



HELLENIC REPUBLIC
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University of Athens

School of Science

Department of Geology & Geoenvironment

Mineralogy and geochemistry of U-V geological materials



Sergios Andronikidis (BSc Thesis)

Supervisor: Prof. A. Godelitsas

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Outline

In the frame of the present Thesis the mineralogy and geochemistry of U-V geological materials has been reviewed and discussed. The importance of this subject arises from the fact that both metals are being explored and exploited for various industrial and technological applications. At the same time, a typical sample of U-V mineralization (mainly carnotite $(K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O)$ - tyuyamunite, $(Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O)$ minerals), occurring in sedimentary formation of Fall River County, South Dakota (USA), has been characterized by means of diffraction (PXRD), micro-analytical (SEM-EDS), spectroscopic (FTIR), and bulk analytical (ICP-MS) techniques. The results obtained are in agreement with the existing literature and contribute in the investigation of U-V ore deposits.

Keywords: Uranium; vanadium; carnotite; carnotite-tyuyamunite; sedimentary; deposits; mineralogy; geochemistry

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1. Introduction

Uranium (mostly U^{6+} and U^{4+}) is a significant chemical element occurring in Earth and forms various types of U minerals and U ore deposits (**Fig. 1** and **Fig. 2**).

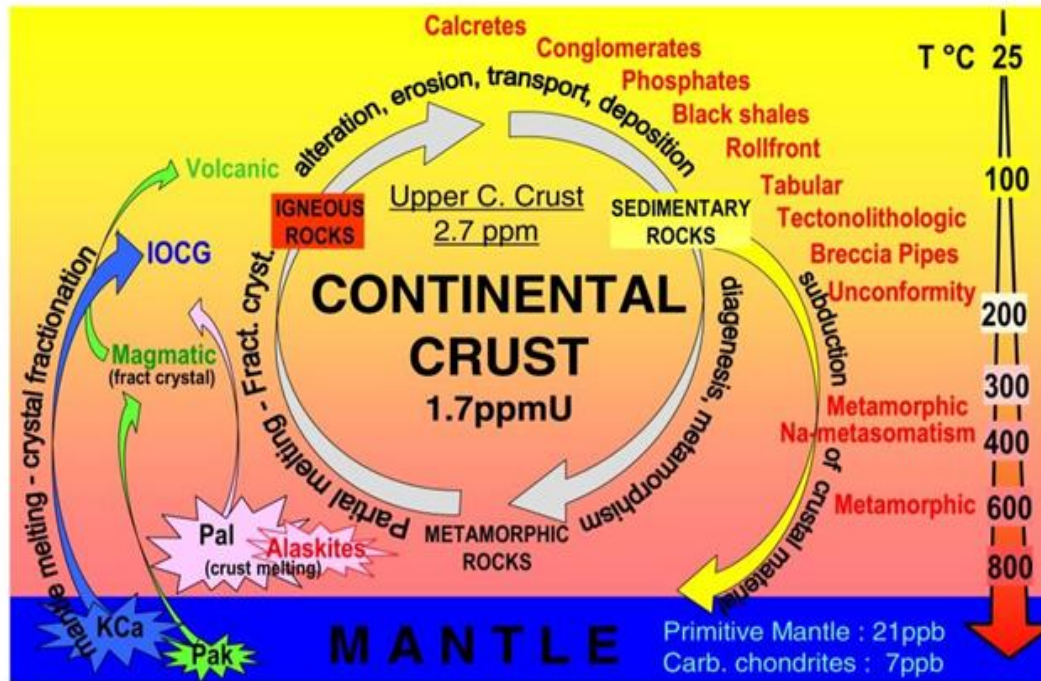


Fig. 1: Uranium geochemical cycles in nature (Cuney, 2009)

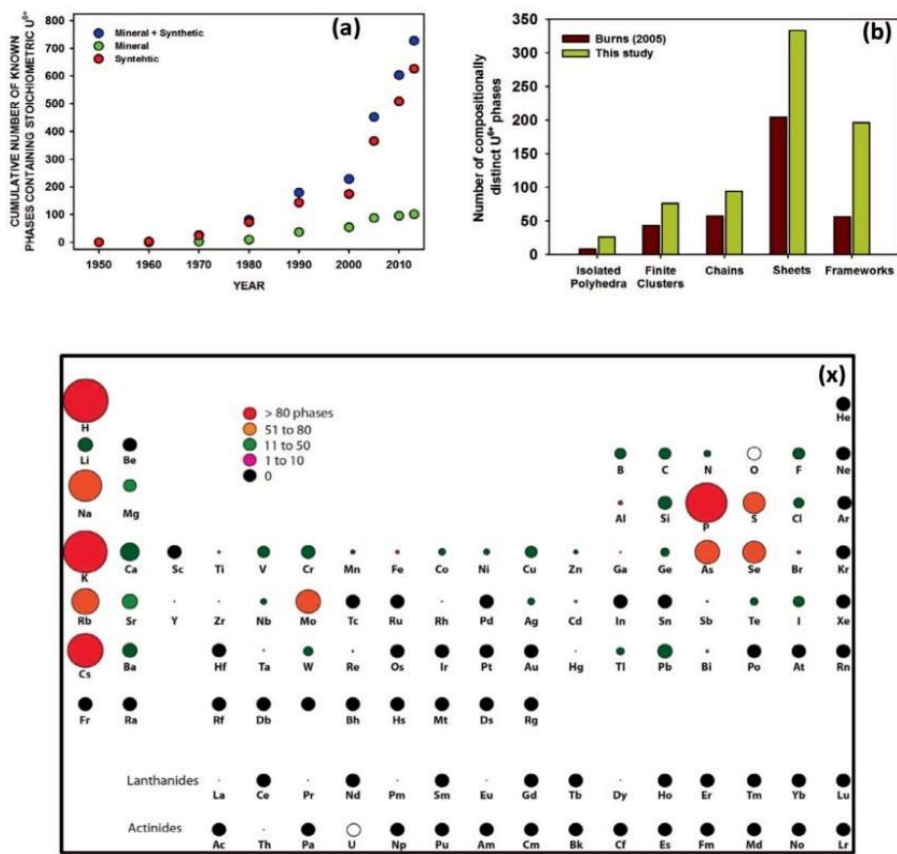


Fig. 2: General information regarding the known U^{6+} compounds & minerals (Lussier et al. 2016)

Except typical U minerals (see e.g. text below), the metal is present, in significant quantities, in a variety of silicate and oxide minerals (Burns and Finch, 1999), showing importance for the mining and metallurgical industry, namely zircon ($ZrSiO_4$), various REE-minerals, and Nb-oxides including columbite ($[(Fe,Mn)Nb_2O_6]$), samarskite ($(YFe^{3+}Fe^{2+}U,Th,Ca)_2(Nb,Ta)_2O_8$), fergusonite ($(Y,REE)NbO_4$) and pyrochlore-group phases such as betafite ($(Ca,U)_2(Ti,Nb,Ta)_2O_6(OH)$).

Besides, U is frequently associated to V in various geological formations. Among U-V geological materials in nature, uranyl vanadates constitute a group of significant minerals,

which are formed under acidic conditions ($\text{pH} < 7$) in various geological environments (Fig. 3).

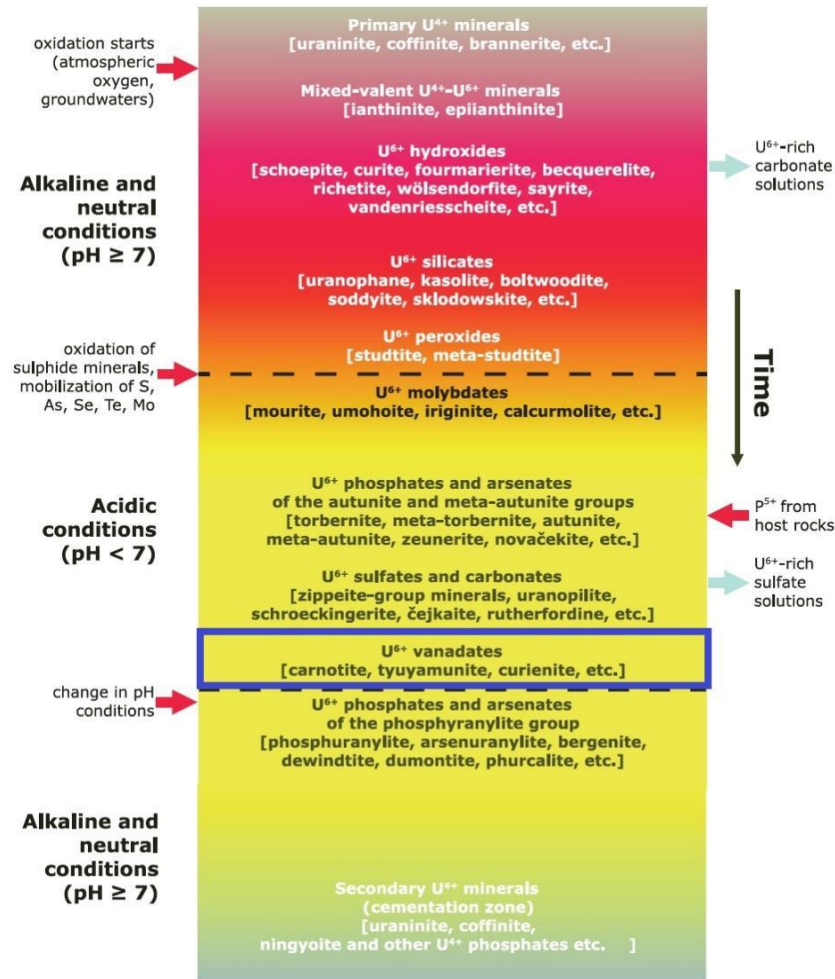


Fig. 3: Paragenetic sequence of U minerals in oxidation zones of U mineral deposits (Krivovichev and Plášil, 2013; Plášil, 2014).

Those minerals are a result of insoluble alteration products of supergene U-oxide minerals (e.g. Langmuir, 1978; Krivovichev and Plášil 2013; Plasil 2014), which are also significant U ore sources. Owing to their insolubility, they retain U in natural systems.

Uranyl vanadate minerals, such as carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) - tyuyamunite, ($Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O$) phases, precipitate when dilute UO_2^{2+} and VO_4^{3-} are present in aqueous systems (e.g. Weeks, 1961; Schindler et al., 2000). Since the late 20th century, at least twelve naturally occurring uranyl vanadates have been discovered on the Earth. Vanadium may occur in different oxidation states and form different mineral species (**Fig. 4**). It is evident that in higher oxidation state -where V forms vanadate anions- the coexistence with U is usual. However, commercial V mainly originates in Fe-ores (V-titanomagnetite) with typical deposits located in South Africa (Bushveld Igneous Complex) and also in Fennoscandia and Greenland. It should be noted that, although V in association with U exists usually as V^{5+} -anions (VO_4^{3-} / vanadates), in titanomagnetite has been found to exist in the form of V^{3+} - and V^{4+} -cations (Balan et al. 2006). Additional V deposits may also occur in other rock types, including shales (**Fig. 5**), where V may co-exist with U (Vind and Tamm 2021).




V^{3+}, V^{4+}	V-Titanomagnetite $V-Fe_{3-x}Ti_xO_4$	
V^{4+} - Vanadyl (VO^{2+})	Cavansite $Ca(VO)Si_4O_{10} \cdot 4(H_2O)$	
V^{5+} - Vanadate (VO_4^{3-})	Carnotite $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$	

Fig. 4: Oxidation states and typical vanadium minerals.

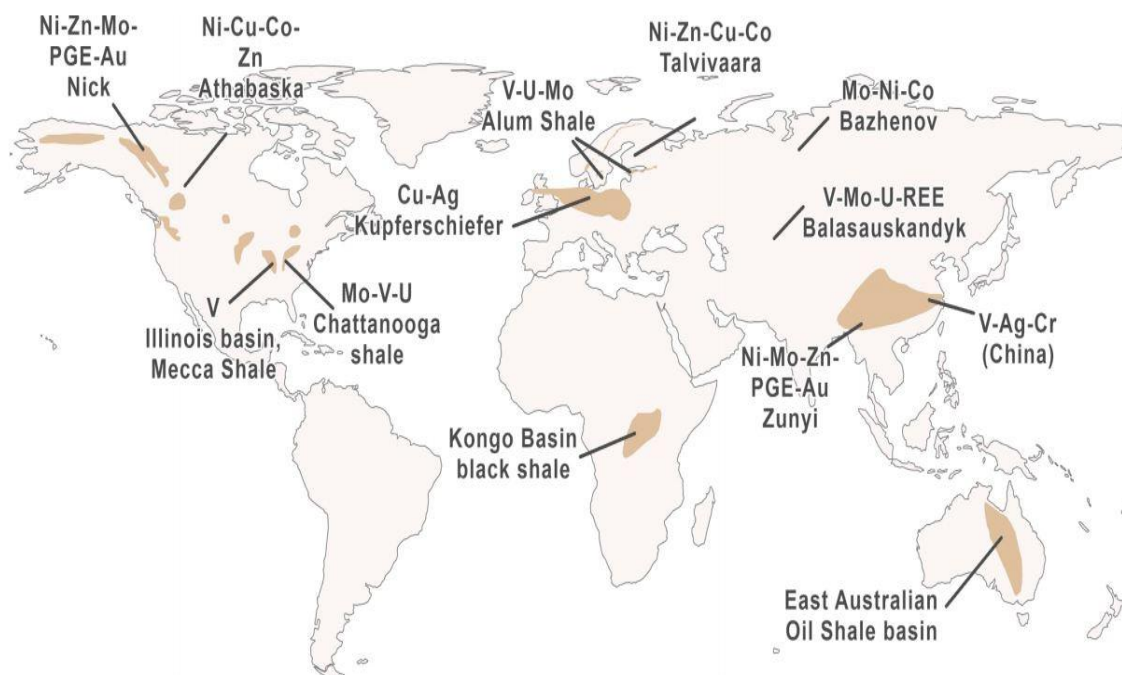


Fig. 5: Major black shale deposits; some contain V and U (Vind and Tamm, 2021)

So far, major U-V sedimentary deposits have been discovered in USA (Colorado Plateau region -around the mutual corners of Utah, Colorado, New Mexico, and Arizona states-, south Texas, and the Wyoming–South Dakota region; see Robb 2005), Australia (Bigrlyi Deposit, Ngalia Basin; see Schmid et. al. 2020) and a new one in Argentina (Ivana Property, Amarillo Grande Project; see **Fig. 6** and Edwards 2020).



Fig. 6: U-V mineralization at Ivana Property, Amarillo Grande Project, Argentina (<https://blueskyuranium.com/projects/rio-negro-province/amarillo-grande-project/photo-gallery/>)

Most of the major U-V deposits mentioned above have are sedimentary-hosted deposits, and the host rock is mainly sandstone (**Fig. 7**).

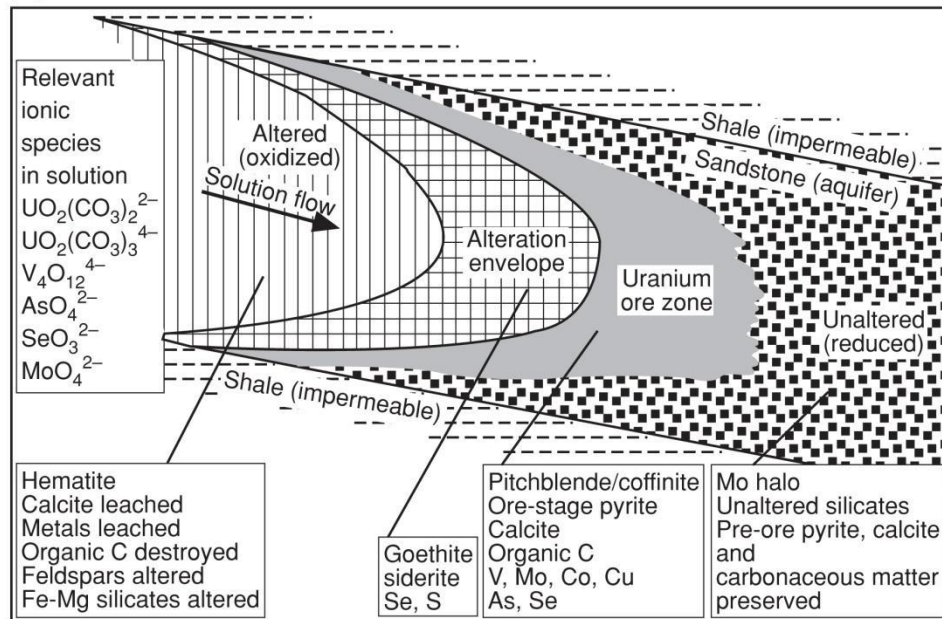


Fig. 7: Cross section through a typical roll front type sandstone-hosted U deposit, such as those in Wyoming, South Dakota, and south Texas / USA (Robb, 2005)

Apart from these features, there are some key differences, especially between the Colorado Plateau-type and Bigrlyi U-V deposits. According to Schmid et al. (2020), the Bigrlyi deposit mineralisation is associated with organic plant matter, unlike the Colorado Plateau deposits, which are associated with fluvial channels in arkosic to micaceous sandstones. Also, U-V mineralisation in Bigrlyi does not always occur together. Furthermore, the Colorado Plateau deposits, comprise hydrated oxides, uranyl vanadates (carnotite $(\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O})$ - tyuyamunite, $(\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5-8\text{H}_2\text{O})$ minerals), phyllosilicates and some rare minerals. Additionally, there are differences in the source of U. Uranium from the Colorado Plateau deposits, is associated with detrital (clastic) Fe-V clays and the source of V was hypersaline brines which strongly affected dolomite precipitation (Northrop and Goldhaber, 1990) whereas the Bigrlyi carbonate mineral was calcite.

The study of U-V geological materials and minerals started rising after 1970, with a first approach in 1976, regarding spectroscopic study of the structure of synthetic carnotite (Fig. 8).

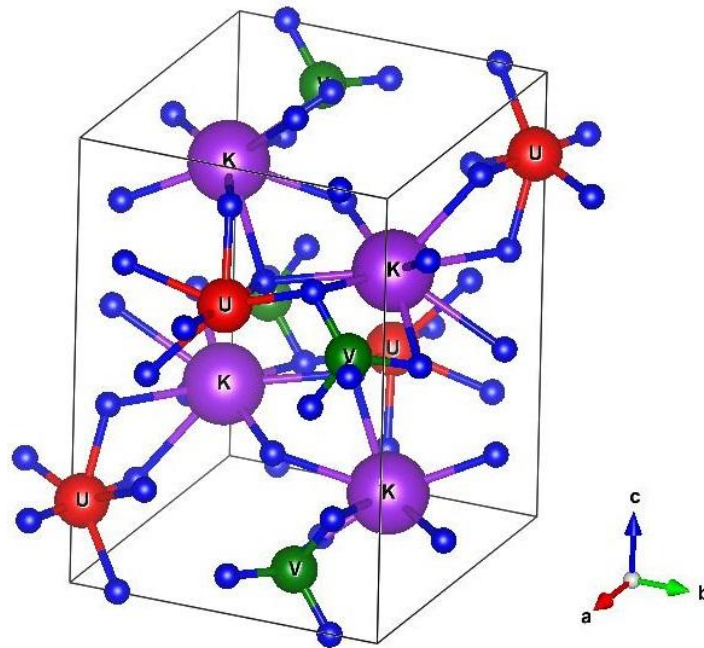


Fig. 8: Crystal structure of carnotite-type phases
(<http://rruff.geo.arizona.edu/AMS/amcsd.php>)

Particularly Baran and Botto (1976) studied, by both infrared (IR) and Raman spectroscopy, stretching vibrations of uranyls and vanadates. Later on, Frost et al. (2005) gave to science the advantage of characterising various natural uranyl vanadates with Raman spectroscopy.

Since 2000s, U-V geochemistry, has played again a significant role in U-V ore deposits and will continue to, because both U and V are needed in the industries of energy and metallurgy. Geochemistry, combined with geophysics and all the technological

advances nowadays are making potential ore deposit discoveries much easier. The scope of this Bsc Thesis was, firstly, to review the mineralogy and geochemistry of U-V geological materials. Secondly, a typical sample of U-V mineralization (mainly carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) - tyuyamunite, ($Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O$) minerals), occurring in sedimentary rocks of Fall River County, South Dakota (USA), has been characterized using diffraction (PXRD), micro-analytical (SEM-EDS), spectroscopic (FTIR) and bulk analytical (ICP-MS) techniques.

2. Materials and Methods

2.1. Samples

The U-V geological material studied, concerns a sample of carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) - tyuyamunite, ($Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O$) minerals, scattered in sandstone matrix, originating in the Fall River, Dakota, USA (Kithil and Davis, 1917; Baker at al. 1952; Bell and Bales, 1954; Bell and Bales, 1955; see **Fig. 9** and **Fig. 10**). According to the U.S.G.S. reports, the most important uranyl - vanadate deposits occur between Craven and Coal Canyon, which are crossed by the Fall River. The geology of Craven Canyon is a repeated stratigraphy of sandstone, shale and mudstone. Carnotite deposits in the Craven Canyon are in the lower parts of Lakota formation and especially in thinly bedded (laminated) sandstone and shale/mudstone, as well as in cracks in sandstone lenses. Those deposits are associated with iron and fossil plants in the sandstone.

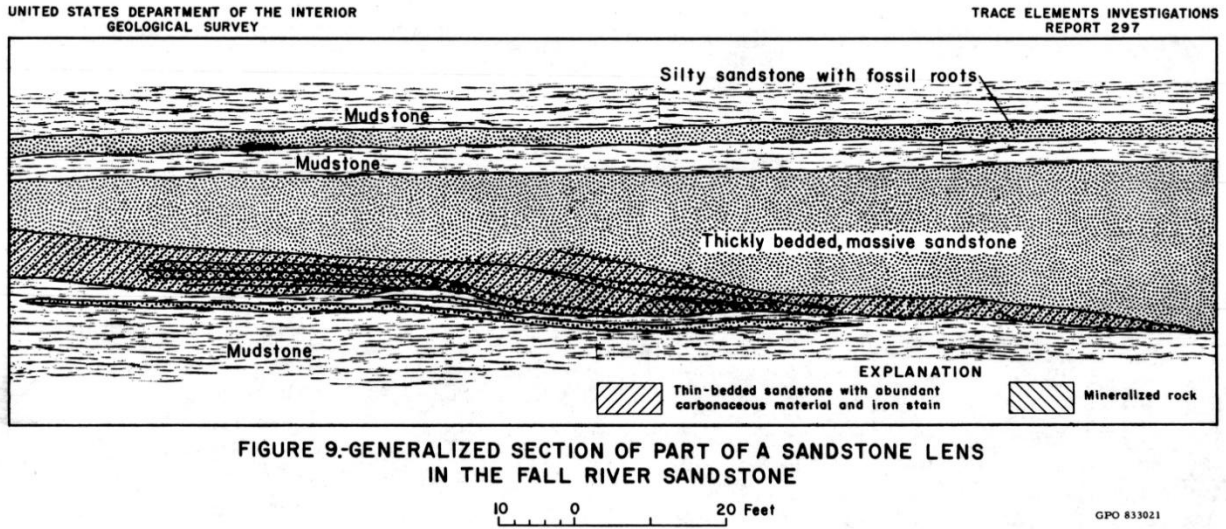


Fig. 9: Generalised section of part of a sandstone lens in Fall River sandstone (Bell and Bales, 1954).

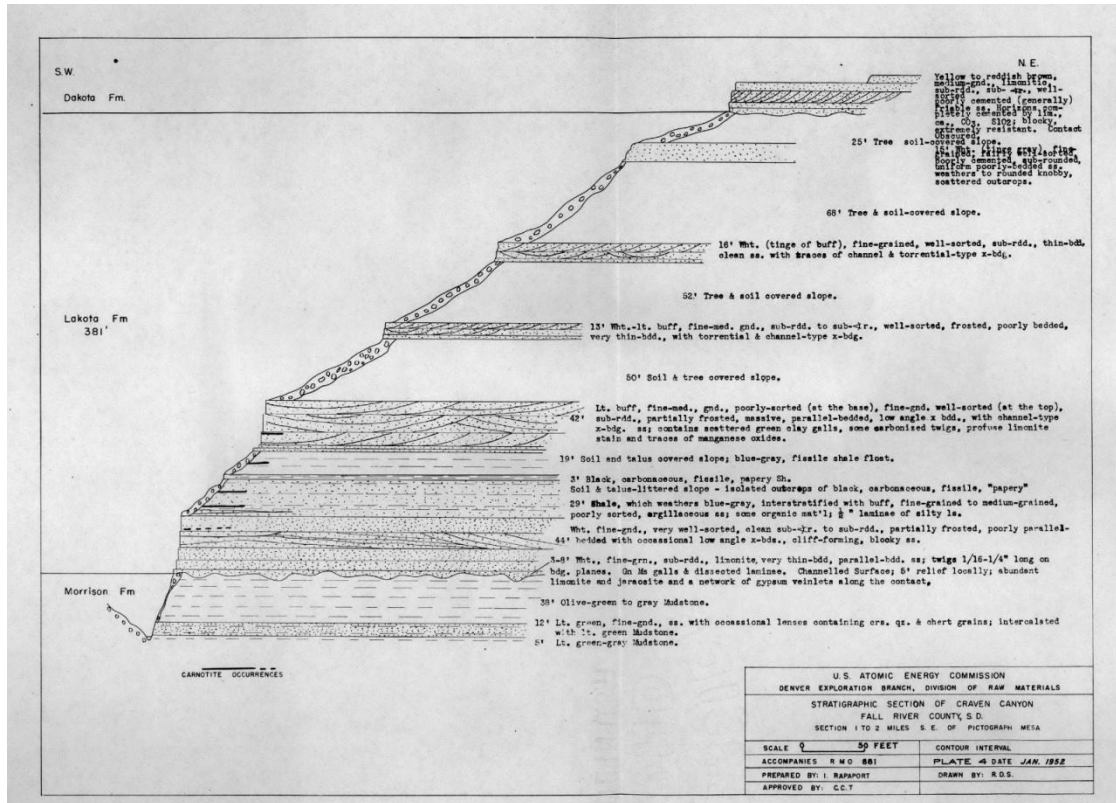


Fig 10: Stratigraphy of Craven Canyon indicating carnotite occurrences (Baker at al. 1952).

2.2. PXRD

The powder X-ray Diffraction (PXRD) study was performed using a Siemens D5005 –now Bruker AXS- diffractometer, $\text{CuK}\alpha$ radiation at 40 kV and 40 mA (**Fig. 11**). The evaluation of the diffractograms was carried out using the EVA 10.0 program of the Bruker DIFFRACplus software package and the MATCH! (Crystal Impact) software.

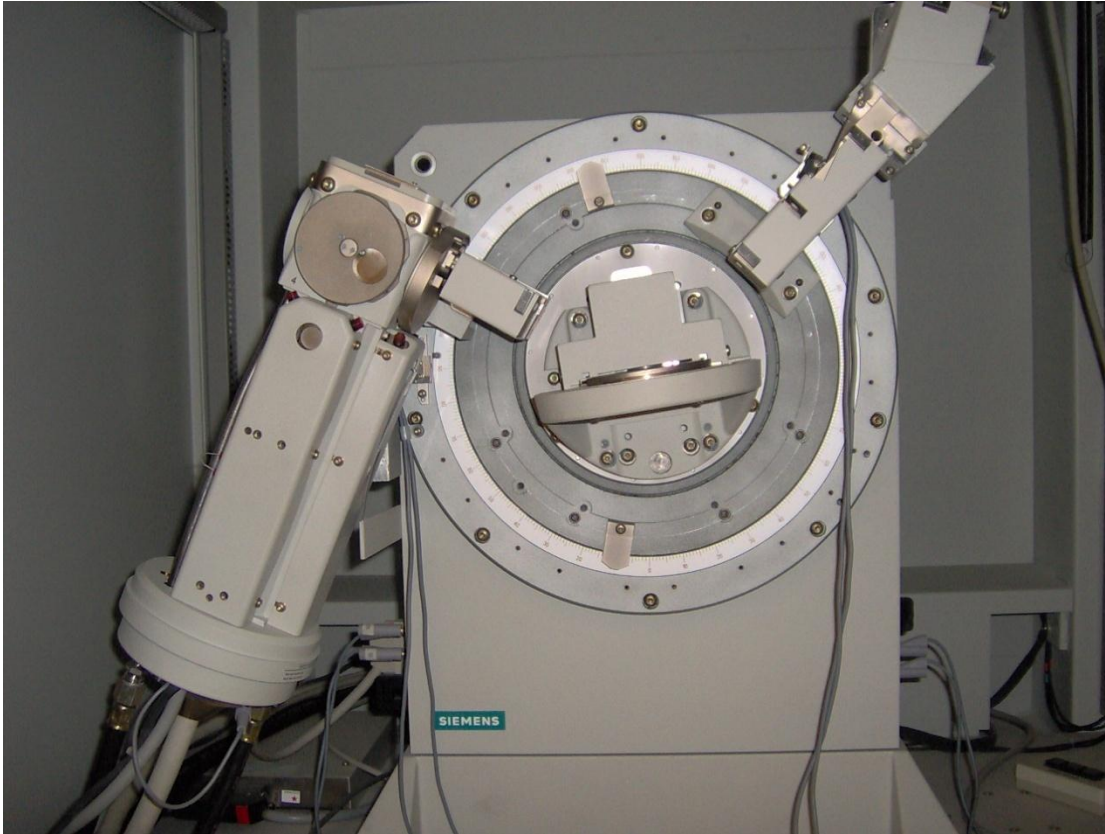


Fig. 11: A typical PXRD system

2.3. SEM-EDS

The Scanning Electron Microscopic study and the corresponding Energy Dispersive microanalyses (SEM-EDS) were performed using a Jeol JSM-5600 equipped with an Oxford EDS (Fig. 12).

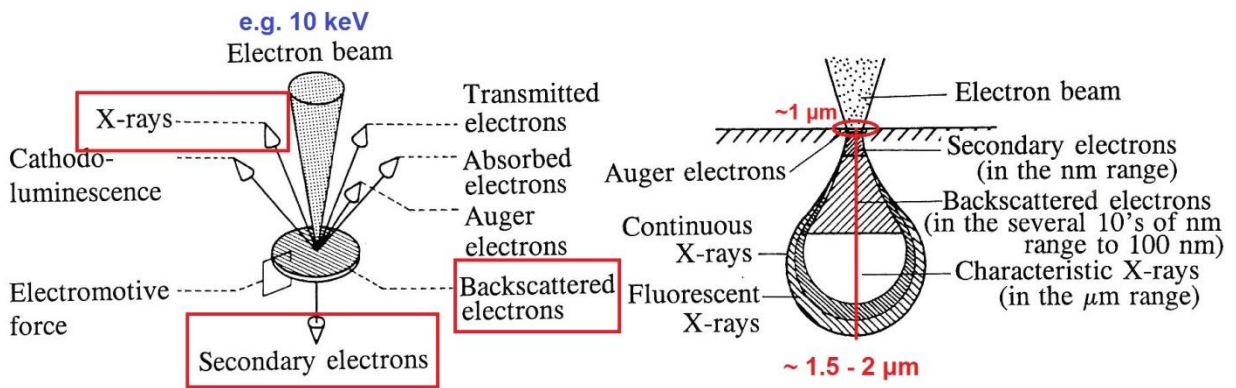
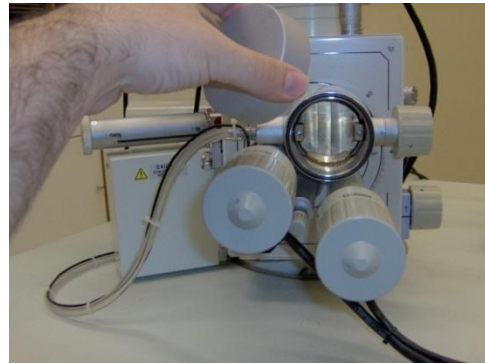
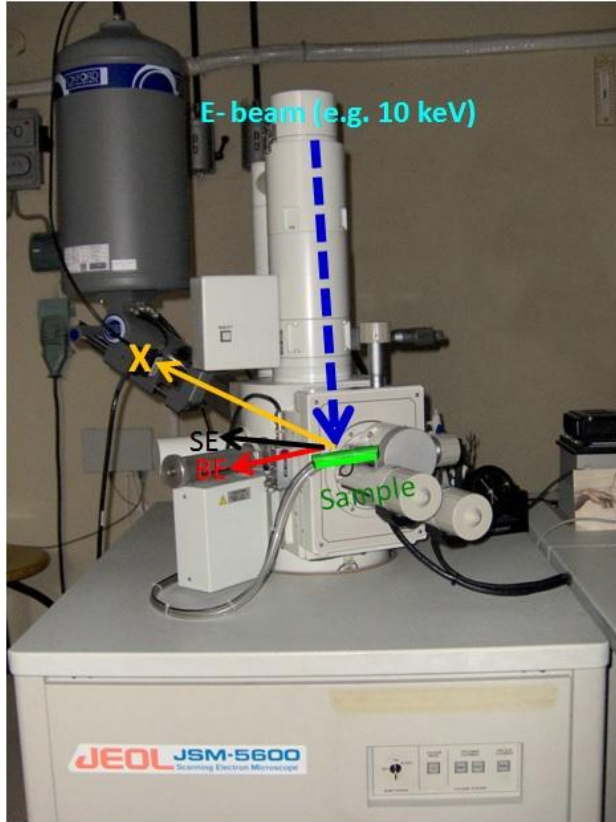


Fig. 12: A typical SEM-EDS system

2.4. FTIR

The Fourier-Transform Infrared (FTIR) measurements were carried out using a Perkin Elmer Spectrum One spectrophotometer (**Fig. 13**). This method is based on the absorption of infrared-light by the molecules of the sample. The masses of the atoms, the shape of the molecular potential energy surfaces and the associated vibronic coupling affect the energies absorbed. The frequencies of the vibrations are associated with a particular mode of motion and a particular bond type. In order for the absorption to occur the frequency of the IR must be the same as the vibrational frequency of a bond or a collection of bonds. The measurement of how much energy was absorbed at each wavelength can be done using a Fourier transform instrument and the generation of a transmittance or absorbance spectrum using a dedicated procedure. The nature of the chemical bonds by which the protons are connected to adjoining atoms determines the proton vibrations. The characteristic wavenumbers in an IR spectrum identifies the vibrations of ions, including uranyls and vanadates (e.g. Ross 1972; Nakamoto 1986).



Fig. 13: A typical FTIR spectrophotometer

2.5. ICP-MS

Bulk analyses for trace elements were performed using a Perkin Elmer Sciex Elan 9000 ICP-MS following a $\text{LiBO}_2/\text{LiB}_4\text{O}_7$ fusion and HNO_3 digestion. The chemical composition of the investigated sedimentary rock was qualified by strict QA/QC procedures including, of course, three analytical replicates. Blanks (analytical and method), duplicates and standard geological and synthetic reference materials provided a measure of background noise, accuracy and precision.

3. Results and Discussion

3.1. Bulk mineralogy (PXRD)

The PXRD results, showing the bulk mineralogy of the studied U-V geological material from S. Dakota (USA), is presented in **Fig. 14**.

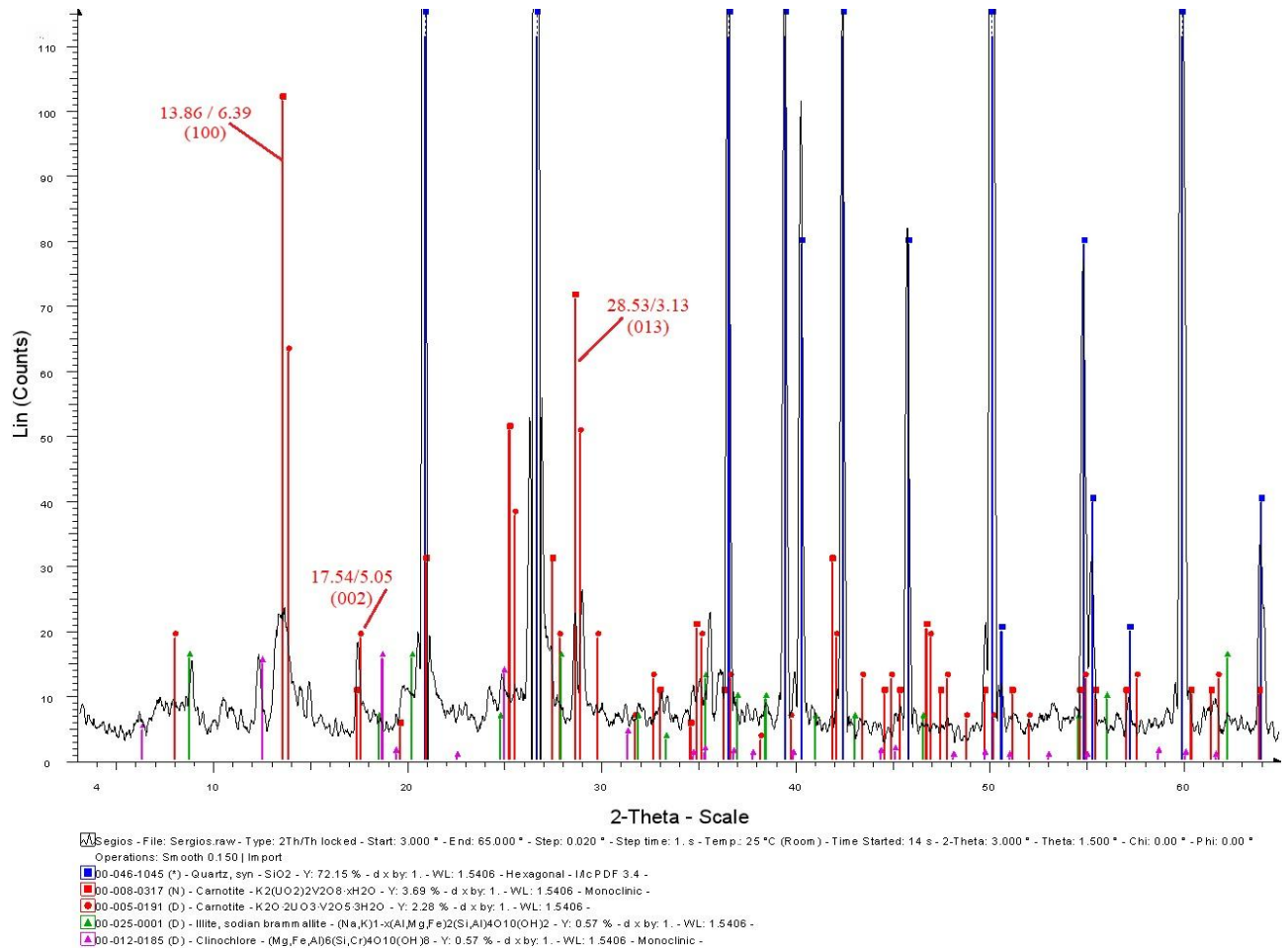


Fig. 14: PXRD pattern of the studied U-V-bearing sedimentary rock

According to the results, the sample contains mostly quartz (because it is actually sandstone) and phyllosilicates (chlorite and clays), whereas there are also traces of carnotite-group minerals ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) - ($Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O$). The main XRD peaks of carnotite-type phases are shown in **Table 1**.

Table 1: XRD peaks of carnotite (Sundberg and Sillen, 1949).

Carnotite

Sundberg I, Sillen L G
 Arkiv for Kemi 1 (1949) 337-351
 On the crystal structure of KUO_2VO_4 (synthetic anhydrous carnotite)
 Locality: synthetic
database_code_amcsd 0012038

CELL PARAMETERS: 6.5900 8.4030 10.4300 90.000 104.200 90.000
 SPACE GROUP: P2₁/c
 X-RAY WAVELENGTH: 1.541838
 Cell Volume: 559.922
 Density (g/cm³): 5.030
 MAX. ABS. INTENSITY / VOLUME**2: 129.6087459
 RIR: 8.390
 RIR based on corundum from Acta Crystallographica A38 (1982) 733-739

2-THETA	INTENSITY	D-SPACING	H	K	L	Multiplicity
13.70	10.14	6.4626	0	1	1	4
13.86	100.00	6.3886	1	0	0	2
17.44	2.31	5.0857	1	1	0	4
17.54	20.50	5.0557	0	0	2	2
17.93	5.91	4.9478	-1	1	1	4
19.54	18.73	4.5438	-1	0	2	2
20.50	4.23	4.3320	0	1	2	4
21.03	7.55	4.2243	1	1	1	4
21.15	17.86	4.2015	0	2	0	2
22.92	10.62	3.8799	0	2	1	4
25.00	2.78	3.5620	1	0	2	2
25.37	31.51	3.5104	1	2	0	4
25.72	8.99	3.4640	-1	2	1	4
27.19	1.62	3.2795	1	1	2	4
27.61	13.43	3.2313	0	2	2	4
27.93	16.83	3.1943	2	0	0	2
28.01	1.72	3.1858	1	2	1	4
28.53	31.42	3.1282	0	1	3	4

28.78	17.27	3.1022	-1	1	3	4
28.94	17.03	3.0848	-1	2	2	4
29.18	11.86	3.0607	-2	0	2	2
29.18	1.21	3.0606	-2	1	1	4
29.93	3.68	2.9859	2	1	0	4
32.97	8.76	2.7170	1	2	2	4
33.18	5.29	2.7004	2	1	1	4
33.19	3.85	2.6993	0	3	1	4
34.65	1.97	2.5885	-2	2	1	4
34.68	12.52	2.5865	1	1	3	4
35.24	2.03	2.5470	-1	3	1	4
35.29	6.17	2.5431	-2	1	3	4
35.30	5.45	2.5429	2	2	0	4
36.31	2.35	2.4739	-2	2	2	4
36.47	1.78	2.4635	-1	1	4	4
36.68	3.53	2.4501	0	3	2	4
36.78	1.06	2.4433	2	0	2	2
36.99	3.99	2.4301	1	3	1	4
41.79	3.27	2.1614	-3	0	2	2
41.94	9.11	2.1542	0	3	3	4
42.11	10.05	2.1457	-1	3	3	4
42.45	3.02	2.1295	3	0	0	2
42.81	4.50	2.1121	2	2	2	4
42.95	1.00	2.1060	2	3	0	4
43.06	5.13	2.1007	0	4	0	2
43.81	1.36	2.0663	-2	3	2	4
44.03	3.08	2.0568	0	4	1	4
44.88	11.93	2.0194	-1	1	5	4
44.94	6.76	2.0172	2	1	3	4
45.39	2.95	1.9983	2	3	1	4
45.45	2.52	1.9956	1	4	0	4
45.66	2.06	1.9870	-1	4	1	4
45.76	5.34	1.9828	-3	1	3	4
46.17	7.87	1.9661	0	1	5	4
46.56	2.45	1.9508	1	3	3	4
46.83	3.00	1.9399	0	4	2	4
46.97	3.21	1.9344	3	1	1	4
47.04	6.40	1.9319	-2	3	3	4
47.09	1.70	1.9300	1	4	1	4
47.30	3.99	1.9220	-3	2	2	4
47.69	1.44	1.9068	-1	4	2	4
47.89	10.21	1.8995	3	2	0	4
47.97	1.28	1.8963	-1	3	4	4
48.22	5.34	1.8873	-2	1	5	4
48.51	3.00	1.8766	0	3	4	4
49.50	1.26	1.8413	2	3	2	4
50.43	1.64	1.8095	1	4	2	4
51.66	1.00	1.7695	3	1	2	4
51.81	2.87	1.7646	1	1	5	4
51.81	1.39	1.7645	-2	3	4	4
52.11	3.23	1.7552	2	4	0	4

52.86	1.74	1.7320	-2	4	2	4
54.23	1.83	1.6913	2	4	1	4
54.45	1.10	1.6852	0	0	6	2
54.98	1.90	1.6701	-1	3	5	4
55.02	1.12	1.6690	-2	0	6	2
55.03	1.01	1.6688	2	3	3	4
55.54	2.93	1.6546	-3	1	5	4
55.74	4.05	1.6493	-3	3	3	4
55.96	3.02	1.6431	-4	0	2	2
56.09	1.19	1.6396	0	3	5	4
56.79	1.35	1.6211	3	3	1	4
57.37	2.86	1.6060	-1	2	6	4
57.64	5.08	1.5991	3	1	3	4
57.88	1.37	1.5931	-2	3	5	4
58.56	1.49	1.5762	-1	5	2	4
58.61	2.27	1.5751	-4	1	3	4
59.06	1.92	1.5641	0	2	6	4
60.50	1.31	1.5303	-4	2	2	4
60.94	1.79	1.5203	2	1	5	4
60.96	1.81	1.5199	1	5	2	4
61.67	1.24	1.5040	0	5	3	4
62.00	1.64	1.4968	4	1	1	4
62.06	1.45	1.4955	3	4	0	4
62.18	2.73	1.4929	4	2	0	4
64.46	1.70	1.4455	-3	3	5	4
64.48	2.23	1.4451	1	2	6	4
64.54	1.16	1.4439	3	4	1	4
65.27	1.22	1.4295	1	5	3	4
65.98	2.21	1.4159	-4	1	5	4
66.39	1.09	1.4081	3	3	3	4
66.41	1.69	1.4077	-1	5	4	4
67.28	1.35	1.3916	-4	3	3	4
67.52	1.34	1.3873	0	6	1	4
68.60	1.26	1.3680	1	6	0	4
68.76	1.18	1.3652	-1	6	1	4
71.81	1.09	1.3145	0	4	6	4
72.27	1.04	1.3073	-1	5	5	4
72.29	1.72	1.3071	4	1	3	4
72.31	1.14	1.3067	2	5	3	4
73.12	1.02	1.2943	-4	4	2	4
73.18	1.08	1.2932	2	2	6	4
74.19	1.95	1.2782	-4	3	5	4
74.65	1.11	1.2714	4	4	0	4
75.62	1.25	1.2575	-5	2	2	4
76.15	1.63	1.2501	-3	5	4	4
76.60	1.67	1.2438	-1	2	8	4
77.49	1.33	1.2317	-2	2	8	4
78.19	1.03	1.2225	5	2	0	4
81.77	1.30	1.1778	-3	2	8	4
86.82	1.05	1.1218	-5	3	5	4

3.2 Microscopic study (SEM-EDS)

The SEM-EDS results, showing natural uranyl vanadate microcrystals, together with their composition, in the studied U-V geological material from S. Dakota (USA), are presented in **Fig. 15** and **Fig.16**. The results are in agreement with the literature concerning carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$) - tyuyamunite, ($Ca(UO_2)_2(VO_4)_2 \cdot 5-8H_2O$) minerals.



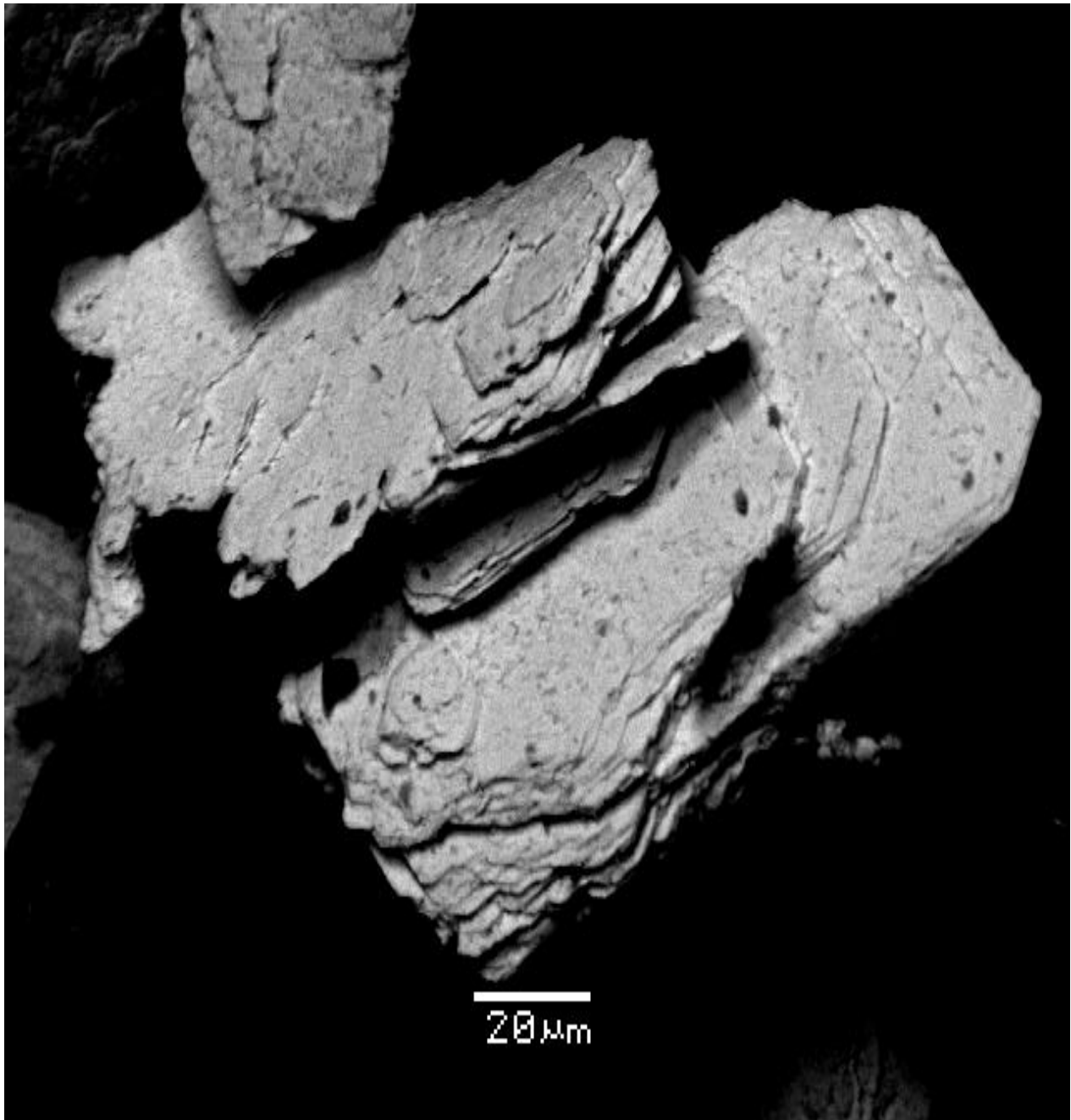




Fig. 15: SEM-EDS images concerning carnotite-group mineral microcrystals into the sedimentary rock.

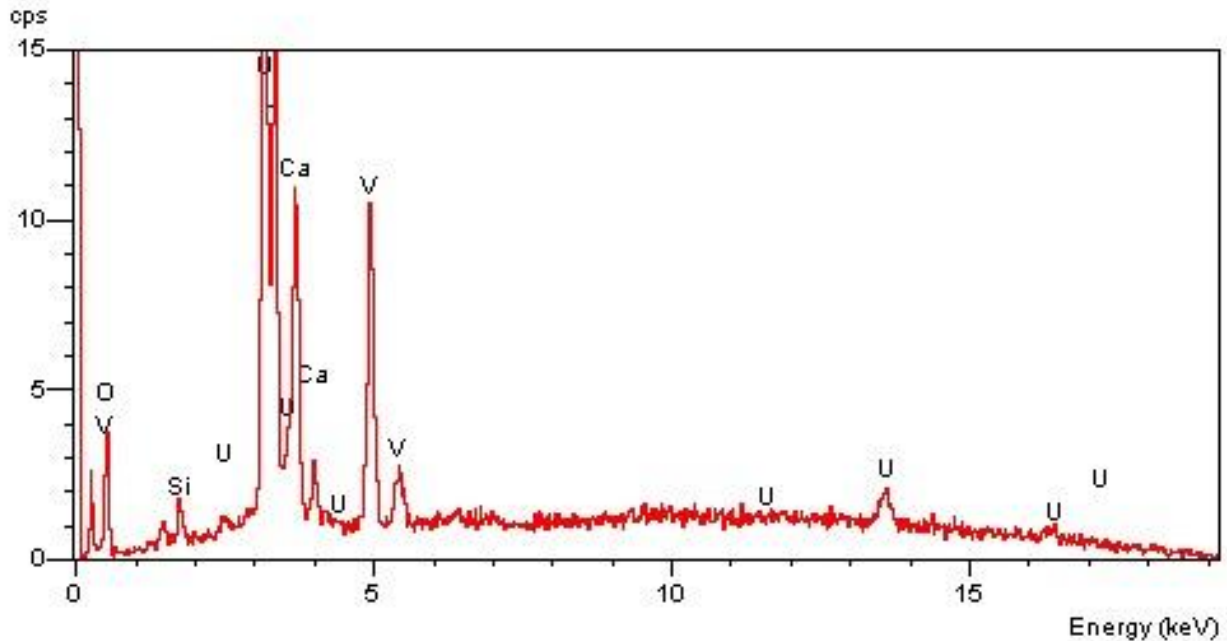


Fig. 16: EDS spectrum concerning carnotite-group mineral microcrystals into the sedimentary rock.

3.3. Spectroscopy (FTIR)

As proven, carnotite-group minerals can be traced by both PXRD and SEM-EDS, apparently. On the other hand, when these phases occur in sedimentary rocks, is difficult to be identified via FTIR method. With this technique, we can record the bond interactions (stretching vibrations) between the atoms of the elements in solid materials. According to Frost et al. (2005), uranyl cations (UO_2^{2+}), respond to an intense band ranging from 800 to 824 cm^{-1} . Another intense band, corresponding to vanadate (VO_4^{3-}) stretching vibrations, is within the range 965 to 985 cm^{-1} . Furthermore, according to a significantly older study

(Baran and Botto, 1976), uranyles respond to 740 cm^{-1} . Taking this fact into account, we can determine the borders of uranyl stretch vibrations of carnotite-group minerals from 740 to 824 cm^{-1} . Finally, it is worth stating that although FTIR spectroscopy is rather low-cost and gives faster results compared to PXRD, it is more difficult to trace uranyl vanadates dispersed into sandstone (Fig. 17).

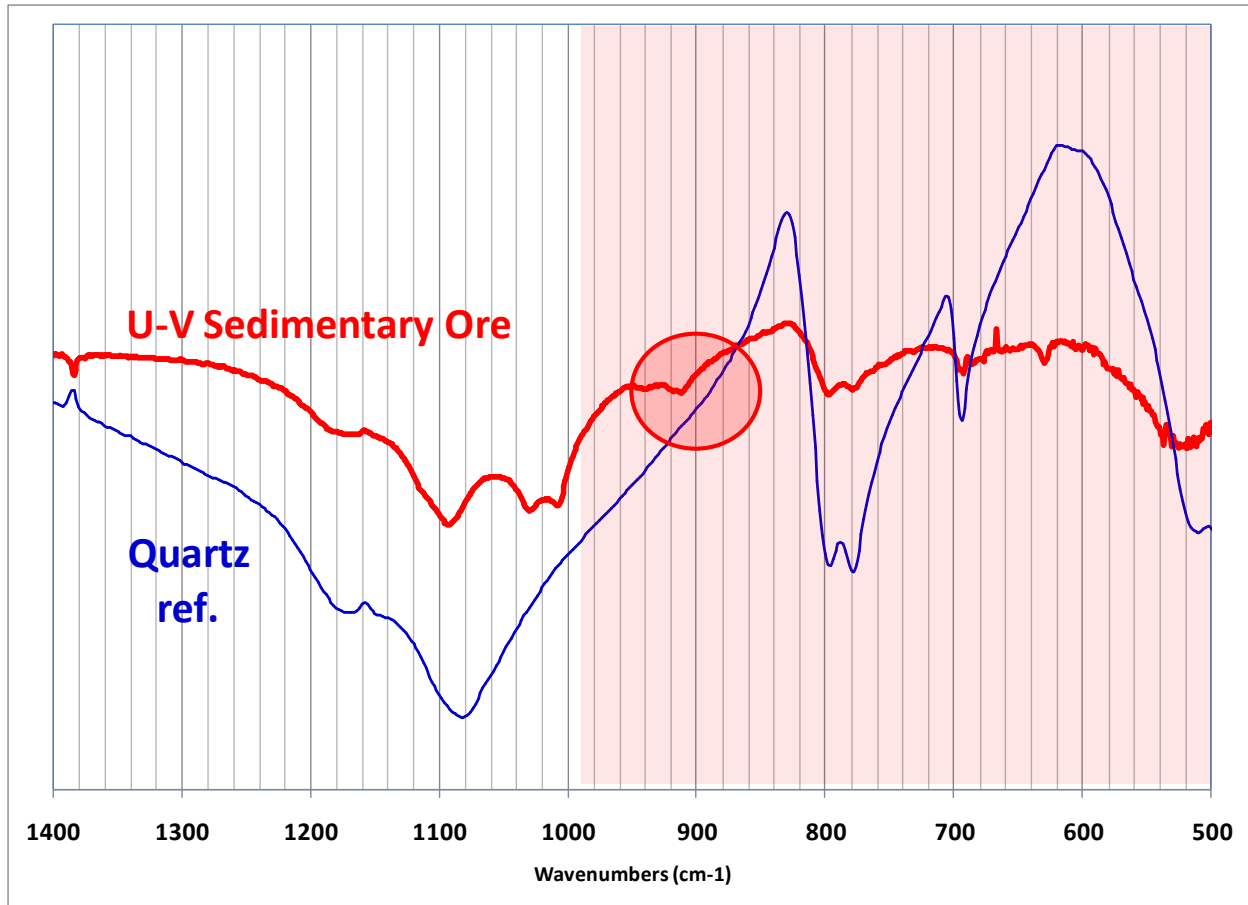


Fig. 17: FTIR spectrum concerning the studied U-V sedimentary rock.

3.4. Bulk geochemistry and REE

The bulk analytical results, concerning trace elements and REE in the studied U-V sedimentary rock, are presented in **Table 2** and **Fig. 18** and **Fig. 19**. According to the results, the studied geological material contains various trace elements without surprising concentrations, close to typical Upper Continental Crust (UCC). Regarding REE geochemical anomalies, it is evident that the material shows a significant negative Eu (Eu/Eu*) anomaly, with a pattern also close to that of UCC.

Table 2: Trace element content of the studied U-V sedimentary rock

TRACE ELEMENTS	ppm	TRACE ELEMENTS	ppm
Zr	320.9	W	1
Ba	71	Be	0.5
Ni	36	Ta	0.4
Sr	17.5	Se	0.25
Rb	11.6	Cs	0.2
Hf	8	Mo	0.2
Zn	6	Hg	0.06
Nb	5.5	Cd	0.05
As	4.1	Sb	0.05
Co	3	Bi	0.05
Pb	2.8	Ag	0.05
Cu	2.6	Tl	0.05
Th	2.3	Au	0.0011
Ga	1.5		
Sn	1		

REE + Y	ppm
La	9.8
Ce	19.5
Pr	2.13
Nd	8.1
Sm	1.42
Eu	0.26
Gd	1.37
Tb	0.24
Dy	1.58
Ho	0.34
Er	1.15
Tm	0.18
Yb	1.12
Lu	0.18
Y	9.8

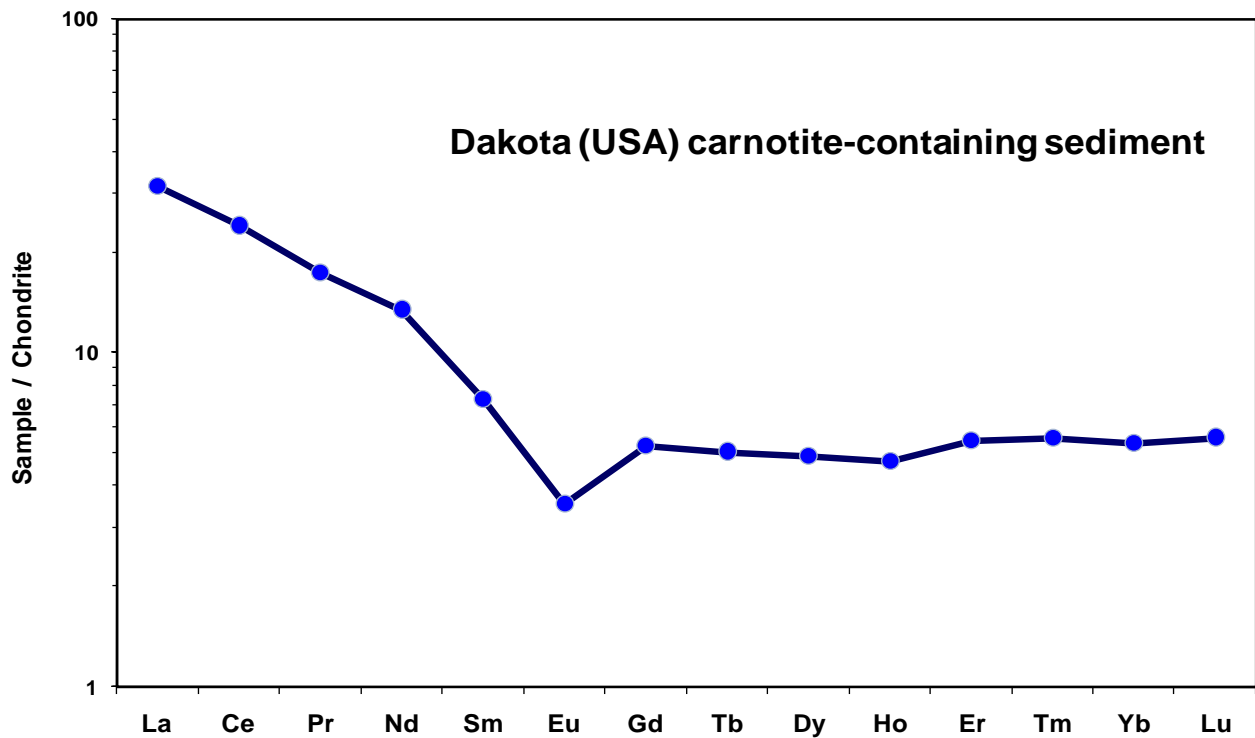


Fig. 18: Chondrite-normalized (McDonough and Sun, 1995) REE pattern for the studied U-V (carnotite)-containing sedimentary rock

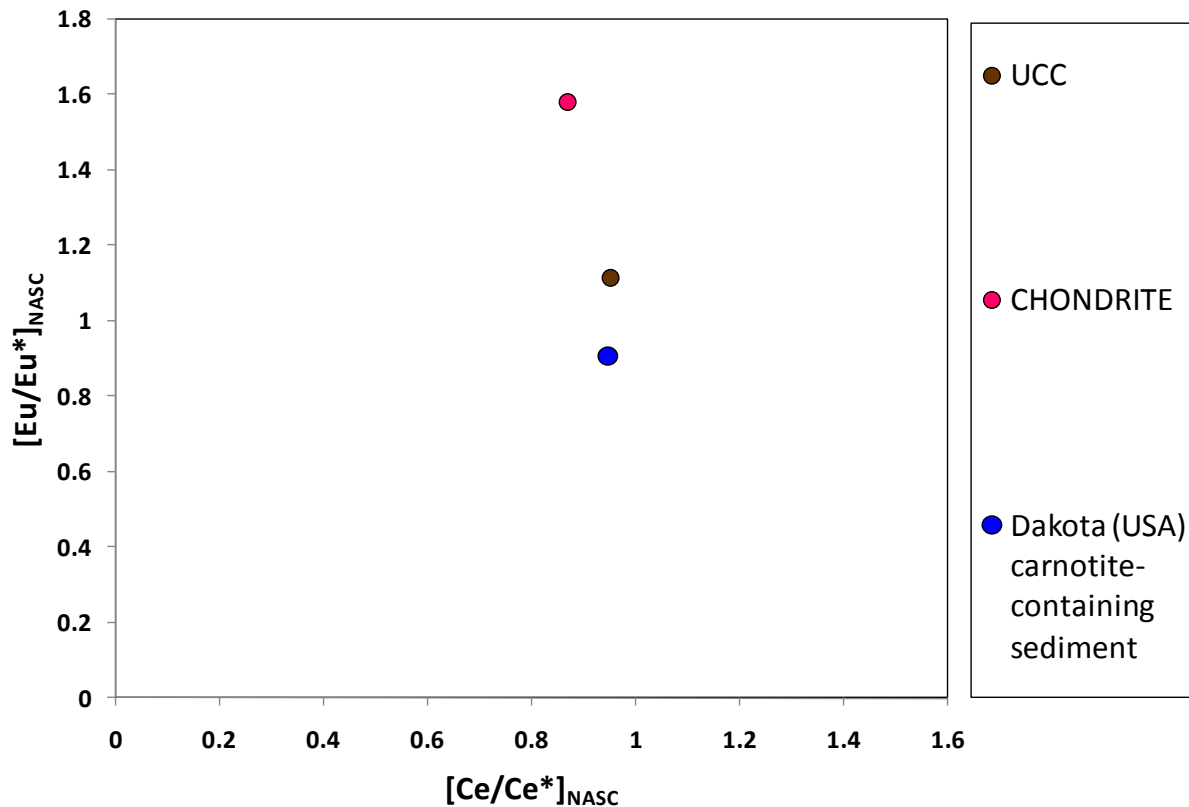


Fig. 19: Binary correlation diagram of Eu vs. Ce anomalies (normalized to NASC; Gromet et al., 1984) for the studied U-V (carnotite)-containing sedimentary rock. Europium anomalies calculated as: $Eu/Eu^* = 2(Eu/Eu_{NASC}) / \{(Sm/Sm_{NASC}) + (Gd/Gd_{NASC})\}$ from Liu et al. (2013). Cerium anomalies calculated as: $Ce/Ce^* = 3(Ce/Ce_{NASC}) / \{(2 La/La_{NASC}) + (Nd/Nd_{NASC})\}$ after German and Elderfield (1990).

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