and petrological features of eclogites from Piława Górna (Góry Sowie Block, SW Poland)

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A several meters thick mafic body embedded in migmatitic gneisses in the Piława Górna quarry comprises heterogeneously retrogressed eclogites. These rocks have a basaltic composition of tholeiitic affinity (Nb/Y av. 0.15 ± 0.03). The chondrite-normalised REE patterns show minor enrichment in LREE ($[La/Yb]_{CN}$: 0.16-1.94) resulting in nearly flat to slightly negatively inclined profiles. These diagrams also display weak fractionation of HREE ($[Tb/Yb]_{CN}$: 1.22-1.45). When compared to N-MORB, the rocks studied display a weak enrichment in incompatible elements (up to ca 4 x N-MORB), a systematic decrease of concentrations from LREE towards the least incompatible elements, and a systematic negative Nb anomaly relative to La and Th (Th/Nb av. 0.22 ± 0.09). The elevated Zr/Nb (28-48) and Y/Nb (5.70-11.27) ratios suggest magma generation from a depleted asthenospheric mantle source (DMM-like) which was presumably fused at shallow levels, within the spinel stability field. However, moderate Ti/V (36-48) and Nb/Yb (0.94-1.67) ratios, and the excess of LREE and Th relative to Nb, indicate an enrichment process which affected the source. As on several discrimination diagrams the studied eclogites show a strong affinity to volcanic arc or back-arc basin basalts, it is presumed that the magmatic protolith of the rocks could have been generated in a supra-subduction setting.

The studied rocks underwent intense metamorphism marked by development of several mineral assemblages. The earliest (the eclogite stage) comprises garnet, omphacite (X_{jd} 0.38-0.41), kyanite, rutile and quartz. It was subsequently overprinted by clinopyroxene and plagioclase symplectites (breakdown of omphacite). Next, at the corona stage garnet was partly replaced by amphibole and plagioclase. It was followed by growth of orthopyroxene and then formation of spinel + plagioclase symplectite at the expense of kyanite, and spinel + orthopyroxene symplectite at the expense of amphibole. The conditions of the eclogite stage are estimated 770-830°C and 2.1-2.6 GPa (conventional geothermobarometers) or 730-840°C and 2.0-2.5 GPa (phase equilibrium modelling). The post-eclogitic, symplectite stage took place at 770-680°C and 1.7-1.4 GPa, whilst the corona stage is constrained to 600-700°C at 0.6-1.2 GPa (phase equilibrium modelling) or 0.7-0.8 GPa (conventional geothermobarometers). The appearance of orthopyroxene, development of symplectites with spinel and late re-equilibration of clinopyroxene and plagioclase, most probably indicate a further pressure decrease below 0.5-0.7 GPa along the retrogression path.

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Geochemical and Nd isotopic record of transition from back-arc setting to rifted margin in metabasites from the Stronie Formation of the Bystrzyckie and Orlickie Mts. (Sudetes, SW Poland)

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The western part of the Orlica-Śnieżnik Dome (OSD) comprises a large orthogneiss body (the Bystrzyckie orthogneiss, ca 500 Ma; Kröner et al. 2001) mantled by the metamorphosed volcano-sedimentary succession of the Stronie and Młynowiec Formations, composed of biotite- to staurolite-grade mica schists and paragneisses with intercalations of marbles and metabasites. The recent studies of Szczepański (2010) and Mazur et al. (2012) indicate that the Młynowiec Formation is a Neoproterozoic sequence (ca 560 Ma) probably related to the Cadomian orogeny and deposited in a supra-subduction tectonic environment, whereas the Early Cambrian Stronie Formation (ca 530 Ma) most probably derived from the erosion of the newly-formed Cadomian orogen and may be considered as an infill of incipient rift basin established after cessation of the Cadomian orogeny.

Metabasalts, which were emplaced coevally with the accumulation of the protolith to the Stronie Formation of the Bystrzyckie and Orlickie Mts., show diverse geochemical features. Immobile trace element and Nd isotope features allow a distinction of dominant, either E-MORB-like (Group 1) or mildly enriched N-MORB-like tholeiites (Group 2), and scarce but genetically important OIB-like alkaline (Group 3) or depleted tholeiitic rocks (Group 4). All magmas were extracted at shallow levels from different mantle sources. The OIB affinity of Group 3 is interpreted to reflect an enriched mantle-type asthenospheric source whilst groups of tholeiitic rocks indicate the involvement of a depleted MORB-type mantle. This depleted mantle was affected by different enrichment processes. Groups 2 and 4 show back-arc basin affinities with a strongly variable subduction zone contribution. For the Group 1 and the subduction-unaffected rocks of Group 2, the decoupling between Nd isotopes and trace element characteristics suggests that shortly prior to melt generation their respective mantle sources underwent enrichment by low-degree alkaline melts.

Based on contrasting back-arc basin- and within-plate-like affinities of the metabasites, and on petrogenetic constraints from the contemporaneous Stronie formation rift basin, it is suggested that the studied magmatic episode might be related to the cessation of the supra-subduction zone activity. This event might have led to slab break-off, opening of a slab window and upward migration of sub-slab enriched asthenosphere. In an extensional regime, magmas generated at shallow levels from heterogeneous mantle regions were emplaced within sedimentary rocks of the overlying rift basin. The vestiges of subduction-related processes and the within-plate style of mantle enrichment seemingly relate the studied magmatic episode to extinction of the subduction zone at the end of the Cadomian orogeny and incipient Early Palaeozoic rifting of Gondwana as proposed by Linnemann et al. (2008).

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Migmatization and regional-scale folding in the Orlica-Śnieżnik Dome, NE Bohemian Massif: constraints from structural and metamorphic records of the Młynowiec Formation

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The Orlica-Śnieżnik Dome (OSD), NE Bohemian Massif, consists of rocks showing different metamorphic grades ranging from low-amphibolite- to granulite- and eclogite-facies conditions (e.g. Don et al. 2003). The geological mapping and structural studies carried out over the years revealed also that metamorphic foliations in the separate domains of the OSD have diverse orientations, with strongly variable strike and/or dip values (e.g. Don et al. 2003; Chopin et al. 2012). New studies on the Młynowiec Formation, a partially migmatized metasedimentary formation of the OSD, provide insights into (1) origin and structural position of differently oriented metamorphic fabrics, (2) reasons for the differences in metamorphic grade of the metavolcano-sedimentary rocks, and (3) P-T conditions of the migmatization event and a possible cause of its merely localized character in the Orlica-Śnieżnik Dome.

The structural record of both non-migmatized and migmatized parts of the Młynowiec Formation corresponds to that obtained for other metapelites of the OSD. The development of the first metamorphic fabric, mainly preserved as inclusion trails in porphyroblasts (D1 stage), was followed by the formation of N-S-trending tight folds and axial planar fabric (D2 stage). The latter is correlated with the flattening strain widespread at the NE edge of the Bohemian Massif. Both tectonic events were presumably related to successive stages of the E-W directed Variscan collision between the Saxothuringian (or Moldanubian) terrane of the Bohemian Massif and the Brunovistulian terrane, with reference to the tectonic reconstructions of the suture zone between these terranes (Jastrzębski 2012).

MnNCKFMASH pseudosection thermobarometry indicates that non-migmatized rocks in the northern part of the Młynowiec Formation area experienced maximum temperatures around 650°C at 6-7 kbar during the D2 stage. At the same time, rocks from the southern part of the Młynowiec Formation underwent higher grade Barrovian metamorphism leading to localized partial melting. The following stages of continental collision were controlled by top-to-the-(N)NE (dextral) movements producing further uplift and cooling to greenschist facies conditions (D3 stage). It is proposed that the continuation of the NE-directed tectonic transport of the OSD involved late interactions with the adjacent Brunovistulian terrane in the east and the Góry Sowie Block in the north, which eventually led to a large-scale folding of the syn-D2 metamorphic fabric in the OSD. In the Młynowiec Formation, this folding event (D4 stage) caused the metamorphic foliation to dip locally at different angles (moderate to high) and different azimuths (NE, N, NW and W). Together with the syn-D2 foliation, the Barrovian zones were folded and inclined towards the W(NW). In consequence, the sequence of syn-D2 Barrovian zones noted in the Stronie Formation can be further traced towards the SE of the OSD, where the metasedimentary rocks of the Młynowiec Formation have been partially migmatized.

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Granulite facies migmatites from the Seve Nappe Complex of west-central Jämtland, Swedish Caledonides: new evidence for HP metamorphism

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The Seve Nappe Complex (SNC) in the Scandinavian Caledonides is composed of medium- and high- grade metamorphic rocks derived from the outer parts of the Baltica margin. Amphibolite facies metasediments and granulite facies gneisses and migmatites are the main lithologies. Rare eclogites and garnet peridotites occur locally. Therefore, it is important to look for alternative evidence of high pressure metamorphism in other localities to unravel a more complete evolution of the SNC. Granulites from the SNC on Åreskutan in west-central Jämtland give us an excellent opportunity to provide important information on the former higher pressure history of these far-travelled nappes. The peak (temperature) metamorphism of the Åreskutan Nappe, according to zircon ion microprobe dating (Ladenberger et. al. 2012) is inferred to have occurred at 442-436 Ma. The latest EMP monazite dating (Majka et. al. 2012) indicates that an earlier high pressure metamorphism occurred at 455 ± 11 Ma (mid-late Ordovician). This age is similar to those reported for eclogites from northwestern Jämtland (Root, Corfu 2012; Brueckner, van Roermund 2007).

Kyanite-bearing leucogranulites were collected from the Åreskutan Nappe (Middle Seve Nappe). Based on Grt-Phg-Ky-Qtz and Phg (Si = 3.38-3.47 apfu) barometers and Grt-Phg thermometer and a modeled pseudosection in the NCKFMMnASH system (for high pressure assemblages: garnet, phengite), the peak pressure conditions were estimated to be 24-32 kbar and 680-720°C. The retrogressive conditions (decompression, partial melting) are inferred from the GASP geobarometer, kyanite-sillimanite transition, biotite-plagioclase assemblages and melt occurrence (phase diagrams). Decompression to ~5-6 kbar is simultaneous with a temperature increase to ~800°C and partial melting. It was followed by cooling to 700°C at 3 kbar and melt crystallization to plagioclase, biotite, K-feldspar and sillimanite. The presence of LP sillimanite replacing HP kyanite in leucogranulites provides evidence of a possibly continuous partial-melt crystallization from high pressure towards lower pressure conditions.

Conventional geothermobarometry together with thermodynamic modeling and extensive field work, the discovery of the kyanite–sillimanite transformation and microtexture analysis lead to the innovative concept that the Åreskutan Nappe experienced HP and HT metamorphism, and not just LP as commonly thought so far. In turn, it suggests that the entire SNC in western Jämtland may have undergone high pressure metamorphism prior to the early Silurian partial melting and emplacement from the hinterland eastwards onto the Baltoscandian platform.

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Metamorphic P-T conditions in metasedimentary rocks of the Kaczawa Complex (SW Poland) based on white mica and chlorite "crystallinity", white mica *b* cell dimension and the chlorite geothermometer

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The Kaczawa Unit of the West Sudetes (NE part of the Bohemian Massif) comprises in its lower (Variscan) part, termed the Kaczawa Complex (KC), low-grade metasedimentary and metavolcanic rocks ranging from Cambrian (and possibly Neoproterozoic) to early Carboniferous in age. The Kaczawa Complex is composed of: (a) thrust slices and likely nappe fragments representing generally coherent metasedimentary-metavolcanic units assigned to the (Pre)Cambrian-Devonian, and (b) mélange bodies containing various fragments of the former units, mostly chaotically distributed in a dark muddy matrix. The latter mudrocks of the KC are interpreted to be sediments gravitationally redeposited within an oceanic trench, which have subsequently undergone deformation and metamorphism during further evolution of the Variscan accretionary prism (Kryza, Zalasiewicz 2008, and refs. therein).

First results on the metamorphic conditions recorded in a mélange and associated metamudstones of the N part of the Kaczawa Mts. were reported by Kostylew (2008). Here we present new data on the P-T metamorphic conditions for mélanges, turbidites, and various fine-grained metasedimentary rocks from various units of the KC.

We have established metamorphic conditions using the illite "crystallinity" (IC) and chlorite/kaolinite (ChC/KaC) indices, using X-ray diffraction (XRD) and standardization procedure according to Warr and Rice (1994). In addition, the white mica *b* cell dimension parameter was calculated (Merriman, Frey, 1999, and refs. therein). In total, 14 samples were collected from various units of the northern, southern and western parts of the Kaczawa Mts. (Złotoryja, Rzeszówek-Jakuszowa, Bolków, Radzimowice, Świerzawa units and in the vicinity of Lubań and Rząsiny). The samples represent various metasedimentary rock types, including the muddy matrix of mélange from Bolków, Rzeszówek and Złotoryja (four samples).

Chlorite geothermometry has been applied for comparison. This method is based on the correlation between tetrahedral Al and Fe/(Fe+Mg) in a single chlorite grain. In total, 116 analyses were obtained using the microprobe technique. The microprobe analyses were recalculated according to four different equations (Kranidiotis, MacLean 1987; Cathelineau 1988; Jowett 1991; Xie et al. 1997). 59 microprobe analyses were performed on 8 samples of mélange and other metamudstones from deep drill cores near Stanisławów (Chełmiec Unit) and 57 analyses on 7 samples of metamudstones from the Rzeszówek mélange (Rzeszówek-Jakuszowa Unit, both units in the northern part of the Kaczawa Mts.).

The IC and ChC/KaC data show that the temperature of metamorphism ranged between 200°C and 300°C, indicating low- to very low-grade metamorphism (low and high anchizone), with a transition to the epizone (~300°C). The temperature of ~300°C was calculated for the sample from Rząsiny (W part of the Kaczawa Mts.), which is interpreted as possibly related to the thermal influence of the Karkonosze Granite to the SW. The white mica *b* cell dimension parameters indicate a medium to high pressure gradient, which is typical of 'Alpine collisional' and 'accretionary' geotectonic settings (Poręba 2011) and agrees with the data obtained by Kostylew (2008).

Chlorite geothermometry provided the most diverse results, with temperatures ranging from ~70 up to 400°C, depending on the calibration method. The most coherent results were obtained using the equations by Cathelineau (1988) and Jowett (1991), with regression coefficients (R^2) up to 1.00 and 0.99, and temperature varied from 224°C to 384°C, and from 236°C to 400°C, respectively. The chlorite geothermometer calculated according to Kranidiotis and MacLean (1987) gave similar results to those obtained from the 'crystallinity' technique, with the temperature ranging from 162°C to 224°C and the R^2 coefficient = 0.76. The chlorite geothermometer based on the equation by Xie et al. (1997) gave the most scattered results, with temperatures ranging from 69°C to 300°C and the R^2 coefficient = 0.12.

Our new data based on the XRD 'crystallinity' technique and the chlorite geothermometer support previous results, suggesting that the metasedimentary rocks of the KC have been metamorphosed under conditions characteristic of the anchizone and epizone. In addition, they also support the model assuming that various parts of the Kaczawa Unit have undergone different paths of metamorphic and tectonic evolution (Kryza et al. 2011). Furthermore, we suggest that applications of various calibrations of chlorite geothermometers should be used with caution, as our results are widely scattered and often differ from those obtained by other methods.

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New blueschist-eclogite province in Svalbard

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During a field expedition to Nordenskiöld Land (SW Svalbard) in the summer of 2011, so far unrecognised high-grade metamorphic rocks were observed. These rocks are represented by high-pressure lithologies, such as the blueschist-eclogite series. These predominantly metamafic rocks could be observed at least at three different tectonic levels and occur typically in the form of isolated bodies of different size enclosed in metasedimentary units.

They consist mainly of reddish garnet and greenish and bluish amphiboles. Other major components are chlorite, epidote, biotite, quartz and albite. Additionally, in some samples glaucophane was observed.

The garnets typically contain large numbers of epidote, albite, quartz, amphibole and titanite inclusions. High contrast back-scattered images and compositional profiles through the garnets show distinct chemical differences between cores and rims. Their composition varies from $Alm_{43}Pyr_1Grs_{50}Spss_6$ in the cores to $Alm_{65}Pyr_3Grs_{32}Spss_0$ in the rims. The change in chemical zoning is either abrupt or more gradual, suggesting two garnet growth events. Preliminary P-T estimates based on thermodynamic modeling in the NCKFMMnASHT system indicate pressure peak conditions below ca 17 kbar and 500°C (obtained from garnet cores).

Tectonically, the whole area is characterized by a moderate, 50°-dipping of S0 and S1 (the main metamorphic foliation) to the north. Deviations from this direction are small and occur only locally. They are mostly caused by the presence of rigid metamafic bodies, around which the common orientation of the bedding and the metamorphic foliation are disturbed. The observed stretching lineations plunge towards the N-NNE and are therefore in very good agreement with the orientation of S0 and S1. Occasionally observed E-W orientated folds have a predominant vergence to the S. Moreover, shear sense indicators such as commonly observed sigma clasts clearly indicate a transport direction from north to south.

The structural geology observations are in good agreement with those made south of the study area, in the northern part of Wedel Jarlsberg Land, but high pressure lithologies have not so far been identified there. On the other hand, these high pressure rocks, exotic in Nordenskiöld Land, may be an equivalent of the high pressure rocks known from Oskar II Land (Motalfjella region) and Albert II Land (Richarddalen region), occurring to the north of the research area. Detailed petrological and geochronological studies to verify this hypothesis are in progress.

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Unique chloride assemblage of exhalative origin from burning coal-mining dump in Radlin (Rybnik Coal Area, S Poland)

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The first chloride minerals (lesukite and iowaite) from the highly thermally engaged col-mining dump of the “Marcel” mine in Radlin (Rybnik Coal Area) were reported by Ciesielczuk et al. (2010), together with millosevichite $(Al,Fe)_2(SO_4)_3$, steklite $KAl(SO_4)_2$ and other sulphates. Further investigations showed that the mineral composition of local exhalative zones is much more complex and of short-distance variability. The most common constituents of the chloride crust are sal ammoniac, kremersite $(NH_4,K)_2[FeCl_5(H_2O)]$ and various NH_4-Mg chlorides. They were found together in an exhalatively active zone, with temperature up to 160°C. Kremersite (a = 13.721(1), b = 9.924(1), c = 7.0389(5); R_{wp} = 5.41%[1], GOF = 2.58, DW = 1.06), though very delicate and thus difficult to analyze, has a composition (EDS, n = 8) close to $[(NH_4)_{1.95}K_{0.04}Na_{0.01}][(Fe_{0.99}Al_{0.01}Zn_{0.01})Cl_{4.95}F_{0.05}(H_2O)]$, with F and I detected only occasionally. Kremersite-rich aggregates are enriched in As (40 ppm), Bi (7.9 ppm), Cd (3.6 ppm), Cu (33 ppm), Mn (320 ppm), Ni (18 ppm), Pb (40 ppm), Sn (34 ppm), Tl (9.6 ppm) and Zn (53 ppm). An admixture of Br was noted in sal ammoniac associated with kremersite, leading to a $NH_4Cl_{0.99}Br_{0.01}$ composition. Sal ammoniac from another part of the dump, however, has the formula $NH_4Cl_{0.91}Br_{0.07}I_{0.02}$. Its unit cell parameter a = 3.8815(1) differs only slightly from that of pure NH_4Cl (PDF 077-2352: a = 3.878). A coexisting NH_4-Mg phase is K-free but Fe-bearing: $(NH_4)Mg_{0.95}Fe_{0.05}Cl_3 \cdot 6H_2O$. PXRD refinements (TOPAS software) show that both the orthorhombic (*redikortsevite*[2]; a = 9.571(2), b = 13.339(1), c = 9.328(1)) and triclinic (a = 6.6721(7), b = 13.3194(7), c = 6.6774(1), α = 89.955(8), β = 91.519(8), γ = 89.938(1); R_{wp} = 5.00%, GOF = 1.97, DW = 1.43) forms of $(NH_4)MgCl_3 \cdot 6H_2O$ are subordinate to a monoclinic unnamed $(NH_4)K_2Mg_3Cl_9 \cdot 18H_2O$ phase, with the following unit cell parameters: a = 16.341(4), b = 22.898(3), c = 9.508(2), β = 90.23(2). Within the lower, *redikortsevite*-enriched zone, rare green botryoidal aggregates of a Cu-bearing $(NH_4)_3[ZnCl_4]Cl$ phase (PDF 074-0718, *Pnma*, a = 8.69(2), b = 9.9(3), c = 12.647(4); R_{wp} = 5.11%, GOF = 1.39, DW = 1.18) were found. Locally they are covered by Cu-rich Mn chloride, likely scacchite (a = 3.543(3), c = 17.7(5)), confirmed via TOPAS refinements together with chloromagnesite (a = 3.578(2), c = 17.3(1)). These materials are associated with hydrocalumite $Ca_2Al(OH)_6[Cl_{1-x}(OH)_x] \cdot 3H_2O$ (a = 10.009(6), b = 11.476(8), c = 16.32(4), β = 104.7(5)), bischofite, lepidocrocite, kieserite, anhydrite

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[1] R_{wp} – residual weighted-pattern, GOF (χ^2) – goodness of fit, DW – Durbin-Watson statistics.

[2] Italicized names correspond to the ones not approved by the International Mineralogical Association.

and unconfirmed belloite $Cu(OH)Cl$. Phases in the NH_4-Zn-Cl system, namely *amminite* $Zn(NH_3)_2Cl_2$ and *chlorozincite* $ZnCl_2 \cdot 4Zn(OH)_2$, from a dump near Gornyak (Kopeisk area, Chelyabinsk Coal Basin), are mentioned by Chesnokov et al. (1998). Lesukite was identified in an alunite-rich sample. Its unit cell parameter a was refined to be equal to 19.813(4) ($R_{wp} = 5.87\%$, GOF = 1.71, DW = 0.85). In one steklite-bearing sample, very rare korshunovskite $Mg_2(OH)_3Cl \cdot 4H_2O$ was confirmed. It coexists, as in case of holotype material, with iowaite (refined parameters: a = 3.145(1), c = 24.55(6)), together with langbeinite $K_2Mg_2(SO_4)_3$ and probably apthitalite $K_3Na(SO_4)_2$. Refined cell parameters of Silesian korshunovskite are: a = 9.02(5), b = 6.20(4), c = 7.48(5), α = 102.2(6), β = 103.9(3), γ = 72.6(9) (R_{wp} = 18.96%, GOF = 6.63, DW = 0.07). The "Marcel" mine dump now stands for the second world occurrence of korshunovskite, previously known only from the Korshunovskoe skarn Fe deposit (Malinko et al. 1982). This is probably also the first documented coal-fire-related site with formation of $Al(OH)_3$ minerals (nordstrandite and bayerite), representing the final step of aluminium chloride hydrolysis, with lesukite as an intermediate phase.

Other identified halides include monoclinic $FeCl_2 \cdot 4H_2O$, probably a precursor of dihydrate form (rokühnite), $[FeCl_2(H_2O)_4][FeCl_4](H_2O)$ phase, the dihydrate analogue of carnallite, and as yet unconfirmed chloraluminite $AlCl_3 \cdot 6H_2O$, cryolite $Na_3[AlF_6]$, *P*-lattice analogue of molysite $FeCl_3$, ralstonite $Na_3Mg_3Al_{13}(OH)_{17}F_{21}(H_2O)_7$, rosenbergite $AlF_3 \cdot 3H_2O$ and erythrosiderite (K-analogue of kremersite). The ammonium-rich chloride crust fluently passes into a K-dominated sulphate crust, composed mainly of millosevichite and steklite, with minor mikasaite $Fe_2(SO_4)_3$, efremovite $(NH_4)_2Mg_2(SO_4)_3$, alum-(Na) $NaAl(SO_4)_2 \cdot 12H_2O$, malladrite $Na_2[SiF_6]$, molysite, yavapaiite? $KFe(SO_4)_2$ and probably $(H_3O)Al(SO_4)_2$ phase. Samples collected around both the crusts contain alum-(K), alunogen $Al_2(SO_4)_3 \cdot 17H_2O$, ammonioleucite $(NH_4,K)AlSi_2O_6$, boussingaultite $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$, gypsum, mascagnite $(NH_4)_2SO_4$, misenite $K_8(SO_4)(SO_3OH)_6$, mohrite $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, picromerite $K_2Mg(SO_4)_2 \cdot 6H_2O$, tamarugite $NaAl(SO_4)_2 \cdot 6H_2O$, tobelite (NH_4-analogue of muscovite), common rhomboclase $(H_5O_2)Fe(SO_4)_2 \cdot 2H_2O$, rostite $Al(SO_4)(F,OH) \cdot 5H_2O$, tschermigite $(NH_4)Al(SO_4)_2 \cdot 12H_2O$, and probably $K_3Al(SO_4)_3$ phase, letovicite $(NH_4)_3H(SO_4)_2$, mirabilite $Na_2SO_4 \cdot 10H_2O$, newberyite $MgHPO_4 \cdot 3H_2O$, Pb chloride of cotunnite ($PbCl_2$) habit, schertelite $(NH_4)_2H_2Mg_2(PO_4)_2 \cdot 4H_2O$, Sn chloride of panichiite ($(NH_4)_2[SnCl_6]$) habit, and tsaregorodtsevite $[N(CH_3)_4]Si_4(Si,Al)_2O_{12}$. In the research area, an assemblage of sal ammoniac, sulfur and minor polymorphs of $(NH_4)_2[SiF_6]$ (cryptohalite and bararite), and a phase in the As-S system, were also found. The presence of acetamide $(CH_3)CO(NH_2)_2$ in some samples is uncertain.

Analysis of chloride- and sulphate- bearing mineralized gas vents on burning dumps may be an easy way to understand mineral-formation processes of NH_4-Mg-Fe-Cl-OH system, connected, e.g. with weathering of serpentine minerals (case of iowaite), but also the alteration of meteorites (Anthony et al. 1997).

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A record of magma differentiation preserved in apatite from the Karkonosze granite, Poland

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The differentiation history of the Karkonosze granitoid pluton has been described using whole-rock and feldspar chemistry (e.g. Słaby, Götze 2004; Słaby, Martin 2008). Fractional crystallization and mixing between mantle- and crust-derived melts were the most important petrogenetic processes. In some rocks late fluid-interaction is also recognized. The whole-rock chemical compositions point to magma mixing as the dominant process, which is also visible in feldspar zonation patterns revealed by CL imaging (Słaby, Götze 2004). The aim of this study is to verify if the same processes are recorded in accessory minerals. Apatite was chosen because it is present in all types of rocks in the pluton and preliminary studies (Przywóski 2006; Słaby 2006) have shown that its chemical composition can be explained by heterogeneity in the magmatic system.

We studied apatite from all stages of magma hybridization. Apatites from granodiorites, which formed from homogeneous, intensive mixing, show the most complex internal zoning, expressed mainly by differences in REE-, Y- and SiO_2-content. The zones are often irregular, discontinuous and separated by resorption boundaries. Oscillatory zoned and homogeneous grains are also present. Similar textures are present in apatites from the primitive porphyritic granite (which experienced only a small degree of mixing). Apatites from magmatic enclaves which represent the later stage of less intensive mixing show textures with less complex, flame-like and patchy zonation. The apatites are mostly divided into BSE-dark cores and BSE-bright rims. Apatites from the latest and least mixed rocks – composite dykes – have mostly patchy textures with only single grains showing distinct irregular zoning.

Apatites from different stages of mixing are compositionally distinctive in certain elements, e.g. Cl, Sr and Mn. Apatites from granodiorites and primitive porphyritic granite have higher Cl and Sr than other types of rocks and are close in composition to apatites from lamprophyres which represent the pure mantle end-member. This could indicate a slight mantle-melt contribution but is not definitive evidence. Higher Sr concentrations in the apatites from the earliest magmatic rocks can be simply a result of differentiation. Y concentrations follow the same trend in almost every type of rock. BSE-dark zones in the apatites from granodiorites, primitive porphyritic granite and composite dykes have Y concentrations that are similar to or slightly higher than the apatites from lamprophyres, whereas those from BSE-bright zones reach concentrations observed in the apatites from highly evolved, crustal granites. Rare earth elements are distributed rather randomly. The apatites from composite dykes, porphyritic granite and granodiorites are more REE-enriched relatively to Y. In these rocks the LREE/REE+Y ratio of apatites is higher than in apatites from lamprophyres, crust-derived granite and enclaves. Total REE contents however do not differ significantly from one rock to another.

Some characteristics, such as Mn, La/Y and LREE/(Y + HREE) ratios of apatites position the granodiorites, primitive porphyritic granite and composite dykes close to the lamprophyres and the enclaves close to the crust-derived granite. Additionally, the apatites from the first three types of rocks are compositionally similar to apatites from mafic I-types granites (Sha, Chappell 1999). In general, apatites from these three rock types have similar characteristics and show some affinity to the apatites from lamprophyres but it is very difficult to distinguish them from each other or to place them in a sequence from a higher to a lower degree of mixing.

From the apatite textures and chemical composition, it is also difficult to recognize a distinctive trend following the progress of magma differentiation and hybridization. Chemical gradients within single grains can be explained by a crystal moving and growing within different types of melts. However, such variability could also be caused by local saturation of apatite (which can then obtain abnormal or simply coincidental composition) or by crystallization of other accessory phases such as zircon or allanite. Indeed, apatite attained full saturation level in the late stages of the pluton formation (Słaby, Martin 2008); therefore the locally crystallized grains would not reflect the distribution patterns characteristic of the whole system. Grains with delicate oscillatory zoning and those containing only two zones (dark core and bright rim) seem, more likely, to have recorded fractional crystallization rather than mixing. Moreover, assuming that the distinct zoning in apatite represents crystallization in two compositionally different magmas, it is hard to say which zones were more influenced by one source than another. The low Y content of the BSE-dark zones suggests a close affinity to mantle-derived melts. However, these zones should have a high LREE-content which is not the case. This fact could also indicate that the mixing was not the only process controlling apatite composition.

This study shows that apatite composition does not follow the simple mixing trends expressed by the whole-rock chemistry and mixing itself cannot explain the compositional variations. Fractional crystallization must have also played an important role during apatite growth. Future studies (e.g. CL, PIXE) are necessary to distinguish these two processes. We also plan to apply polytopic vector analysis to verify mathematically whether the chemical composition of apatites is a mixture of two or more end-members.

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Preliminary geochemical characteristics of A-type granites from the Baga-Gazriin Chuluu pluton (Central Mongolia)

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The Baga-Gazriin Chuluu (BG) granitic body is situated 220 km SSW of Ulan Bator and covers an area of ca 120 km^2. It intruded in the Early Mesozoic (latest Triassic) into the area shaped by the Altaid orogeny. Recent studies (e.g. Buchan et al. 2002; Wilhem et al. 2012) proved that the formation of the present geological structure of Mongolia was a result of complex accretion-subduction processes, which took place over several hundred million years, from Latest Proterozoic to Mesozoic. The investigated plutonic body is situated ca 30 km to the SW of the Adaatsag Ophiolite, a fragment of oceanic lithosphere preserved after the closure of the Mongol-Okhotsk Ocean. The BG granites are accompanied by numerous greisen veins, tungsten-tin mineralization and display enrichment in REE (Machowiak et al. submitted).

The BG granites can be subdivided into three textural varieties: 1) coarse-grained equigranular, locally porphyritic, 2) medium-grained porphyritic, and 3) fine-grained equigranular or porphyritic (so-called haplogranites). Regardless of textural diversity, they usually display a monotonous mineral composition, with K-feldspar ($Or_{90}Ab_{10}$), quartz, plagioclase ($Ab_{90}An_{10}$), biotite and muscovite as the rock-forming phases. The samples, which were influenced by metasomatic processes, contain also topaz, fluorite, REE minerals and lithium micas - zinnwaldite and lepidolite (Machowiak, Stawikowski 2012).

The granites show high SiO_2 (73.6-80.2wt%) and alkali ($K_2O + Na_2O$ = 7.3-10.1wt%) concentrations. Based on the K_2O content and the classification diagram of Rickwood (1989), they can be defined as high-K rocks. Their MgO and P_2O_5 concentrations are extremely low and always below 0.1wt%. The BG granites display high contents of Rb (279-877 ppm, av. 380) in contrast to very low levels of Sr (2-39 ppm, av. 14), Ba (5-277 ppm, av. 69) and Eu (0-0.44 ppm, av. 0.17). As a consequence, they reveal high Rb/Sr (8-88, av. 45.5) ratios. The BG granites are characterized by relatively high concentrations of rare earth elements (REE). Excluding the aplite veins, the sums of all analysed REE ($\sum$REE) in the studied samples are 160-428 ppm (av. value for all samples: $\sum$REE = 255). The $\sum$LREE values are in the range 73-369 ppm (av. 210), the $\sum$HREE spread between 11-75 ppm (av. 54) and $\sum$LREE/$\sum$HREE ratios vary from 1.82 to 6.48 (av. 3.88).

Most of the BG granite samples display a lanthanide tetrad effect. According to the commonly used interpretation, this is a result of magma-fluid interactions in evolved granites at a final stage of crystallization (e.g. Irber 1999; Zhenhua et al. 2002; Ishihara et al. 2008).The level of tetrad effect ($TE_{1,3}$) was calculated using the method proposed by Irber (1999), where $TE_{1,3} > 1$ for REE patterns with the tetrad effect (for a clearly visible effect, $TE_{1,3} > 1.1$) and $TE_{1,3} \approx 1.00$ for REE patterns without the tetrad effect. The values of $TE_{1,3}$ calculated for the BG granites are > 1.1 in all analyzed samples.

The values of major element parameters calculated for the BG granites (e.g. high alkali, LILE, HFSE contents, high Fe/Mg ratios) as well as the increased Nb, Ta, Y, W, Sn and REE contents in these rocks suggest that the BG granites are A-type granites. However, the latter term has been applied in recent years to a broad spectrum of rock compositions and has become ambiguous and imprecise. On the other hand, the geochemical composition of the studied rocks indicates that they correspond to calc-alkalic ferroan granites, following the new classification proposed by Frost and Frost (2011).

The BG leucocratic magmas were most probably formed by partial melting of continental crust. The absence of enclaves in the granites indicates that relatively little contamination by surrounding rocks or mafic magma recharge affected the felsic magmatic system prior to or after its emplacement. The crustal protolith of the BG granites must have been relatively poor in aluminum, e.g. it was an orthogneiss with calc-alkaline composition (Machowiak et al. submitted).

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The role of outer membrane vesicles in biogeochemical cycles of elements in Kupferschiefer black shale (Fore-Sudetic Monocline, SW Poland)

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Outer membrane vesicles (OMVs) are extracellular structures produced by most gram-negative bacteria. They are liberated from the outer membrane and contain lipopolysaccharides, outer membrane proteins and phospholipids as well as periplasmic proteins (Włodarczyk, Matlakowska 2010). The formation of outer membrane vesicles by bacteria is a naturally occurring phenomenon, observed in the microorganisms belonging to different genera and isolated from different environments. Membrane vesicles constitute a kind of secretion and transport system. They are utilized in several processes, including delivery of toxins, dissemination and protection of antimicrobial factors, protein and DNA transfer. Membrane vesicles play a role in interspecies and inter-kingdom communication, and are a major component of biofilms. Moreover, they can contain enzymes important in the degradation of extracellular compounds and take part in electron transfer (Włodarczyk, Matlakowska 2010).

Recent studies have confirmed the ability to form membrane vesicles by indigenous microorganisms inhabiting the surface of the Kupferschiefer black shale (Matlakowska et al. 2012). Among tested microorganisms were strains of *Pseudomonas* sp., *Bacillus* sp. and *Acinetobacter* sp. It was shown that OMVs were the main component of the biofilm matrix developed on fine laminae within the black shale that are rich in organic matter. The OMVs were between 50 and 500 nm and were surrounded by a matrix of extracellular material (Fig. 1).

The role of membrane vesicles occurring on the surface of black shale is not yet known. Probably it is an adaptation mechanism of indigenous microorganisms to extreme conditions prevailing on the surface of black shale. It is speculated that the potential role of membrane vesicles is involvement in the early stages of biofilm formation by aggregation of single cells and facilitating their adhesion to the shale. OMVs usually are the most likely source of the basic components of the extracellular matrix. However, recent studies showed for the first time the biominerals which occur inside the OMVs. The EDS microanalysis of the electron dense bodies within OMVs revealed the presence of P, Ca, Mg, Si, Al, (see Fig. 2).

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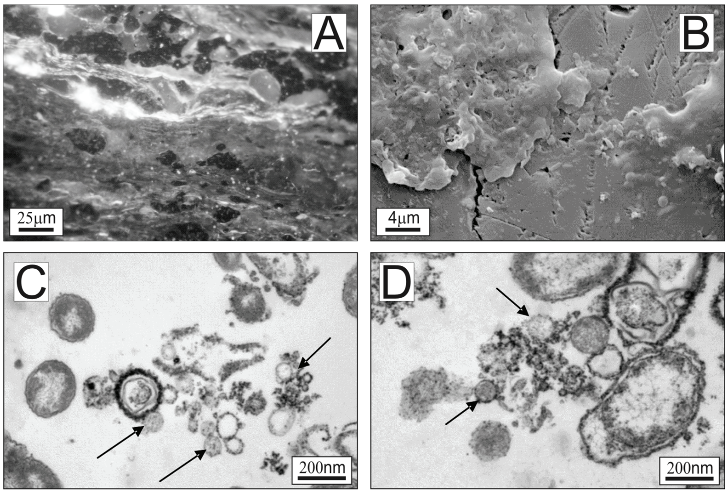

Fig. 1. Biofilm and outer membrane vesicles (OMVs) developed under laboratory conditions. A) biofilm (white stripes) covering the Kupferschiefer shale, UV reflected-light image; B) SEM image of the biofilm covering the sulphides in the Kupferschiefer shale; C-D) transmission electron images (TEM) showing details of the examined biofilms. The OMVs are arrowed.

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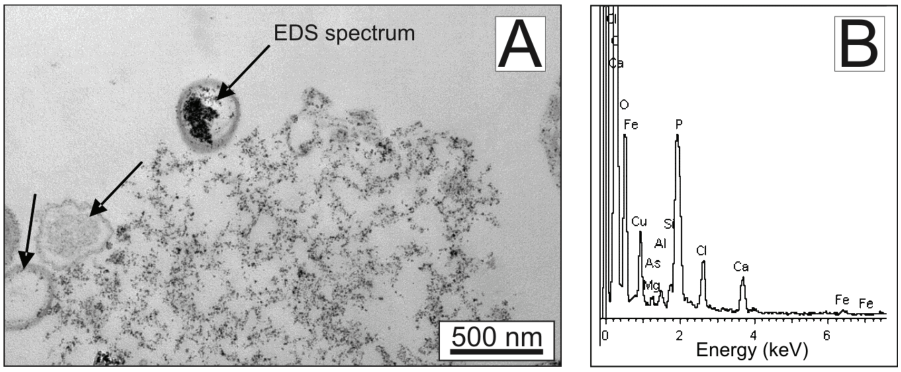

Fig. 2. TEM image of the biofilm fragment. A) mineralized OMVs, indicated by black arrows, B) EDS spectrum of biominerals occurring in OMVs (arrowed).

These results provide new insight into the activities of bacterial membrane vesicles and their role in the geochemical cycles of P, Ca, Mg and Al. A possible benefit of the production of outer membrane vesicles by microorganisms, and especially the biomineralization of Si and Al in OMVs, is the increased surface area available for metal adsorption and neutralization of the toxic effects of high concentrations of elements such as Cu, As and Ag. On the other hand, the ability of bacteria to immobilize Al and Si and other elements has important environmental implications for their transfer from the aqueous phase to the sediment, because after bacterial death the cell-bound elements may develop as mineral microdeposits responsible for an enhanced content of selected elements in sedimentary rocks. During syngenetic mineralization, e.g. early silicification, the small amount of the biominerals, arranged within well-defined OMV forms, may by used as a trace of the presence of life in extreme environments, including the oldest sedimentary rocks known on the Earth, as well as extraterrestrial materials.

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Aeschynite and euxenite group minerals in pegmatites from the NE part of the Karkonosze Massif

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Introduction

Based on the statistical discrimination proposed by Ercit (2005) and Ewing (1976), the following minerals were identified – aeschynite-(Y) and nioboaeschynite-(Ce) from the aeschynite group (AGM), and polycrase-(Y) from the euxenite group (EGM), respectively. All data given below stem from electron microbe analyses calculated on 6 oxygen atoms per formula unit.

Polycrase-(Y)

Polycrase-(Y) is the most common phase from the AGM-EGM. It has been found in three localities. It forms subhedral or euhedral inclusions in quartz ca 10 μm in diameter, often accreted in clusters of irregular shape. It is associated with zircon, quartz, cheralite, xenotime, minerals of the pyrochlore supergroup and aeschynite-(Y); with the latter it seldom forms epitaxial intergrowths. Sometimes polycrase-(Y) with fergusonite-(Y) forms probably secondary phases replacing zirconolite. Polycrase is usually altered, especially at the margins of the grain, and sometimes is replaced by liandratite or a mineral with the chemical composition of pyrochlore.

The A-site occupancy is highly variable. Oxide abundances are: 6.79-21.62wt% Y_2O_3 (0.25-0.69 apfu), 7.92-15.68wt% $\sum REE_2O_3$ (0.17-0.34 apfu), 0-4.71wt% CaO (0-0.34 apfu), 1.29-10.54wt% UO_2 (0.01-0.17 apfu), 0.64-3.31wt.% ThO_2 (0.01-0.08 apfu). U/(U+Th) is very high and ranges from 0.53 to 0.92. The content of Fe is high and varies from 0.96 to 4.55wt% FeO (0.05-0.25apfu).

The B-site occupancy changes as well. The analyses gave: 15.55-36.02wt% TiO_2 (0.77-1.63 apfu), 6.89-23.80wt% Nb_2O_5 (0.21-0.71 apfu), 9.56-31.15wt% Ta_2O_5 (0.16-0.60 apfu). The amount of Si reaches up to 4.80wt% SiO_2 (0.33 apfu) in the altered part, but with the chemical composition still falling in the aeschynite-euxenite field. Polycrase-(Y) from the Karkonosze massif contains significant amount of Zr, up to 3.29wt% ZrO_2 (0.10 apfu) and Sn, up to 1.23wt% SnO_2 (0.03 apfu).

Aeschynite-(Y)

So far, aeschynite-(Y) has been identified in two pegmatites. It occurs with cassiterite, polycrase-(Y), thorite, zircon, and LREE phosphates. Especially interesting is aeschynite-(Y) from the ball pegmatite. Analytical totals for this grain are from 95.0 to 99.3 for the W-poor and W-rich part, respectively.

Analyses of the A-site cations show 21.28-24.92wt% Y_2O_3 (0.68-0.79 apfu) and 11.97-14.21wt% $\sum REE_2O_3$ (0.23-0.28 apfu). The U and Th contents are low and range from

0.99 to 4.40wt% ThO_2 (0.01-0.06 apfu) and 0.80-2.16wt% UO_2 (0.01-0.03 apfu). The U/(Th+U) varies from 0.25 to 0.47. Amongst other elements, the presence of Fe is notable. Its contents are very low, in comparison to other AGM-EGM from Karkonosze, and do not exceed 0.72wt% FeO (0.04 apfu).

The B-site is mainly characterized by the presence of Ti (37.27-45.38wt% TiO_2, 1.69-2.00 apfu). The analyses also revealed a very high variability in W content, from 6.20 to 18.25wt% WO_3 (0.09-0.27 apfu). The mineral is strongly depleted in Nb ($\leq$ 2.82wt% Nb_2O_5) and Ta ($\leq$ 0.27wt% Ta_2O_5).

Nioboaeschynite-(Ce)

A single grain of Ca-rich nioboaeschynite-(Ce) with maximum dimension ca 250 µm was found. The margins of the mineral are altered – enriched in Fe and slightly depleted in YREE. There are small inclusions of ishikawaite. The grain, except at its margins, is homogeneous but porous.

The analytical totals are high, 97.3-99.0wt%. In the A-site occupancy the YREE contents are relatively low and vary between 19.33 and 15.21wt%, $\sum YREEO_3$ giving 0.34 and 0.44 apfu, respectively. The content of Ca is significant, up to 4.50wt.% of CaO (0.29 apfu), especially relative to YREE. Uranium and thorium concentrations are rather low and amount 0.25-2.19wt% ThO_2 (0-0.04 apfu), 1.57-3.04wt% UO_2 (0.02-0.04 apfu), and U/(U+Th) ranges from 0.56 to 0.87 and is rather high, closer to EGM than AGM from Karkonosze. Amongst other cations, noteworthy are the elevated amounts of Pb (3.04-4.14wt% PbO, 0.05-0.07 apfu) and Fe (1.55-4.81wt% FeO, 0.08-0.25 apfu).

The B-site occupancy includes 46.18-54.76wt%. Nb_2O_5 (1.46-1.29 apfu), 5.19-8.16wt% TiO_2 (0.24-0.37 apfu) and 3.39-4.83wt% Ta_2O_5 (0.06-0.08 apfu). Besides the typical B-site cations, the grain contains significant amount of Si, up to 3.47wt% SiO_2 (0.21 apfu), Al (1.03-1.76wt% Al_2O_3, 0.07-0.13apfu), and P up 0.42wt% P_2O_5 (0.02 apfu).

Conclusion

Three minerals from the aeschynite-euxenite group minerals were briefly described. Generally, all these minerals are very rare phases in the pegmatites from Karkonosze, but in some pegmatite bodies they are the main Nb-Ta-Ti accessory phases. The chemical analyses revealed the unusual presence of Si, Al, Zr, P, and W in some phases. There is a positive correlation between Al and Si, indicating that at least part of Si comes from sub-microscopic impurities of aluminosilicates. On the other hand, the presence of Si in the crystal lattice of the AGM-EGM groups requires further investigation. Due to the lack of clear evidence, it is probable that the presence of Zr is not caused by a zircon-bearing intergrowth, but by its occupation of the six-fold position in the crystal lattice. Phosphorus is a common element in various Nb-Ta-Ti minerals from the Karkonosze massif, replacing Nb and Ta. Tungsten is a common element in the AGM-EGM, and its abundance of ca 18wt% WO_3 is one of the highest W contents in aeschynite-(Y) described in the literature (Aurisicchio et al. 2001). In this case it is likely that W replaces Ti; there is a very strong correlation between the contents of W and Ti and no correlation between W and Nb or Ta.

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Petzite (Ag_3AuTe_2) – a new telluride mineral from the Radzimowice deposit (Sudetes, SW Poland)

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At the Radzimowice Au-As-Cu deposit, auriferous mineralization occurred in sheeted quartz veins representing a hydrothermal transition between porphyry and epithermal type (Mikulski 2005). The economic ore mineralization resulted from two main hydrothermal stages. Early mesothermal quartz–Fe mineralization with As sulphides and refractory gold was cataclastically deformed and overprinted by low-sulphidation epithermal character mineralization with base-metal sulphides, non-refractory gold and carbonates. They were followed by Te-Bi-Au-Ag minerals and a late association of sulphosalts (Mikulski 2007). Tellurium minerals appear in parageneses with bismuth minerals (native bismuth, bismuthinite – Bi_2S_3, maldonite – Au_2Bi), non-refractory gold (electrum), Ag-Pb-Bi sulfosalts, magnetite and gangue of carbonates and finely-crystalline quartz (Mikulski 1999). The tellurium minerals occur as polymineral inclusions (up to 100 micrometer in size) in arsenopyrite, as fine-scale replacements (up to 200 micrometer in size) after arsenopyrite-chalcopyrite aggregates, and intergrowths with associated minerals. According to microanalytical investigation, the main tellurium mineral at the Radzimowice deposit is hessite (Ag_2Te). It may form intergrowths with members of different phases from the rucklidgeite ($PbBi_2Te_4$) – volynskite ($AgBiTe_2$) and altaite ($PbTe$) series that are in close association with Ag-Pb-Bi sulfosalts such as gustavite ($AgPbBi_3S_6$) and other phases from the gustavite group and the lillianite series (Mikulski 2007). Minerals from the gustavite group have chemical compositions between those of pavonite ($AgBi_3S_5$) and galena, with inclination to matildite ($AgBiS_2$).

At present, the new telluride mineral – petzite was recognized in a sample of massive quartz-sulphide ore found at the mining dump in the northern part of the deposit. The sample was provided by AM. Detailed microprobe investigations were performed both at PGI-NRI and UW according to standard procedures. Petzite appears in close association with earlier described tellurides, bismuth minerals, electrum and Bi sulphosalts. It forms irregular, very tiny (2 to 10 μm in size) intergrowths within a bigger aggregates (up to 20-30 μm in diameter) of electrum, hessite and Bi-Pb-Ag sulfosalts of variable composition. The chemical composition of electrum (Au-Ag alloys) varies from 61.8 to 71.7wt% Au and from 36.2 to 28.3wt% Ag. Petzite from Radzimowice has a chemical composition close to its empirical formula Ag_3AuTe_2. It contains from 40.12 to 42.19wt% Ag, from 32.35 to 32.67wt% Te and from 23.61 to 24.23wt% Au. Additionally, small admixtures of Fe (up to 1.15wt%) and Se (up to 0.09wt%) were determined.

At the Radzimowice deposit, the presence of the Ag- and Bi-tellurides in paragenetic association with gold, sulfotellurides, Ag-Bi-Pb sulfosalts and carbonates indicates that those minerals crystallized in close to neutral conditions at temperatures < 371°C (maldonite melting point) and probably < 250°C (Afifi et al 1988).

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Synthesis of libethenite $Cu_2(PO_4)OH$ and olivenite $Cu_2(AsO_4)OH$ solid solutions

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Libethenite $Cu_2(PO_4)OH$ and olivenite $Cu_2(AsO_4)OH$ are secondary minerals formed in the hypergenic zone of copper deposits. Their type locality is Lubietowa (Slovakia), where mining was active till the XIX century. Both belong to the same isomorphic series. However, libethenite crystallizes in the orthorhombic system and olivenite is monoclinic. Optical microscopy revealed that they are products of chalcopyrite transformation.

The objective of this project is the synthesis of libethenite, olivenite and their solid solutions by a wet method. In the natural environment these solid solutions have never been found. We hypothesis that this is related to the differences in the solubility of the solid solutions: they are probably more soluble than the end members.

All syntheses were run by mixing $(NH_4)H_2PO_4$, $Cu(NO_3)_2{\cdot}3H_2O$ and $Na_2HAsO_4{\cdot}7H_2O$ in stoichiometric proportions, at 65°C and in acidic conditions of pH=3. The products of synthesis were characterized by X-Ray diffraction which revealed systematic shifts of diffraction peaks. Unit cell parameters were also calculated for every product and systematic changes in crystal morphology were characterized with SEM. In all cases, the formation of blue, metastable precursors of mixed composition was observed, the recrystallization of which depends strongly on temperature.

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CO_2 sequestration by mineral carbonation using serpentinites from the Sudetes, SW Poland: insights into a development of new methods of Ni, Co, Mn, Cr, and PGE extraction from serpentinites and low-grade Ni lateritic ores

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Carbon capture and storage by mineral carbonation using olivine- and serpentine-rich rocks as a feedstock are still considered an emerging technology of CO_2 sequestration. The mineral carbonation methods comprise (I) *in situ* sequestration of CO_2 within mafic or ultramafic massifs, (II) *ex situ* direct mineral carbonation using fine-grained crushed rock, and (III) *ex situ* indirect sequestration of CO_2 following significant pre-treatment of the feedstock. In our study we test the possibility of utilising the indirect mineral carbonation using serpentinites from the Central Sudetic Ophiolite in Poland and applying recyclable ammonium salts to chemical pre-treatment of the feedstock (Wang, Maroto-Valer 2011). The pre-treatment results in a release of Mg ions that are available for further reaction with the captured CO_2. In addition, there is a scope for usage and further development of the technology to extract Ni, Co, Mn, Cr, PGE (Platinum Group Elements) occurring in the Sudetic serpentinites. In order to effectively sequester 1 tonne of CO_2, 2.1 or 1.6 tonnes of serpentine or olivine, respectively, would be required (*ibid.*).

Serpentinite is a common rock type in the Central Sudetic Ophiolite. The largest massifs (Jordanów-Gogołów, Braszowice-Brzeźnica and Szklary) that occur around the Góry Sowie Block are the major inferred reserves that could potentially be used as a feedstock in mineral carbonation processes. The measured serpentinite resources in four deposits (Nasławice, Jordanów, Jordanów I and Tomice) are estimated at 80.4 mln tonnes (Szuflicki et al. 2012). The Szklary serpentinite massif is one of the most interesting, due to its high rock resources, up to 14.6 mln tonnes (potential feedstock) and Ni lateritic ores with medium ore-grade of 0.8 wt.% Ni. The annual serpentinite production in Poland is close to 1.06 mln tonnes (*ibid.*).

Annual CO_2 emission in Poland amounts up to 328 mln tonnes. The Turów power station, located ca 200 km W from the Szklary massif, emits 10.8 mln tonnes CO_2 per year. Therefore, in order to effectively sequester the Turów`s annual emission at least 22.7 mln tonnes of the feedstock serpentinite (assumed that serpentine constitutes 100vol.% of the rock) is required. This simple calculation shows that serpentinite resources in Poland are insufficient to sequester CO_2 emitted by one large power plant over 10 years. However, if the sequestration processes were linked with hydrometallurgical extraction of Ni, Co, Mn, Cr, and PGE metals, the whole venture could prove economically viable and possibly cost effective.

The Sudetic serpentinites consist of antigorite, lizardite, talc, chlorite, magnesite, olivine, Mg-Al-chromite, ferrichromite, and Fe-Ni sulphides. The weathered serpentinites are rich in hydrated Fe-oxides, hematite, SiO_2-group minerals, magnesite, and Ni-rich phyllosilicates. The serpentinites contain varying amounts of primary olivine and in some samples from the Szklary massif up to 10-15vol.% of anthophyllite and/or tremolite have been identified (see Ostrowicki 1965). High amounts of the late amphibole and other minerals reduce the effectiveness of mineral carbonation, and the amount of potentially active minerals (i.e. serpentine and olivine) decreases to ca 85vol.%.

Systematic geochemical data of the Sudetic serpentinites are scarce. The concentrations of NiO and Cr_2O_3 range from 0.35 to 0.17wt.% and from 0.56 to 0.15wt.%, respectively (Ostrowicki 1965; Natkaniec-Nowak, Pitera 1986; Dubińska et al. 1995; Gunia 2000; Niśkiewicz 2000). The concentration of Co varies from 110 to 96 ppm (Dubińska et al. 1995). The PGE content in Lower Silesia serpentinites is low and ranges from 10 ppb to 3.69 ppm (Popiel, Waleńczak 1978; Sachanbiński, Łazarienkow 1994).This could be compared with the PGE concentrations from other ultramafic massifs, e.g. the total amount of PGE in dunites and harzburgites from the Veria ophiolite complex in N Greece, ranges from 25 to 9 ppb (Tsoupas, Economou-Eliopoulos 2008). The PGM study from Jordanów-Gogołów Massif shows that some parts of this massif are PGE enriched (see Speczik, Piestrzyński 1995) but additional mineralogical and geochemical studies are required to confirm these findings.

It is estimated that the annual CO_2 emission from the 460 MWh power-unit (taking ca 0.824 tonnes CO_2/MWh) amounts to 3.32 mln tonnes. This implies that 7.3 mln tonnes of feedstock serpentinite is necessary for mineral sequestration of CO_2. Taking into account that the process is 85% effective, the annual production of Ni, Cr, Co can be estimated at least at 8067 tonnes of Ni, 6205 tonnes of Cr and 595 tonnes of Co (Table 1). Considering current metal prices, the annual economical effect of the extraction of the metals during the CO_2 mineral sequestration is estimated at 211 mln USD, including 33 mln USD for sequestration of the 3.32 mln tonnes of CO_2. The use of the low-grade Ni lateritic ores from the Szklary Massif enhances significantly the economic effect. Hydromagnesite and amorphous silica are also market products that can be used in agriculture and industry. These materials are ecologically harmless and can be also used during recultivation of mining areas.

Table 1. Estimation of recovery of Ni, Cr, Co and PGE_{TOT} from Sudetic serpentinites during mineral sequestration of 3.32 mln tonnes of CO_2. In the calculation, the 85% ratio of efficiency of the metal extraction was applied.

Metal	**Max. concentration [g/tonne]**	**Min. concentration [g/tonne]**	**Max. metals extraction [tonnes]**	**Min. metals extraction [tonnes]**
Ni [0.35-0.17 wt.% NiO]	2800	1300	17374	8067
Cr [0.56-0.15 wt.% Cr_2O_3]	3800	1000	23579	6205
Co	110	96	683	596
PGE_{TOT}	3.69	0.01	22.87	0.06

The feedstock pre-treatment utilising ammonium salts (Wang, Maroto-Valer 2011) used along with hydrometallurgical technologies opens the possibility of metal (e.g. Ni, Co) extraction as by-products of mineral carbonation. The Cr and PGE are refractory metals and in order to extract them smelting technologies are required. The localization of the Sudetic serpentinite deposits in the area where CO_2 can by supplied by Turów power plant and/or newly planned power station in Legnica, that will use brown coal from the Legnica-Ścinawa deposits, gives us a unique opportunity to use brown coal for the production of electricity with the zero emission of CO_2.

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Nb-rich andesites from Uherský Brod area (Moravia): petrogenesis and tectonic setting

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Potassium-rich andesitic rocks from the Uherský Brod area of the Western Outer Carpathians (Moravia, Czech Republic) show geochemical features intermediate between the calc-alkaline magmatic rocks of the Carpathian-Pannonian Region and alkaline magmatism of the Bohemian Massif (for details see Pécskay et al. 2006; Trua et al. 2006; Harangi et al. 2007; Seghedi, Downes 2011; Ulrych et al. 2011; Nejbert et al. 2012). Their age is estimated from K-Ar determinations at 14.8 ± 0.2 to 11.0 ± 1.2 Ma (Přichystal et al. 1998; Pécskay et al. 2006), which corresponds well with the age of the andesites from the Pieniny area, Poland (Birkenmajer, Pécskay 1999, 2000; Birkenmajer 2003).

According to the TAS classification, the Moravia rocks are basalts, trachybasalts, trachyandesites and trachydacites. A melanocratic basanite from Starý Hrozenkov, with abundant phenocrysts of clinopyroxene and olivine, is classified as ankaramite. The phenocryst assemblages of the Uherský Brod rocks are represented by plagioclase, amphibole, clinopyroxene, biotite, and Fe-Ti oxides. The phenocryst mineralogy is generally comparable to andesites from the Pieniny area and to the calc-alkaline suites from the Carpathian-Pannonian Region. The Moravia andesites have high contents of incompatible trace elements, e.g. up to 122 ppm Nb, 249 ppm Zr, and 31 ppm Th. The high concentrations of these elements are a magmatic feature of the andesites and are reflected by the presence in the matrix of abundant grains of a Nb-rich member of the chevkinite-group of minerals (CGM), niobian ilmenite (up to 1.76wt% Nb_2O_5), and a Nb-rich oxide with composition close to zirconolite.

The CGM have SiO_2 contents ranging from 19.1 to 20.3wt%, TiO_2 from 14.5 to 18.3wt%, Ce_2O_3 from 14.4 to 20.4wt%, CaO from 3.9 to 6.2wt%, and FeO from 7.3 to 9.8wt%. The Nb_2O_5 and ZrO_2 contents are between 1.5 and 4.1wt% and 1.6 and 3.7wt%, respectively (all are WDS microprobe data). The CGM occur as dispersed small crystals within the matrix, with a size range from submicroscopic (< 0.1 μm) to 50 μm in diameter. Larger grains are strongly zoned and the outer rims are progressively ThO_2 enriched (up to 1.4wt.%). On the discrimination plot of Macdonald and Belkin (2002), they generally plot within the perrierite field, just below the boundary dividing the perrierite and chevkinite subgroups; additionally some analyses plot within the chevkinite field.

The zirconolite crystals have a platy habit and are rich in Nb_2O_5 (11.27-14.74wt%), TiO_2 (18.87-20.43wt%), ZrO_2 (16.39-24.51wt%), ThO_2 (3.31-7.75wt%), Ce_2O_3 (5.43-8.14wt%), FeO (8.41-9.80wt%) and CaO (5.71-6.59wt%). The SiO_2 contents range from

0.59 to 1.09wt%. Zirconolite is associated with both chevkinite and monazite, but a chevkinite-monazite association has not been observed.

The unusual composition of the andesites from Moravia and their location on the SE extension of the Elbe Fault Zone, which penetrates the basement of the Western Outer Carpathians, give us a unique opportunity to link their geochemical features with their tectonic setting. The primary magmas of the andesites were generated in highly metasomatised lithospheric mantle of the European plate. Metasomatism at Moravia was strongly influenced by multiple infiltrations of deeper mantle melts and/or fluids (Nejbert et al. 2012). These metasomatic events possibly took place in several stages: (i) probably before 1 Ga, (ii) during the Variscan orogeny and (iii) Alpine orogeny. However, the most intensive metasomatism probably occurred during the Early Cretaceous rifting responsible for, e.g. the picrite-teschenite magmatism forming a major province from Moravia to SE Poland (Włodyka 2010). The high concentrations of the incompatible elements were enhanced by the small volume melting of the mantle. This model also helps to clarify the tectonic setting of the andesites that occurred within the Western Outer Carpathians in the Pieniny Mts. In the case of Pieniny, melts were also generated within highly metasomatised lithospheric mantle of the European plate, but the metasomatism was ancient subduction-related (Trua et al. 2006). The partial melting of the lithospheric mantle may have been triggered by decompression during reactivation of the mantle-rooted NW–SE-trending fault zones, e.g. Elbe Fault Zone in the case of the Moravia andesites, and analogously along the assumed SW extension of the Kraków-Myszków Zone in the case of the andesites from the Pieniny area.

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The precipitation of secondary copper sulphides during bioweathering of the Kupferschiefer black shale (Fore-Sudetic Monocline, SW Poland)

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The bioweathering of the highly mineralized Kupferschiefer black shale by heterotrophic bacteria represented by *Pseudomonas* sp., *Acinetobacter* sp., *Bacillus* sp. and *Microbacterium* sp. was studied in laboratory under aerobic conditions. The bacterial strains were isolated from the Lubin Mine, Fore-Sudetic Monocline, Poland. During an experiment extensive biofilms growing on the Kupferschiefer shale were observed. At early stages of the experiment, the biofilms were localized mainly along parts of the shale that were enriched in organic matter. The growth of these biofilms triggered extensive bioweathering of the highly mineralized Kupferschiefer shale, which led to mobilization of P, Al, Si, Ca, Mg, K, Fe, S, Cu, As and Pb (Matlakowska et al. 2012). The Kupferschiefer bioweathering was realized through complex direct and indirect interaction of the bacteria with the minerals and organic matter. These interactions are reflected in biomineralization of bacterial cells and growth of secondary sulphates, carbonates and phosphates on the examined Kupferschiefer, as shown by SEM study. Most intriguing was the occurrence of sulphide aggregates within bioweathering mineral products, especially if we consider that the bacteria used in the experiment do not belong to the group of sulphate-reducing bacteria.

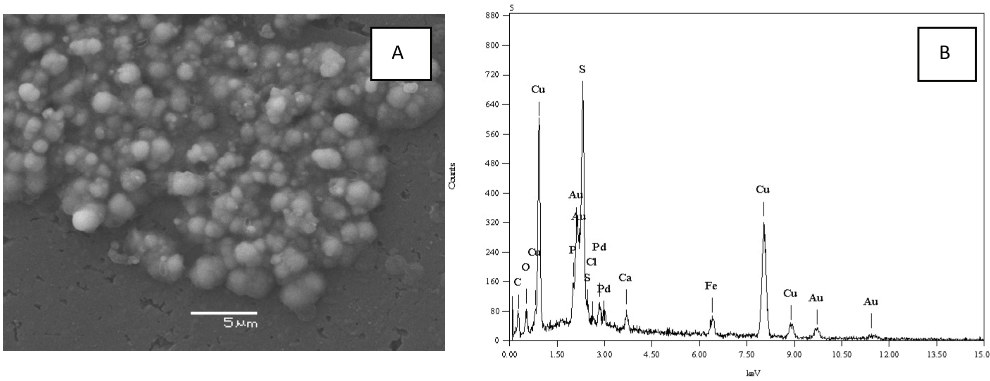

Fig. 1. (A) Secondary sulphide aggregates developed under laboratory conditions on the surface of Kupferschiefer shale during bioweathering.
(B) EDS spectrum of secondary sulphides presented on Fig. A.

The accumulations of Cu-sulphides were identified at the interface between dolomite aggregates and the clayey matrix (Fig. 1). The Cu/S apfu ratio of newly crystallized sulphides is close to 1.7. This is in good agreement with the Cu/S ratio occurring in anilite (Cu_7S_4; Cu/S ~1.75) and roxbyite (Cu_9S_5, Cu/S ~1.7). Both are known from red-bed copper deposits and from polymetallic, low-temperature hydrothermal deposits (Guilbert, Park 1986).

The secondary sulphides recognised in mineral assemblages crystallized under laboratory conditions resemble supergene sulphides (chalcocite, covellite, digenite, and djurleite) common in blanket deposits (Sikka et al. 1991; Anderson, 1955). The origin of such sulphides is related to the Cu mobilisation in an oxidized zone followed by crystallization of the secondary sulphides close to the water table environment, where the primary sulphides determine the redox state (e.g. Brimhall 1985; Guilbert, Park 1986). The supergene sulphide mineralization was mainly driven by abiotic processes (Brimhall et al. 1985) but bacteriogenic processes also played an important role (Sillitoe et al. 1996; Enders et al. 2006). Besides Cu-sulphides, the other sulphide minerals can by crystallized in supergene environments, e.g. framboidal pyrite and Fe-poor sphalerite (Bawden et al. 2003). The extremely low $\delta^{34}S$ values, sometimes as low as -70‰, are taken as unequivocal evidence of bacterial activity during their growth (*ibid.*).

The mechanisms of secondary sulphide precipitation on the shale surface observed during this study are unknown, although two processes can by proposed. Crystallization of secondary copper sulphides can be connected either with microbial activity or be crystallized during purely abiotic mineralization processes. The absence of sulphate-reducing bacteria in the community used in the experiment supports abiotic mechanisms. The Cu^{2+} mobilized during bioweathering of the Kupferschiefer interacts with primary Fe-Cu sulphides, such as chalcopyrite, bornite and pyrite, which leads to crystallization of secondary Cu sulphides (for details see Brimhall et al. 1985). The other possible mechanisms of secondary copper sulphides precipitation may indirectly involve bacterial activity and can be connected with microaerobic conditions created in pits or within the biofilm observed on the surface of the Kupferschiefer black shale. Probably there are microniches created by colonies of bacteria, characterized by microaerobic conditions, which together with solubilised organic matter are known to be strong reducing factors.

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Mineralogy of (Y,REE,U,Th)-(Ti,Nb,Ta) oxide minerals in a muscovite pegmatite from the Suwałki Anorthosite Massif, NE Poland

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The Suwałki Anorthosite Massif (SAM), occurring in the basement of the East-European Platform in NE Poland, is composed of anorthosite, norite, gabbronorite, ferrodiorite, and ilmenite-magnetite rocks (Juskowiak 1971; Kubicki, Siemiątkowski 1979; Kubicki, Ryka 1982; Wiszniewska 2002; Nejbert, Wiszniewska 2005). The host rocks of the SAM are rapakivi granites and metamorphic rocks that were recrystallized during amphibolite and/or granulite facies metamorphism (Kubicki, Ryka 1982). Granite and pegmatite veins, with thicknesses ranging from a few cm to ca 8 m, cut all known crystalline rocks in the basement of the East-European Platform, as evidenced by core materials from numerous deep boreholes (Juskowiak 1971).

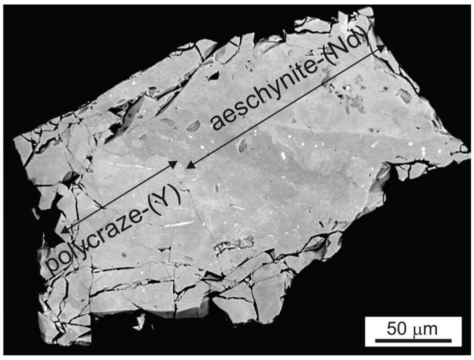

Fig. 1. BSE image of a complex polycrase-(Y) and aeschynite-(Nd) grain from the GSA-2 sample, Suwałki Anorthosite Massif.

The texture and mineralogy of the granite and pegmatite veins are varied and depend on their thickness. The thickest veins show well developed zoning, and four zones can be distinguished. These are, starting from the contact with the host rock: (I) fine- to medium-grained aplite zone, (II) coarse-grained blocky feldspar zone, in places with clearly visible feldspar-quartz graphic intergrowths, (III) quartz – automorphic feldspar intergrowths, and (IV) massive quartz core. Thin veins reveal more simple textures. They are dominated by fine- to medium-grained granite. Moreover, coarse-grained pegmatites in contact with the host anorthosites have also been recorded. The mineralogy of the pegmatite and granite veins is dominated by K-feldspar, albite, quartz, biotite, muscovite, and Fe-Ti oxides.

In more evolved pegmatites muscovite dominates over biotite, and one such sample (GMS-2) was selected for a detailed mineralogical study of the accessory minerals. The selected sample was coarse-grained K-feldspar-muscovite pegmatite showing a well preserved thermal contact with the host anorthosite. The CHIME age of the examined pegmatite, based on 60 monazite analyses, yielded 1438 ± 48 Ma. The K-feldspar, red in color, from 3 to 4 cm in size, is associated with muscovite aggregates up to 1 cm in diameter. The sample was crushed and divided into grain fractions before accessory mineral separation by using magnetic and heavy liquid (LST Fastfloat polytungstate) techniques. The chemical composition of the minerals was determined using a Cameca SX-1000 microprobe; the analyses of (Y,REE,U,Th)-(Ti,Nb,Ta) oxides were recalculated to 6 oxygen atoms per formula unit.

The accessory phases in the examined pegmatite comprise apatite, zircon, monazite-(Ce), cheralite, rutile, pyrite, chalcopyrite and barite. The complex (Y,REE,U,Th)-(Ti,Nb,Ta) oxides occur as large grains, at least 300 μm in diameter. They are probably highly metamicted due to a high uranium content (compare Tomašić et al. 2004), but primary zoning in some grains is still preserved (Fig. 1). Based on the statistical approach proposed by Ewing (1976) and Ercit (2005), numerous aeschynite-(Nd) and polycrase-(Y) grains were recognized in all non-magnetic fractions. In some cases, the polycrase-(Y) core was overgrown by aeschynite-(Nd). small amounts of uranopolycrase and Nb-rich rutile were also found.

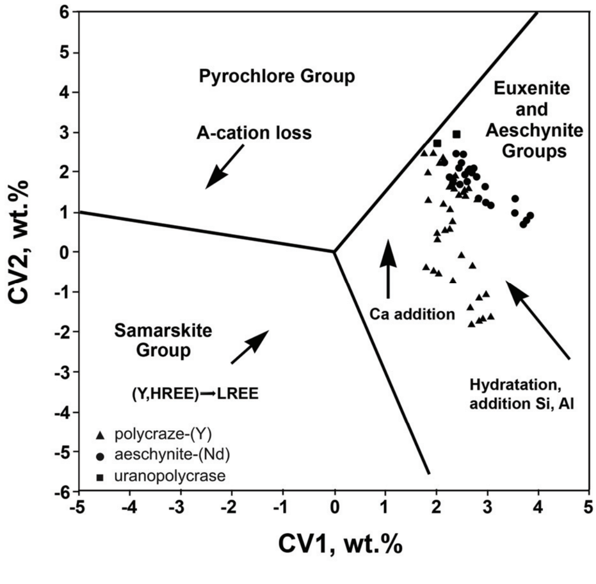

Fig. 2. Composition of the oxides from GSA-2 sample plotted on the diagram of Ercit (2005) for discrimination of pyrochlore, samarskite, and euxenite-aeschynite mineral groups

The aeschynite-(Nd) grains have TiO_2 contents ranging from 19.84 to 22.74wt.% (0.89-1.08 apfu), Nb_2O_5 from 18.08 to 26.34wt.% (0.52-0.71 apfu), Ta_2O_5 from 2.61 to 5.10 (0.04-0.08 apfu), UO_2 from 8.01 to 17.08wt.% (0.10-0.24 apfu), ThO_2 0.92-5.98wt.% (0.01-0.09 apfu), Nd_2O_3 from 3.34 to 6.24wt.% (0.07-0.13 apfu), Ce_2O_3 from 2.68 to 5.09wt.% (0.06-0.11 apfu), Y_2O_3 from 2.18 to 3.87wt.% (0.07-0.13 apfu), CaO from 3.03 to 4.99wt.% (0.21-0.32 apfu), and FeO from 0.39 to 1.53wt.% (0.02-0.08 apfu). The U/(U+Th) varies from 0.71 to 0.91. The total REE are from 13.52 to 21.83wt.%. SiO_2 reaches up to

7.17wt.% (0.44 apfu), and these enhanced contents reflect possible hydration and addition of Si during metamictization. On the discrimination diagram of Ercit (2005) the analyses plot within the aeschynite-euxenite groups field (Fig. 2). Application of the Ercit (2005) discrimination formulae for the aeschynite group [LREE > 0.326* TiO_2 – 0.06 Nb_2O_5 + 3.1 [wt.% oxide] shows that only half of the analyses should be classified as representing aeschynite group minerals. The predominance of Ti over Nb in the B site, and UO_2/ThO_2 > 1 ratio recognized in the other analyses suggest that the rest of the examined grains are polycrase-(Y) (for details see Ewing 1976, Ercit 2005). Uranopolycrase (0.41 U apfu) was observed as small intergrowths within polycrase-(Y).

The results revealed for the first time the complex mineralogy of the accessory phases in the SAM pegmatites. The majority of the pegmatites in the SAM probably belong to the primitive (barren) type. The studied muscovite-rich pegmatite is more evolved, and can be classified in the muscovite – rare-elements (MSREL-REE) or euxenite subtype of the rare-element class (REL-REE) (Černy, Ercit 2005). According to petrogenetic classification, the pegmatite belongs to the NYF family (*ibid.*).

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Origin of zircons in metabasites from the Izera-Karkonosze Massif

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In the Izera-Karkonosze Massif of the Saxothuringian terrane, ca 500 Ma metagranites were cut by a swarm of basic veins which represent mostly within-plate alkali basalt, more rarely within-plate tholeiite and N-MORB-like basalt geochemistry. The veins were then deformed and metamorphosed together with the host rocks (Nowak, Żelaźniewicz 2000; Żelaźniewicz, Nowak 2003). Two different types of zircon, labelled types I and II, and differing in colour, size and habit, were identified in eight samples of the Izera metabasites. Zircons of type I are colourless, transparent, euhedral to subhedral grains from 100-300 μm in size. They are bright in CL images and usually display distinct core-rim structures: inherited cores are surrounded by rims of well-developed oscillatory zoning. Zircons of type II appear as both subhedral to euhedral, short-prismatic crystals and anhedral fragments of larger euhedral crystals, possibly broken during rock-crushing preparation. They are brown, non-transparent or have turbid cores and often contain numerous micro-inclusions and a spongy texture. The type II zircons are bigger (100-600 μm) than the type I zircons and dark in CL images. Nevertheless, their internal structures can be observed. Most of the brown zircons have a relatively large core, about 2/3 of the grain size, surrounded by a thinner rim of distinct oscillatory zoning. The inner parts of the zircons usually are almost homogeneous, though some have irregular domains differing slightly in CL emission or have poorly visible sector zoning. Some brown zircons show sector zoning, sometimes of hourglass type with narrow rims of very low CL. None of the samples revealed zircons in thin section, but very small zircon grains (< 50 μm sized) were occasionally seen in BSE images. Subhedral to euhedral zircon grains occur as inclusions in amphibole, quartz and plagioclase, but rarely in chlorite, epidote and K-feldspar. However, anhedral zircons mostly associated with titanite and ilmenite were observed in a metabasite sample which contains only zircons of type II.

Zircons of type I and II represent at least two different age generations of this mineral. Grains of type I yielded a U-Pb age of ca 500 Ma in the oscillatory zoned parts and ages of 680-600 Ma and 560-550 Ma in the oldest cores. Zircons of type II yielded U-Pb ages of ca 390-365 Ma (Nowak et al. 2011). The features of the type I grains, such as a normal habit and pronounced oscillatory zoning are typical of zircons from felsic magmatic rocks. The results of U-Pb dating are almost identical with the intrusion age of a protolith for the Izera metagranites, estimated to be 515-480 Ma (Korytowski et al. 1993; Oliver et al. 1993; Philippe et al. 1995). Such a coincidence indicates that the zircons of type I are probably inherited xenocrysts incorporated into the basic magma via assimilation of material derived from the local granitic crust. The origin of the type II zircons is ambiguous. Their characteristics may indicate either a magmatic origin from basic melt or precipitation from a hydrothermal fluid or a fluid-saturated residual melt. These zircon crystals preserved magmatic oscillatory-zoned growth domains particularly visible at the margins of grains. However, the middle parts of the majority of grains seem to be modified by hydrothermal fluids. Spongy and inclusion-rich centres of the zircons probably may have crystallized under similar conditions together with titanite, ilmenite, quartz, K-feldspar and biotite in the metabasites, especially in highly deformed parts of the veins. Locally, strong deformation of the metabasites could facilitate the migration of fluids coming from the surrounding metagranites. Nevertheless, the REE patterns, the Th/U ratios (0.4-1.8), and the weak oscillatory zoning in the rims of type II zircons suggest that these zircons crystallized from a magmatic melt rather than from metamorphic fluids. The slightly flattened HREE patterns of the type II zircons are connected with the coeval crystallization of other HREE-scavenging minerals such as pyroxene. The differences in the REE concentrations and the profiles between the types I and II zircons probably reflect crystallization from magmatic melts which differed in their composition. However, the zircons of type II show low values of $\delta^{18}O$ (4.42-5.25‰) which are below the mantle value of $\delta^{18}O$ (5.3 ± 0.3‰, Valley et al. 2005). These low $\delta^{18}O$ values of the zircons from the Izera metabasites can suggest interaction of the rocks with hydrothermal fluids during crystallization of zircons of type II. The results obtained are not yet sufficiently conclusive and require confirmation through further research.

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Genesis of Cenozoic volcanic rocks based on the study of selected xenoliths from Lower Silesia

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Cenozoic volcanic rocks in SW Poland are part of the Central European Volcanic Province (CEVP), which belongs to the vast Circum-Mediterranean Anorogenic Cenozoic Igneous province (Lustrino, Wilson 2007). The Lower Silesian occurrences are the north-easternmost zone of volcanic activity in those provinces, and are related to the Eger (Ohře) Rift (Birkenmajer et al. 2007; Puziewicz et al. 2011). The age of the Cenozoic volcanic activity ranges from Eocene to Pliocene and is strongly related to tectonic movements that occurred during the Alpine orogeny (Badura et al. 2006; Puziewicz et al. 2011).

The origin of the Cenozoic volcanic rocks has been explained as a result of mixing of melts originating from three mantle members: depleted mantle (DM), enriched mantle (EM) and high-μ (HIMU-FOZO type) (Ladenberger et al. 2006). In the area of the Eger Rift and the entire Bohemian Massif there is no obvious evidence for mantle plumes (Plomerova, Babuska 2010). Therefore, the geochemical components can be linked with three different regions in the upper mantle: lithospheric mantle, asthenospheric mantle and a boundary between those two layers – as was previously postulated (Ladenberger et al. 2006). The studies presented in this paper involved an examination of xenoliths transported by magma as potential sources of information on the localization of partial melting in the upper mantle.

The study area included the region between the towns of Złotoryja, Jawor and Świerzawa. For detailed petrological investigations, seven occurrences were chosen (Wołek (WH), Muchowskie Wzgórza (MW), Owczarek (O), Czartowska Skała (CzS), Wilcza Góra (WG), Kozia Góra (KG) and Jeziorna (J)). While generally xenoliths were found in all outcrops, mantle xenoliths (peridotites and pyroxenites) were found in only five (WH, MW, O, WG, J).

The research included petrological, geochemical and isotopic analyses of volcanic rocks and their xenoliths (more than 600 samples were collected). Petrological observations were performed on 121 thin sections, and modal compositions were estimated for over 40 different xenoliths (using two independent methods). Whole rock analyses (ICP-MS conducted at Acme Labs, Canada) were made of 18 volcanic rocks and 7 xenoliths. The chemical compositions of major elements in single mineral crystals were analyzed using electron microprobes (in Warsaw, Hannover and Toulouse), and trace elements were measured by LA-ICP-MS (Toulouse). More than 3000 analyses were obtained. The isotopic compositions (^{143}Nd/^{144}Nd, ^{87}Sr/^{86}Sr) of 20 samples were analyzed by TIMS at the UAM Poznań Isotopic Laboratory, and Pb isotopic ratios for 10 samples were measured by MC-ICP-MS at Acme Labs.

The volcanic rocks are mafic in composition. Based on TAS classification, they are basanites, but alkali basalts and nephelinites also occur rarely (Nowak 2012). Generally, the rocks are characterized by rather constant chemical, mineralogical and isotopic compositions, similar to other rocks from the CEVP (Ladenberger et al. 2006; Haase, Renno 2008). Locally, younger rocks (ca 20 Ma) differ from the older ones (ca 30 Ma) in lower SiO_2 and Al_2O_3 contents, mg-number and higher amounts of TiO_2, P_2O_5, CaO and Na_2O. Based on geochemical data, possible models of partial melting of lithospheric mantle were constructed. According to the rare element compositions from whole-rock analyses, the magma sources contained amphibole-bearing garnet peridotite (KG, WG, WH) and amphibole-bearing (or -absent) spinel peridotite (MW, O, CzS, J). Indeed, mixing of those two components cannot be excluded.

Five types of xenoliths were identified: peridotite xenoliths, pyroxenite xenoliths, ultramafic cumulates, crustal xenoliths and megacrysts. The peridotite xenoliths are mainly harzburgitic in composition. Sporadically, dunites and wehrlites also occur. The chemical and modal compositions of the main phases in the xenoliths (olivines (Ol), orthopyroxenes (Opx)) suggest that most of the lithospheric mantle was rather refractory and mineralogically uniform. However, in the xenoliths, besides the main phases, which can be related to first generations of minerals (more than ca 63% of the studied minerals), five further mineral generations were recognized. They have been interpreted as the results of processes such as: mantle metasomatism (both: cryptic and modal types; ca 16.5%), partial melting and magma ascent (ca 5%), xenolith-host rock interactions (ca 2%) and later post-volcanic and weathering processes (ca 12.5%). Rare hydrous minerals (amphiboles and phlogopite), found in xenoliths from WH and WG (Nowak et al. 2012), are the best proof of mantle metasomatism, and represent locally enriched lithospheric mantle. The presence of pyroxenite xenoliths or pyroxenite veins in peridotite xenoliths as well as ultramafic cumulates and megacrysts is evidence that some additional magmas from the asthenospheric mantle influenced the lithosphere. Such magmas could represent a HIMU-FOZO component.

P-T calculations were performed for both the volcanic rocks and their xenoliths, using the spreadsheets of Putirka (2008). In the volcanic rocks, averaged pressure (P) estimates vary between 0.1 and 1.2 GPa, whilst the temperature (T) values vary from ~1200ºC up to ~1330ºC. Averaged (T) calculations for the mantle xenoliths are much lower, ca 790-1000ºC (by 1Px thermometers), up to ~1180ºC (by 2Px thermometers) (Brey, Köhler 1990; Witt-Eickschen, Seck 1991). Pressure values are between 0.4 and 4.0(?) GPa. Due to the rarely observed equilibrium between diagnostic minerals, and low concentrations of some elements (e.g. Ca in Ol), the results for pressure (P) raise doubts. Also, hypothetical temperatures of magma source were calculated. The results range from 1320ºC to 1480ºC, and are much higher than the estimates from the mantle xenoliths.

In case of three outcrops (WH, WG, MH), for two hypothetical depths, 50 and 70 km, the time of magma ascent was calculated (by two independent methods). The results vary between a min. 1 day and max. 100 days, but those estimates could be influenced by the presence/absence of shallow crustal magma chambers (Nowak 2012). Unfortunately, the methods applied could not eliminate this factor.

In conclusion, the chemical and mineralogical compositions of the volcanic rocks studied do not differ much from other rocks belonging to the CEVP. The petrological observations and the calculations presented above are the basis of the petrological model, which shows the evolution of lithospheric mantle in the study area since the Eocene up to the late Miocene (Nowak et al. 2011). The peridotite xenoliths mostly represent cold, probably refractory lithospheric mantle. Such depleted mantle could not have individually produced the Cenozoic magmas. However, Cenozoic magmas of asthenospheric origin (HIMU-FOZO component?) during their ascent changed the composition of the lithospheric mantle. Locally fertile mantle (EM) could also have melted during the late stages of volcanic activity and could have contributed to changes in composition of the youngest volcanic rocks. The present research has confirmed the three-component mixing model proposed by Ladenberger et al. (2006), although the studies of the xenoliths have shown that time was a very important factor in such mixing.

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Mineralogy, geochemistry and genesis of the Anna Khatoon Cu deposit north of Tabriz (East Azarbaijan province)

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Sediment-hosted copper deposits are known from several points of Miocene geological units in the East Azarbaijan province. The Anna Khatoon Cu deposit is located north of Tabriz, in the northwest of Iran. The host rocks of the Anna Khatoon deposit in this part of west Alborz-Azarbayjan include redbed sediments (Ghom Redbeds) of Miocene age that extend over a large area between Nahand and Ivand. These sediments overlie limestones of Cretaceous age, and are covered by red and yellow marls interbedded with conglomerate and sandstone units of Pliocene age.

The Ghom Redbeds, 1200 m thick, include alternations of red oxidized (iron oxide minerals) sandstones and conglomerates that partly convert to light grey coloured varieties (with plant fossils) and make reduced horizons. In addition, this unit has considerable deposits of evaporites, such as gypsum and salt. Also Miocene salt domes are related to this unit. In most cases, the layers of siltstones, shales, sandstones and even conglomerates with woody fragments and plant fossils between the thick sequence of continental deposits with oxidized conditions, caused a reduced environment that was responsible for hosting the copper minerals (Brown 1997). The main ore minerals in this deposit are copper carbonates such as malachite, azurite and some copper sulphides such as chalcocite (Durieux, Brown 2007). It seems that creating conditions for a reducing sedimentary basin was the most important factor in the process of mineralization in this area (Stensgaard 2011).

Some of the most important parameters for this mineralization can be defined as:

- most deposits contain significant amounts of organic matter (Cox et al. 2007);
- in most cases, evaporitic rocks such as gypsum and anhydrite are found in close proximity to the ore minerals (El Desouky et al. 2007).

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A shape fabric analysis in deformed metaconglomerate of the Jegłowa beds, Strzelin Massif, SW Poland

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A deformed metaconglomerate cropping out near Jegłowa (40 km south of Wrocław, Poland) comprises densely packed, aligned, prolate pebbles, which are composed of polycrystalline quartz. The shape of 189 weathered-out pebbles has been described in terms of the long (X), intermediate (Y), and short (Z) axis of an approximating ellipsoid. The equivalent radius of the pebbles is in the range 0.4 to 1.8 cm, with a geometric mean value of 0.8 cm and its distribution shows an asymmetry towards high values. The geometric means of the measured X/Y, Y/Z and X/Z ratios are respectively 2.6, 1.4, and 3.7, resulting in a harmonic mean k-value of 2.8. The distribution of the axial ratios is approximately log-normal. No dependence of the axial ratios and the k-values on the equivalent radius is observed. The axial ratio of the central vacancy in the Fry plots measured for the XZ sections reaches values from 3.4 up to 6.5 and in YZ sections from 1.2 to 1.7. Thus, the k-parameter lies in the range 1.4 to 9.0.

In our numerical experiment, a randomly oriented assemblage of oblate ellipsoids with X = 1.5-4, Y = 1.5-2 and Z = 1 subject to a finite homogeneous strain of 4:1:1 shows a distribution of the X/Z ratio that is similar to that measured for the Jegłowa metaconglomerate.

In conclusion, it is suggested that the observed variability of the final pebble shapes could have arisen as a result of one deformation episode.

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Permian bimodal volcanism in the North-Sudetic Basin: new insights into the emplacement processes, sequence and petrology of volcanic rocks of the Świerzawa area

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The Świerzawa area in the NE part of the North-Sudetic Basin was the site of late-orogenic, early Permian bimodal volcanism, characteristic also of many other late Palaeozoic intramontane basins across the European Variscan Belt. However, the Świerzawa area is famous for spectacular outcrops of columnar jointed rhyolites, as well as for post-magmatic mineralization. Previous studies (Kozłowski, Parachoniak 1967 and references therein) provided basic constraints on the geology and petrography of the volcanic rocks and the sequence of volcanic events. The rhyolites from Wielisławka and Dynowice were recently dated at 293 ± 2 Ma and 294 ± 3 Ma, respectively, using the SHRIMP method on zircons (Szczepara et al. 2011). This contribution contains an overview of recent advances in petrological and volcanological studies from this area, including the emplacement sequence of the volcanic rocks, and the mineral chemistry and geochemistry of the volcanic rocks.

In the Świerzawa area, rhyolitic volcanism volumetrically predominated over basaltic-andesitic volcanism. The rhyolites form two main units/bodies. The southern unit comprises the Wielisławka Hill rhyolites with the famous, spectacular exposure known as the Organy Wielisławskie. There, flow foliation forms a concentric structure with a perpendicular or oblique system of well-developed columnar joints, defining a radial pattern. Most probably, the Wielisławka rhyolites are the remnants of a subvolcanic intrusion (?laccolith), or the basal to central part of an eroded rhyolitic lava dome. Small blocks of breccias abundant on the eastern slope of Wielisławka support emplacement of the rhyolites as a subaerial silicic dome.

Located 1 km north of Wielisławka, there is a more extensive (8.5 x 3 km), ca 150 m thick outcrop of felsic rocks. This unit consists mainly of massive rhyolites. Field and thin-section observations show also well-developed carapace facies lithologies in the northern parts of this rhyolitic body. The carapace facies consists of perlitic, weathered obsidian and spherulitic rhyolite with abundant, spectacular agates filling lithophysae and vesicles. These rhyolites resulted from lava effusions. In addition, volcaniclastic deposits of rhyolitic composition occur in an abandoned quarry on Owczarnia Hill in the western part, and in small exposure in the southern part of Wołek Hill. The structures of deposits at Owczarnia and their microscopic features suggest an epiclastic rather than pyroclastic origin, i.e. they are volcanogenic sandstones and conglomerates rather than tuffs. However, the deposits from Wołek are probably of pyroclastic origin. The small (3 x 4 m) size of this isolated exposure impedes a more detailed interpretation.

The mafic rocks of the study area are basaltic andesites. According to geological maps and field observations, these rocks partly cut the rhyolitic sequence and form shallow-level subvolcanic intrusions rather than lava flows; evidence is also provided by lava-sediment breccias (peperites) abundant at some localities. It seems that mafic volcanic activity postdated silicic volcanism, which is opposite to the sequence proposed by Kozłowski and Parachoniak (1967).

The rhyolitic suite is represented by red, pinkish, massive to platy jointed, locally flow-laminated rhyolites. These rocks have a porphyritic, fine- to medium-grained texture. The groundmass of the rhyolites of the core facies of lava flows is felsitic, sometimes microspherulitic and cryptocrystalline. The carapace facies of lava flows comprises perlitic, spherulitic, lithophysae-bearing (with agates) or amygdaloidal (quartz-filled) rhyolites. The basaltic andesites are dark-brown with massive, plagioclase-phyric or microcrystalline, aphyric texture. The margins of intrusions are represented by amygdaloidal rocks with intersertal groundmass.

Phenocrysts in the rhyolites are quartz, alkali feldspar (Or_{54-99}), plagioclase (An_{35}), dark mica (biotite with subordinate phlogopite and annite), with microphenocrysts of apatite, zircon, and Fe-Ti oxides. One can find also post-magmatic minerals such as albite, kaolinite, illite and various types of silica-group minerals including agate. Alkali feldspar phenocrysts (and kaolinite pseudomorphs after this mineral) predominate over plagioclase phenocrysts with the exception of rhyolites from Zawodnia Hill where this ratio is reversed. Phenocrysts in the basaltic andesites are plagioclase (An_{37-61}) and albite pseudomorphs after plagioclase, and iddingsite or clay mineral pseudomorphs after mafic minerals. Alkali feldspar (Or_{48-66}) and Fe-Ti oxides occur also in the groundmass. Other post-magmatic minerals, such as chlorite, calcite and quartz and other silica-group varieties, fill the amygdales.

Whole-rock geochemistry confirms the bimodal nature of the volcanism. The classification diagram for altered volcanic rocks of Pearce (1996) shows two distinct clusters, trachyandesites and rhyolites, that straddle the border between alkaline and sub-alkaline suites. Harker diagrams show some well-defined magmatic trends (Fe_2O_3, Al_2O_3,P_2O_5 and TiO_2 vs SiO_2) and alteration-related trends (Na_2O and K_2O vs SiO_2), the latter, controlled by the replacement of feldspars (mainly plagioclase) by clay minerals. Spider diagrams reveal rather complex relationships between mafic and felsic rocks, e.g. lower contents of many incompatible elements in the felsic rocks. The new data together with previously published results (Awdankiewicz 2006) suggest that the basaltic andesites were generated from a mantle source and were affected by fractional crystallization processes. The rhyolites rather resulted from a different parental magma and underwent differentiation in a crustal magma reservoir. However, these conclusions require further confirmation,
e.g. using geochemical modelling.

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REE and Y behaviour during breakdown of coexisting monazite-(Ce) and xenotime-(Y) in granite from the High Tatra Mts.

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The breakdown of monazite has been noted many times from the Tatra granites (e.g. Broska, Siman 1998; Michalik, Skublicki 1998; Szopa 2009) and Alpine metagranites according to the typical reaction of monazite decomposition proposed by Finger et al. (1998): 3Mnz + Ann + 4Pl + 3Qtz + fluid ↔ Ap + 3All + Ms. REE-rich epidote to allanite crystals are the result of monazite-(Ce) breakdown to apatite-(CaF) and allanite during metamorphic and hydrothermal processes. In this paper, the products of xenotime-(Y) breakdown are noted and compared with the much more common breakdown of monazite-(Ce) from the High Tatra granite (Fig. 1A).

The REE-rich epidote-group minerals are the main products of monazite-(Ce) and xenotime-(Y) decomposition in biotite monzogranite from the Morskie Oko Area, the High Tatra Mts. The REE-rich epidotes are present as elongated, xenomorphic crystals, occasionally showing patchy textures due to irregular zonation with respect to REE and Y. Together with apatite-(CaF) and pure epidote, they form coronas on monazite/xenotime crystals. The chemical composition of the epidotes that form the coronas could be distinguished in BSE images (Fig. 1A).

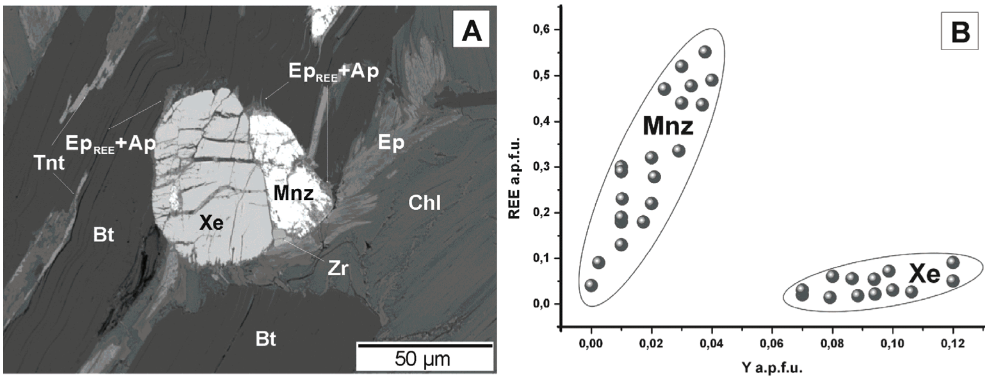

Fig.1 (A) BSE image of monazite-(Ce), xenotime-(Y) and their mineral coronas. (B) Chemical composition plot of REE-rich epidote from the decomposition coronas of primary phosphates: after monazite-(Ce) (Mnz) and xenotime-(Y) decomposition (Xe). Explanations: Xe – xenotime, Mnz – monazite, Bt – biotite, Chl – chlorite, Zr – zircon, Tnt – titanite, Ep – epidote, Ep$_{REE}$ – REE-rich epidote

The investigated epidote/allanite group minerals were formed as a result of the influx of an alkali- and Ca-rich, F-bearing fluid (Upadhyay, Pruseth 2012). Decomposition of both phosphate minerals by active fluids probably started at the same time. The coronas were formed as a mixture of both monazite-(Ce) and xenotime-(Y) mineral products on their relict grains. Electron microanalyses reveal two types of REE rich-epidotes/allanites, differing in chemical composition (Fig. 1B). The average chemical formulae for REE-rich epidote formed after monazite-(Ce) and xenotime-(Y) decomposition are $(Ca_{1.60}Ce_{0.24}Nd_{0.07}La_{0.07})_{\Sigma=1.98}(Al_{1.79}Fe^{3+}_{1.19}Mn_{0.01})_{\Sigma=2.99}Si_{2.94}O_{12}|O(OH)_{0.5}$ and $(Ca_{1.62}Y_{0.12}Gd_{0.04}Mg_{0.02})_{\Sigma=1.90}(Al_{2.0}Fe^{3+}_{0.85}Mn_{0.02})_{\Sigma=2.87}Si_{2.96}O_{12}|O(OH)_{0.5}$, respectively.

During alteration of the phosphates, widespread chloritization of biotite was observed. Three different geothermometers were used to determine the temperature, following the (1) Cathelineau and Nieva (1985), (2) Kranidiotis and MacLean (1987) and (3) Jowett (1991) protocols. The chlorite geothermometers reveal two ranges of temperature: (1) 332-360°C and 312-325°C, (2) 319-330°C and 305-312°C, (3) 340-366°C and 321-333°C.

The study shows that the primary, magmatic phosphates might have been altered during a late Variscan fluid-induced metamorphic overprint. The observed monazite-(Ce) and xenotime-(Y) decomposition reaction was caused by Ca, Al, F and Si-rich fluids. The chlorite geothermometers gave two, the most likely, intervals, with average temperatures ca 350°C and 320°C respectively, interpreted as possible temperature intervals of REE- and Y-rich epidote corona formation during igneous phosphate breakdown.

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Composition and weathering of Zn-Pb slags from Bytom-Piekary Śląskie area: a case of heavy metal concentration and mobility

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Slag heaps are typical landscape components of the Bytom-Piekary Śląskie area. Their formation started in the 13th century, together with the development of Zn-Pb-Ag ore mining (Kotucha 2008).

Highly porous Zn-Pb slags are composed of pyroxenes, feldspars, melilites, spinels, sulphides and metallic phases. Pyroxenes usually form zoned, idiomorphic to subidiomorphic crystals, having the composition of diopside-petedunnite solid solution $(Ca_{0.86-0.91}Fe^{2+}_{0.10}Na_{0.00-0.09}Pb_{0.00-0.02})(Mg_{0.00-0.82}Mn_{0.00-0.28}Fe^{2+}_{0.00-0.013}Fe^{3+}_{0.01-0.04}Zn_{0.02-0.58}Ti_{0.09}Al_{0.02})(Si_{1.86-1.96}Al_{0.04-0.08}Fe^{3+}_{0.06})O_6$. They are intergrown with melilite crystals $(Ca_{1.82}Mg_{0.04}Na_{0.09}K_{0.01})_{\Sigma=1.96}(Mg_{0.60}Al_{0.30}Zn_{0.05}Fe^{3+}_{0.03}Mn_{0.01}V_{0.01})_{\Sigma=1}(Si_{1.83}Al_{0.17})_{\Sigma=2}O_7$. Feldspars are represented by composite crystals composed of bytownite-anorthite cores $(Ca_{0.76-0.99}Na_{0.02-0.21}K_{0.00-0.04}Ba_{0.00-0.01})(Al_{1.75-1.99}Fe^{3+}_{0.00-0.05})Si_{2.00-2.16}O_8)$, overgrown by plumbian K-feldspars, enriched in barium $(K_{0.70-0.66}Ca_{0.08-0.76}Na_{0.10-0.20}Ba_{0.04-0.19}Pb_{0.01-0.05}Zn_{0.04}Mg_{0.00-0.02})(Al_{1.08-1.60}Fe^{3+}_{0.05-0.09})Si_{2.26-2.81}O_8)$. Spinels with a compositional spectrum from magnetite–Ti-magnetite to more complex $(Zn_{0.36}Fe^{2+}_{0.34}Mg_{0.20}Mn_{0.05}Na_{0.01})_{\Sigma=0.96}(Fe^{3+}_{1.41}Al_{0.52}Ti_{0.06})_{\Sigma=1.99}O_4$ crystals are dispersed in the silicate matrix and usually show a dendritic morphology. In places, layer-like concentrations of subidiomorphic magnetite--magnesioferrite and hematite grains are observed. Galena and sphalerite remnants are also observed. Locally the metallic droplets of Fe-As were found. Two types of glass were distinguished: Pb-rich (25-53wt% PbO) and felsic, rich in silica (73-86wt% SiO_2).

In the typical slag the total amount of Fe_2O_3 (concentrated in spinels and hematite) is about 15-16wt%, whilst the Zn concentration is 0.8-3.0wt% and its main carriers are pyroxenes, spinels and glass; Pb is in the range of 0.13-0.38wt% (concentrated in glass and feldspars), while the As content reaches 0.2wt% and is concentrated in Fe-As intermetallic compounds and sulphides.

Weathering of the slags is expressed in the formation of white coronas composed of calcite, aragonite, rapidcreekite, gypsum and pyroaurite. The typical weathering zone show an enrichment in As (1.5wt%), Cu (0.21wt%) and Au (307 ppb). Zinc concentration reaches 0.6wt%, whilst Pb does not exceed 0.13wt%. Secondary gypsum could locally concentrate Zn up to 3wt%. REE analyses suggest no or restricted mobility during weathering.

Leaching tests demonstrated the mobility of As in the weathered zone (32 x higher concentration of As than in the case of leachate from fresh slag). Zn is preferentially leached from the fresh slag, whilst Pb is leached from both fresh and weathered slag.

The type of secondary phases suggest oxidizing conditions and low pH during slag weathering (Lottermoser 2010).

The documented mobility of As, Zn and Pb from the slags causes an environmental risk; however the present location of the heap prevents mixing of contaminated water with formation waters. However, the slags are currently used as material for road construction, which could cause great environmental problems in the future. Taking into account the concentration of Zn, As and Au in the secondary products as well as the common presence of Fe-spinels the potential recycling of wastes should be considered.

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Potassic-fluorian richterite from the Międzyrzecze sill

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There are two main occurrences of K-rich amphiboles: the first is in ultrabasic xenoliths from kimberlites and the second is in lamproites. K-richterites from kimberlitic xenoliths contain only minor amounts of Fe and negligible Al, Ti, Cr and F. Lamproitic amphiboles are typically rich in Ti (up to 8wt% TiO_2) and exhibit a compositional range from titanian K-richterites to titanian K-magnesio-katophorites. K-rich amphiboles of crustal origin are extremely rare (Martin 2007). Textures and experimental works suggest their near-solidus or subsolidus origin.

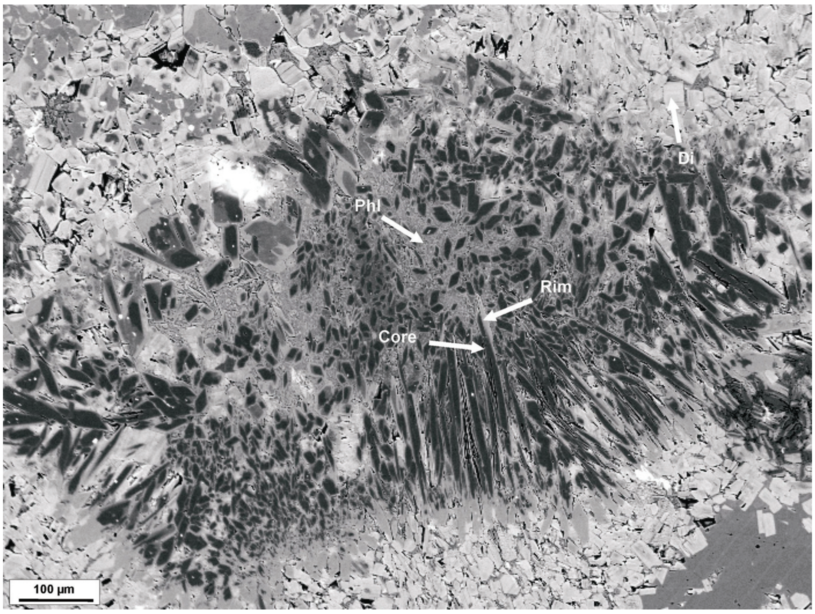

Fig. 1. BSE image of the ocelli in fine-grained glimmerite chilled rims around limestone xenolith; explanations: Di - diopside; Phl - phlogopite; Core/Rim – richterite

In alkaline rocks (picrite, picroteschenite, teschenite and syenite) from the western part of the Outer Polish Carpathians, the composition of amphiboles varies from kaersutite (pargasite/magnesiohastingite) through ferrokaersutite to hastingite, and towards NaCa-amphiboles (taramite, katophorite, richterite, winchite). In general, the compositional trend in the amphiboles approaches the Na-amphibole field (arfvedsonite). In the picrite sills, amphiboles range in composition from kaersutite and ferrokaersutite through Mg-hastingsite, Mg-katophorite to richterite (evolution at low f_{O_2}). In these rocks NaCa-amphiboles occur as narrow rims on Ca-amphibole cores (Włodyka 2010).

Individual crystals of potassic-fluorian-richterite have been found only in the strongly altered olivine glimmerite sill at Międzyrzecze Górne near Bielsko-Biała. The small, 12 m thick sill was emplaced into the Upper Jurassic (Tithonian) Cieszyn Limestones. A section through the sill shows a division into two main parts, whose origin can be explained by flow differentiation of olivine. In the external, olivine-free part, up to 2 m thick, the presence of a Ca-skarn xenolith was recorded. It forms a large lens, with a thickness over 2 m, length of 12 m and width of 5 m. The main part of the skarn is composed of pectolite crystals, enclosing abundant poikilitic inclusions of Ti-garnet and aegirine as well as diopside, natrolite, datolite, titanite and Sr-apatite.

Richterite occurs in a fine-grained glimmerite chilled rim of ~10 cm around the limestone xenolith. A characteristic feature of these rims is the presence of ocelli textures (Fig. 1). The ocelli show globular shapes, display rounded to elongated forms and are approximately 1.0 mm in diameter. The contact between this type of ocelli and the host groundmass is marked by diopside-rich segregations. They consist of radial crystals of richterite directed inside the ocelli, and interstitial phlogopite-biotite. They probably originated by crystallization from the contaminated mafic melts at the magma-limestone interface.

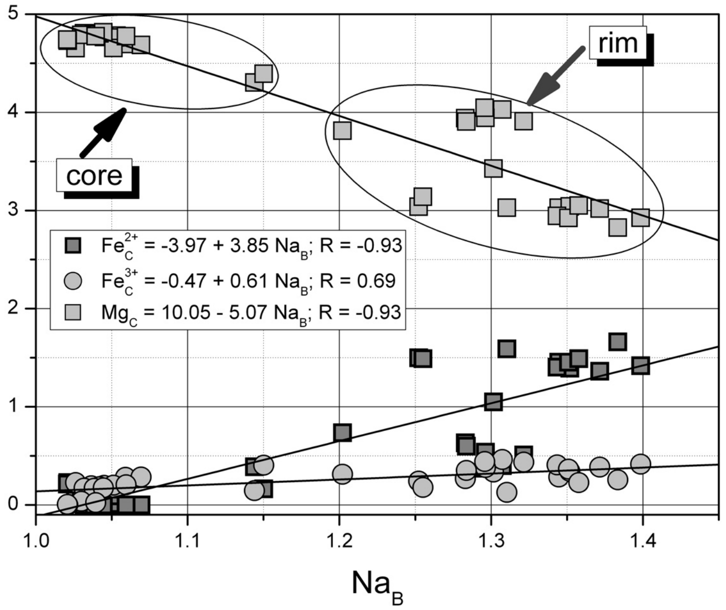

Fig. 2. Relation of Na_B to $(Fe^{2+}, Fe^{3+}, Mg)_C$ for potassic-fluorian richterite from the Międzyrzecze sill

NaCa-amphiboles form acicular, zoned crystals (Fig. 2); their cores are richer in F, Mg and Ca than the rims, which are richer in OH, Ti, Fe, Na and K. They are Mg-rich, with Mg/(Mg+Fe) and F/(F+OH) ratios ranging from 0.97-0.87/0.31-0.21 (core) to 0.83-0.59/0.23-0.14 (rim). These compositional variations can be expressed by the following crystal-chemical formula: $(K_{0.66-0.96}Na_{0.31-0.02})(Ca_{0.97-0.60}Na_{1.03-1.40})(Mg_{4.79-2.90}Fe_{0.20-2.00}Mn_{0.01-0.08})(Si_{7.93-7.08}Al_{0.00-0.74}Ti_{0.07-0.18})O_{22}(F_{0.64-0.28}OH_{1.36-1.71})$. The chemical data on the zoned richterite crystals reveal that the change in chemical composition from the core to the rim takes place along the substitutions: $Na^{B}Fe^{3+(C)}Ca^{B}_{-1}Mg^{C}_{-1}$ (arfvedsonite vector), $Fe^{C}Mg^{C}_{-1}$ and $TiSi_{-1}$ as seen in Fig. 2.

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XIXth Meeting of the Petrology Group of the Mineralogical Society of Poland

METEORITES: INSIGHTS INTO PLANETARY COMPOSITIONS

EXCURSION GUIDE

The 164 kg Morasko meteorite after cleaning, showing regmaglypted surface.

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Field excursion to the “Morasko Meteorite” Reserve

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During the field excursion, we will visit the site of the Morasko craters and discuss the problems of the meteorite fall onto the soft glacigenic sediments which have been raised in several publications. Also, interesting geomorphological aspects and age relationships of the deposits in which the craters were formed will be presented.

Specific problems to be presented and discussed during the field excursion are as follows (see also Muszyński et al.: Morasko meteorite – the current state of knowledge, this volume):

1. The history of discovery of the Morasko meteorite

The first find of Morasko was in 1914. The related iron of Przełazy was found in 1847 and of Jankowo Dolne in 1990. Considerable progress in scientific documentation was made by Pokrzywnicki (between 1955 and 1964), Hurnik et al. (1976), and Stankowski and co-workers (1995-2008).

2. Geological setting, distribution and morphology of the Morasko craters; glacitectonics

Moraska Góra is built of deformed Neogene and Pleistocene deposits (the oldest > 0.5 Ma), and its palaeomorphological rise is older than the last glaciation (Stankowski 2001).

During the ice maximum extent of the last glaciation (Vistulian, ~20000 BP), shallow glacitectonic deformation took place and morphological features similar to present day features were formed. The degradation of permafrost in Moraska Góra and surroundings occurred between 14,000 and 10,000 yr BP. Evorsive depressions and kettle-holes, predominantly longitudinal and irregular in shape, started to fill with organic deposits before the Holocene (Tobolski 1976; Stankowski 2008). The age of the deepest organic infill in the thermocarst depressions is documented palynologically and by ^{14}C dating (Stankowski 2001).

In a small area NE of the Moraska Góra summit, several regular oval depressions are found, with circumferential ridges of different shape. The age of their organic infill is much younger than that in cryogenic ones from pre-Holocene times.

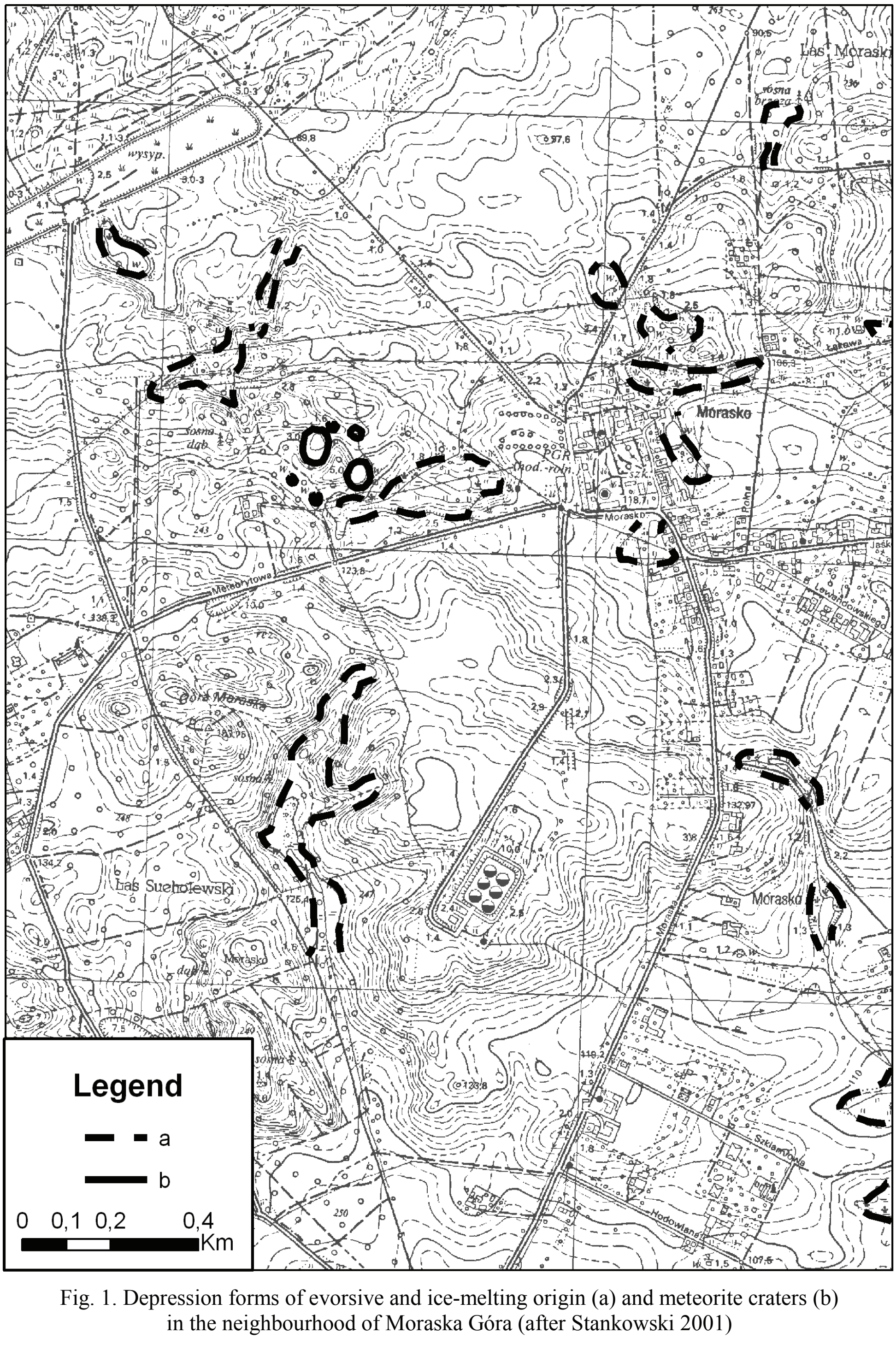


Fig. 1. Depression forms of evorsive and ice-melting origin (a) and meteorite craters (b) in the neighbourhood of Moraska Góra (after Stankowski 2001)

3. Distribution of the meteorite finds

The great majority of finds of Morasko are confined to a relatively small area on the northern slope of a terminal moraine from the last glaciation. No find has been reported north of the moraine, except two doubtful irons which were reportedly found in the town of Oborniki, and lost before detailed examination could be made (Pokrzywnicki 1964). Most meteorite fragments were found at a depth of ~50-80 cm. However, the latest findings indicate that the meteorites can occur deeper than 160 cm (Pilski et al. 2012).

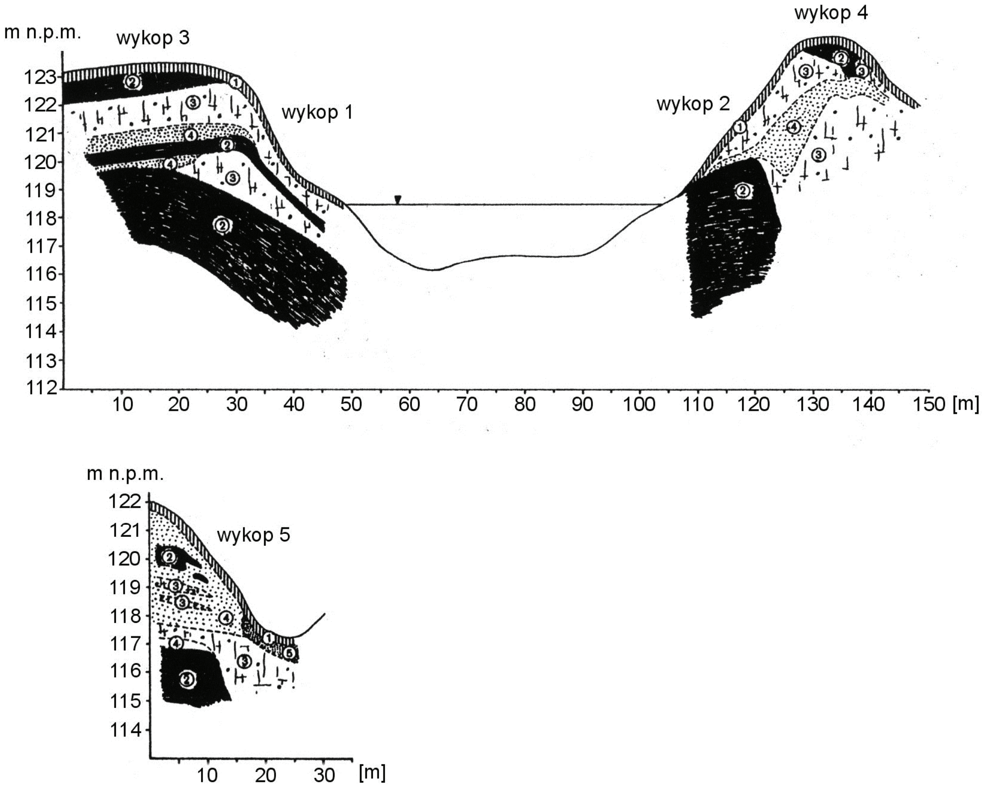
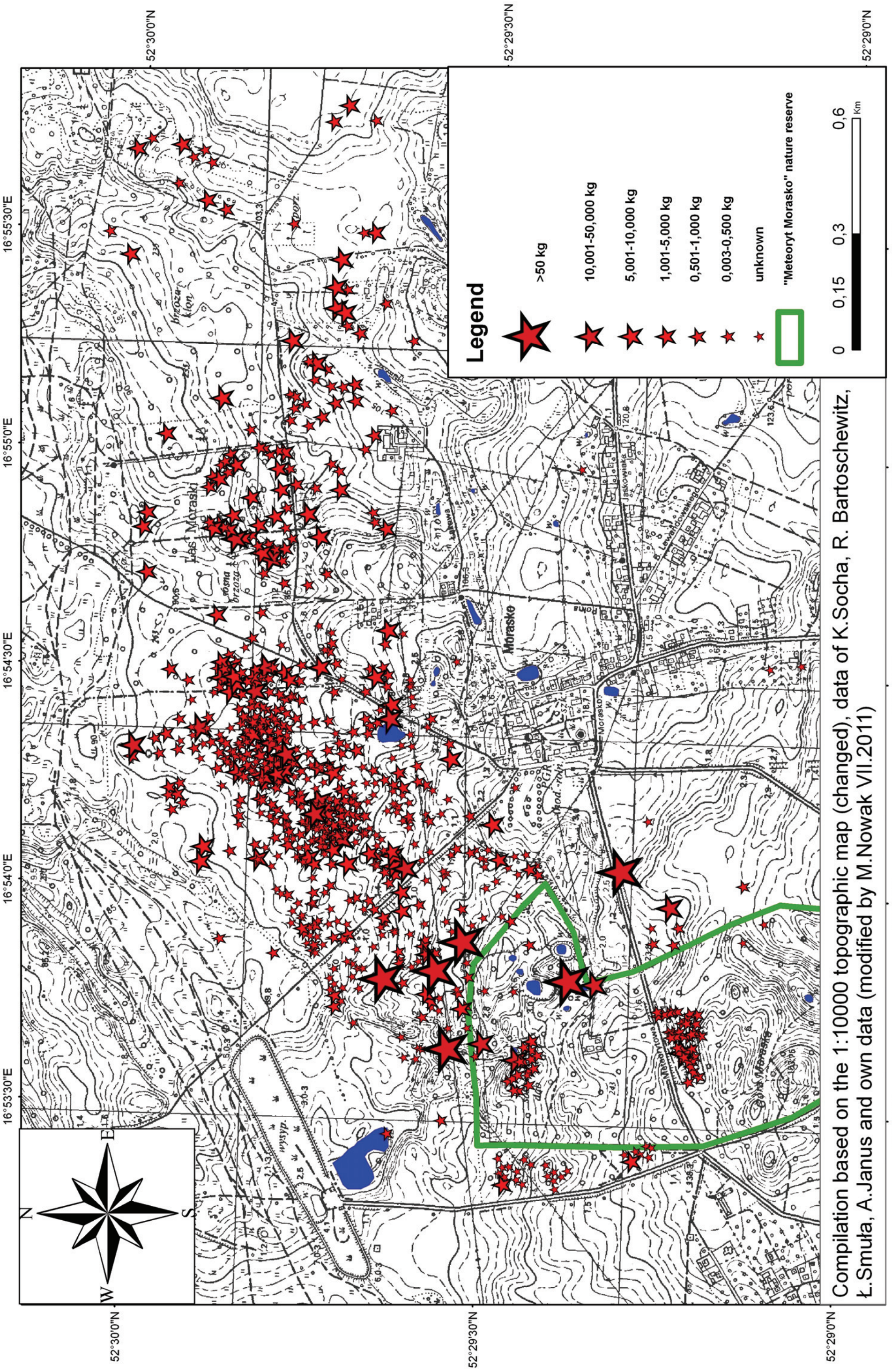


Fig. 2. Schematic cross-sections through depressions A (above) and F (below), (after Karczewski 1976). 1 – soil, 2 – Poznań variegated clay, 3 – sandy loam, 4 – clayey sand, 5 – organodetrital deposits

4. The Morasko strewn field

The distribution of the Morasko iron finds is shown in Fig. 3. The three iron falls, Morasko, Przełazy and Jankowo Dolne, broadly lie along a WSW-ENE line, with the largest Morasko fall situated approximately midway between Przełazy and Jankowo Dolne.



Compilation based on the 1:10000 topographic map (changed), data of K.Socha, R. Bartoschewitz, Ł.Smuła, A.Janus and own data (modified by M.Nowak VII.2011)

Fig. 3. The Morasko iron: distribution of meteorite finds (after Muszyński et al. 2012)

5. Petrography, mineralogy and chemistry of the meteorites

All three irons, Morasko, Przełazy and Jankowo, display many similarities in petrography, mineralogy and chemical features. All three belong to group IAB, but show exceptionally low Ir and high Ge contents. They are composed mainly of coarse-grained kamacite and taenite, with accessory cohenite and schreibersite. A distinct feature in all three irons is the presence of characteristic nodules, usually ca 1-1.5 cm in size, composed of graphite and troilite, with minor silicates, sulphates, oxides and phosphates. Shock changes are found in many small individual meteorite fragments (Karwowski 2007; Jastrzębska 2009).

6. Micrometeorites and meteoritic dust in soil

Micrometeorites and meteoritic dust have been proven at many localities within the Morasko strewn field (unpublished data). Marini et al. (2004) have shown that tiny fragments of meteorites can form at various stages of impact. They can form from metal-rich vapour, melt or due to disintegration of larger solid particles (Fig. 4).

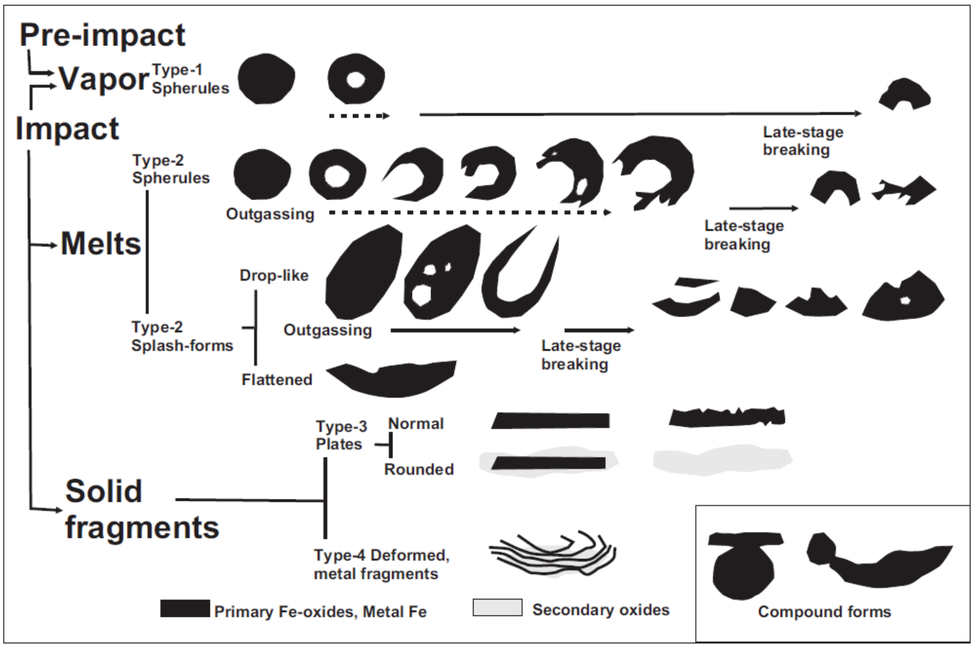


Fig. 4. Various genetic types of "magnetic fines" (after Marini et al. 2004)

7. Meteorite weathering

Iron meteorites show various degrees of weathering, depending on their location and local conditions (Fig. 5). In the case of the Morasko iron, weakly weathered fragments are found at shallow depth in loams, whereas those from sandy and clayey deposits at deeper levels are much more strongly altered. The weathering products include Ni-rich iron hydroxides, and chlorides, sulphates, phosphates and carbonates. Locally, microaggregates of a Ge-rich (up to 5at.%) metal phase are found within secondary hydroxides (Karwowski, Gurdziel 2009).

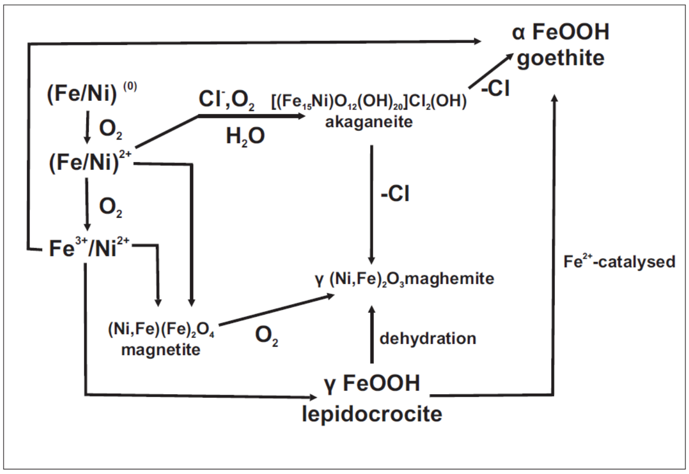


Fig. 5. Scheme of weathering of iron meteorites (after Golden et al. 1995)

8. Timing of the meteorite fall

According to Tobolski's (1976) palynological estimates, ^{14}C, OSL and TL data (see Stankowski, this volume), organic accumulation in the Morasko Reserve depressions started no earlier than the middle stage of the Atlantic period (Table 1). Based on available data, the Morasko meteorite shower took place about 5000 yr BP. The latest investigations of the age of weathering crusts of the Morasko iron by Stankowski (see this volume) confirm the relatively young age of the Morasko fall.

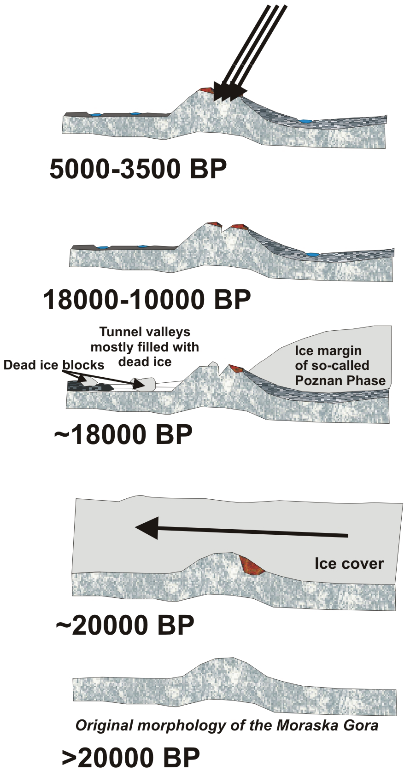
Table 1. Morasko meteorite craters - radiometric data and palynological estimations (after Stankowski, Muszyński 2008).

Years BP	Beginning of crater organic infilling				
	Palynological estimations (Tobolski 1976; Milecka, unpublished)	^{14}C datings (Gliwice and *Poznań* laboratories) Craters:			
		A	B	C	E
0	5000-5500		260±80 690±95	640±90 690±150 990±160	610±75 650±110
1000					
2000			2690±170		
3000					3360±100
4000		*4465±35* *4495±35*	*4760±40*		
5000					
6000					
7000					
8000					
9000					
10000	Permafrost degradation not later than 10000 years BP (Kozarski 1963)				

^{14}C data for mineral/organic boundary in different boreholes, elaborated by Pazdur (Gliwice) and Goslar (Poznań; in italics).

9. Morasko iron shower model

Summarizing the available observations, we may conclude that the three iron meteorite falls, Morasko, Seeläsgen (Przełazy) and Jankowo Dolne, represent a single meteorite shower dated at ca 5000 Ma. They originated from a large and rather homogeneous meteoroid. A model showing the geological and environmental circumstances preceding the impact of the Morasko iron shower, after Stankowski (2001), is presented in Fig. 6.



Between 5000-3500 BP the Meteorite Morasko shower fell-craters were formed and their organic infilling could started.

The permafrost degradation development of kettle-holes. Beginning of organic infilling of kettle-holes (14000 and later) but not younger then 10000 BP.

Prolongation of evortion, active erosion of melting waters and accumulation of glaciogenic sediments. Out of glacial cover permafrost exist and active periglacial processes occur.

Shallow young deformations and ice abrasion surfaces developed during the maximum extend of the last ice-sheet reaching so-called Leszno Phase. Subglacial meltwater erosional forms have begun to create.

Pre-Vistulian hill glacitectonically deformed in older glaciacions and denudationally transformed.

Fig. 6. Sketch showing the geological and environmental circumstances preceding the impact of the Morasko iron shower (after Stankowski 2001, modified)

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Doświadczenie

Poznaliśmy historię kamienia, a to dziedzictwo jest naszym udziałem. Działamy na rynku już od 70 lat. Mimo ogromnego doświadczenia wciąż się uczymy, wzbogacamy naszą wiedzę a posteriori ciężką, codzienną pracą. To my, jako pierwsi w dziejach ludzkości rozpoczynaliśmy pozyskiwanie oraz dystrybucję pięknych marmurów carraryjskich. Mimo zmieniającej się mody, my wciąż dostarczamy kamień naturalny z powodzeniem zaspakajając wyszukane gusta naszych klientów. Nie straszne nam są żadne nowe trendy rządzące światem designu. Nie szukamy łatwych dróg, unikamy podróbek i tandety. Stosując tę prostą filozofię z łatwością dostarczamy materiały kamienne najwyższej jakości do licznych i szeroko podziwianych obiektów użyteczności publicznej oraz domów rozsianych na wszystkich kontynentach. Warto zaufać naszemu doświadczeniu.

Szeroka gama produktów

W naszej ofercie mamy około 200 rodzajów kamienia w ciągłej sprzedaży. Większość z oferowanych materiałów naturalnych pochodzi z Włoch, jednak część z bardzo odległych i egzotycznych zakątków Świata. Z radością prezentujemy Państwu najnowsze i najbardziej elitarne odkrycia z naszych kamieniołomów ukrytych w lasach tropikalnych, suchych i niedostępnych pustyniach lub mroźnych i dzikich bezludziach. Nie ustajemy w poszukiwaniach nowych, jeszcze nie eksplorowanych odmianach znanych standardów kamieniarskich. Każdego roku poszerzamy i dostosowujemy naszą ofertę do Państwa wymagań i oczekiwań.

Ekskluzywne materiały

Dla naszych wymagających klientów zawsze mamy wyjątkowe okazy, kamienie niedostępne w żadnym innym salonie kamieniarskim, kamienie o unikalnych cechach, egzemplarze ocierające się o miano "kolekcjonerskie". Naszym zadaniem jest dopasowanie kamieni pod indywidualny gust. Dobranie materiału zarówno pod względem wyglądu, jak również pod względem zastosowania eksploatacyjnego. To dla nas przyjemność móc Państwu doradzać.

Dyspozycyjność

Zawsze mamy dla Państwa czas. Umawiamy się na indywidualne spotkania. Słuchamy Państwa potrzeb, doradzimy i zrobimy wszystko aby Państwo podzielili nasz niekłamany zachwyt nad pięknem kamienia naturalnego i aby to piękno połączyło nasze wspólne losy na lata...

Zapraszamy do naszych oddziałów:

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