

Uranium Minerals in the Radlovac Series Metasediments at Mt. Papuk, Croatia

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Abstract

Applying a combination of different methods – X-ray diffraction, scanning electron microscopy, gamma-spectroscopy and X-ray spectroscopy, a suite of uranium minerals, meta-torbernite, meta-uranospinite and meta-zeunerite was identified in metasediments of the Radlovac series at the Mt. Papuk area, Croatia. The accessory minerals galena, zircon, rutile, chalcopyrite and cuprite, as well as an unidentified Ni-bearing phase are also present.

The mineral assemblage indicates a sequence of epigenetic and supergene processes affecting the Radlovac series.

1. INTRODUCTION

From the early 1960's to the late 80's, extensive exploration for uranium ore took place in the former Yugoslavia, including Croatia (BRAUN, 1984). Prospecting activities by the Croatian Geological Survey identified several locations in the Slavonian Mts. (Croatia) with an increased level of radioactivity (BRAUN et al., 1983), particularly in the area of Mts. Psunj and Papuk. The Carbon age of the metasediments of Radlovac creek – known as the Radlovac series – has been determined from the fossil flora (BRKIĆ et al., 1974). The position of this series, which includes rocks with higher background radioactivity, is shown in Fig. 1.

The tectonic setting and structural fabric of these and associated rocks have been described by JAMIČIĆ (1976, 1979).

The Radlovac series is a metachist formation, and an increased level of radioactivity has been identified in

several, apparently unrelated locations. This is also true for deeper strata (samples from the prospecting boreholes). A detailed synthesis of this research was given by JURKOVIĆ (2003).

In 1984 the Institute of Mineralogy and Petrology of the Faculty of Sciences in Zagreb attempted X-ray diffraction analysis of the uranium-bearing minerals in the Radlovac metachists. Due to the complex mineralogical structure of the rocks, the separation methods available at that time (magnetic separation, granulometry, high-density liquids) did not yield satisfactory results, and the minerals responsible for the increased radioactivity were not unambiguously identified, even though both the light and heavy mineral fractions as well as composite rock samples were analyzed. However, it was inferred that the activity was due to the presence of uranyl arsenates of calcium, copper, iron or barium (ŠČAVNIČAR, 1984³). Therefore, the aim of the present study is to determine the uranium-bearing minerals of those samples, using contemporary and state-of-the-art XRD, EDXRF, SEM with EDX spectrometer and gamma spectrometric methods.

2. MATERIALS AND METHODS

Some of the original samples, which were analysed in 1984, were still available to the authors. These samples (which show the strongest background activities) were taken from low-grade metamorphosed sedimentary rocks of the Radlovac series in Mt. Papuk, which crops out near the Ninkovac creek. The host rock has a schistlike structure and contains muscovite, quartz, pyrophyllite, chlorite, albite, microcline, chloritoid, and, occasionally, calcite and dolomite. This mineral assemblage indicates a sequence of low-grade metamorphism. Uranium, originating from the surrounding weathering zones, was deposited in the form of U-oxysalts in these rocks.

The radioactivity of the analyzed samples was determined by gamma spectrometry. Prior to gamma-

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³ ŠČAVNIČAR, S. (1984): Rentgenografska analiza mineralnog sastava radioaktivnih uzoraka stijena iz Slavonije.– Unpubl. report, Archive of the Croatian Geological Survey.

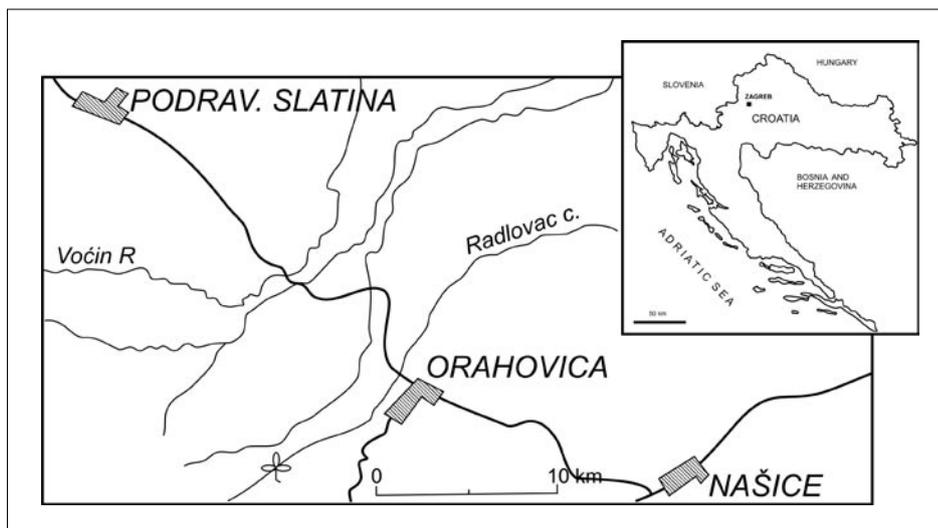


Fig. 1 Location map of the Radlovac series in the Mt. Papuk area.

spectrometry measurements, samples were placed into counting vessels of known geometry, sealed and stored for at least 4 weeks to allow ingrowth of gaseous ^{222}Rn (half-life of 3.8 days) and its short-lived decay products to equilibrate with the long-lived ^{226}Ra precursor in the sample. At the end of the ingrowth period, samples were counted on an InInspector gamma spectrometer ('Canberra' portable HPGe detector coupled with a 8192 channel analyser). The system was calibrated using standard reference materials supplied by the International Atomic Energy Agency (stream sediments IAEA-306, IAEA-313 and IAEA-314). Counting time was 80,000 seconds and recorded spectra were analyzed using the Canberra GENIE 2K software. The activities of ^{40}K were calculated from the 1460.75 keV-peak. Activities of ^{226}Ra were calculated from the 609.4 keV peak of its ^{214}Bi progeny as well as ^{228}Ra activities from 911.1 keV-peak of its ^{228}Ac progeny. Activities of ^{235}U were calculated from 186 keV peak (after subtraction of the overlapping ^{226}Ra peak, which was calculated previously from ^{214}Bi). Activities of ^{238}U were calculated from the ^{235}U activities assuming the $^{235}\text{U}/^{238}\text{U}$ activity ratio of 0.0460. This procedure was detailed by BARIŠIĆ (1989). ^{40}K activity of 309.3 Bq/kg corresponds to 1% of total potassium, ^{238}U activity of 12.44 Bq/kg corresponds to 1 ppm of uranium, while the ^{232}Th activity of 4.06 Bq/kg corresponds to 1 ppm of thorium (BARIŠIĆ, 1996).

Samples with the highest activities were used for XRD investigations. The diffraction patterns of all samples were collected on a Philips 'Xpert diffractometer using $\text{CuK}\alpha$ radiation. Powder diffraction data were collected in the range of $4\text{--}63^\circ 2\theta$, and a step size of 0.02° . The obtained d -spacings and relative intensities of the patterns obtained were compared with reference values (JCPDS 01-077-0124, 01-086-1787, 00-018-0309). The diffractograms were analyzed using the Philips proprietary computer code enabling a precise pattern analysis and the identification of very weak diffraction peaks.

For elemental analysis, each sample was disaggregated in an agate mortar, pressed into pellets and measured by energy dispersive X-ray fluorescence method (EDXRF; OREŠČANIN et al., 2006, 2007). Samples were irradiated by X-rays generated from a ^{109}Cd annular source. The incident angle was 50° . Detection of the characteristic X-ray radiation from the sample was done with a liquid-N cooled Si(Li) detector (Canberra) with the following characteristics: detector size = 30 mm^2 , Si thickness = 3 mm, Be window = $25\text{ }\mu\text{m}$, FWHM for 5.9 keV ^{55}Fe 165 eV, the emerging angle was 74° , and the distance was 1.5 cm. Spectra were collected by Genie – 2000 software (Canberra, Meriden, CT, USA). Collecting time was 10,000 s. Spectral data were analyzed by Canberra's WinAxil software. Elemental concentrations in the thick targets were calculated using the 'Fundamental parameters' method from the WinFund package, with IAEA SRM SL-1 and SOIL 7 as the standards. The concentration (w_i) of each element (i) was calculated according to the following formula:

$$w_i = N_{ij} / (K_{ij} D_{ij} F P_{ij} A_{ij,m} H_{ij,m} I i_0 t),$$

where N_{ij} is the net peak area of the characteristic X-ray line j ; K_{ij} – calibration constant calculated on the basis of the standard reference material; D_{ij} – detector efficiency at E_{ij} energy; $F P_{ij}$ – number of fundamental parameters; $A_{ij,m}$ – attenuation of the X-rays due to matrix (m); $H_{ij,m}$ – enhancement of the X-rays due to the matrix (m); I – intensity distribution of the characteristic lines and of the continuum in the excitation; i_0 – factor taking into account the overall intensity of the source (the activity of the radio isotope); t – measurement time.

Scanning electron microscopy (SEM) of the samples was done using a Tescan SE microscope VEGA TS5136 equipped with Oxford detectors for secondary and back-scattered electrons. The operating voltage of the SEM was 20 kV, the current was 20 nA. The microscope is capable of elemental microanalysis through an EDS detector and the INCA 250 software package.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

X-ray diffraction analysis was run on available samples and the presence of minerals belonging to the meta-autunite group was verified. As it was impossible to obtain pure mineral phases, there were numerous overlaps of diffraction peaks of the uranium minerals and other mineral phases such as quartz, micas and feldspars. However, the meta-autunite mineral group could be unambiguously identified based on their strongest lines. The unit cell could not be calculated from this data set, which – even if available – would not provide information on the mineral species due to the complex crystallochemical characteristics of the group. As in the earlier investigation (ŠČAVNIČAR, 1984³), the samples investigated here contained muscovite, quartz, pyrophyllite, chlorite, albite, microcline, chloritoid, and occasionally dolomite and calcite. These minerals account for all diffraction peaks identified in the XRD patterns, except for one line of variable intensity around 8.8 Å. This peak belongs to the most intensive line in the powder XRD pattern of the meta-autunite mineral group. This line was also identified in most of the samples analyzed previously, but its intensity varies from barely discernible to conspicuous.

The powder pattern of the chloritoid minerals presents a major difficulty in the identification process of uranium minerals present in the samples. Some chloritoid group minerals have a strong diffraction line (of 10–20% intensity) at 8.9 Å, and its resolution from the line at 8.8 Å, belonging to the meta-autunite minerals, is difficult, if at all possible. Chemical analysis would probably have provided the requisite information for mineral identification, but such an analysis was not

feasible due to the substantial intergrowth of the various mineral phases present in the samples.

3.2. Scanning electron microscopy investigation

For the SEM analysis of the Radlovac series rocks, the samples were only sputtered with carbon and scanned for surface roughness (i.e. the surface topography of the sample). The different mineral phases were identified based on the atomic numbers of the elements in the mineral crystal structures. In this way, the heavy elements could be identified very easily. In the samples collected for the previous investigation, SEM scanning revealed the presence of numerous aggregated fragments of uranium minerals. The fragments are hypidiomorphic to idiomorphic with a platy appearance. The plates grow in a subparallel arrangement and a tetragonal symmetry is clearly visible in octagonal sections. The plates have nearly perfect cleavage parallel to the base (Fig. 2a and b).

The crystals are 2–20 µm in length, their aggregations up to 0.5 cm in size. Smaller crystals have rectangular (Fig. 3a), the larger ones octagonal sections, which can be diagonally elongated (Fig. 3b).

Several, rounded fragments of zircon were identified in sample ZMAGO-1-4-3a.

3.3. Energy dispersive X-ray analysis

The energy dispersive X-ray analysis (EDX) showed that the principal elements in the uranium mineral structures are U, As and Cu in one group of samples, and U, P, Cu and Ca in the other group. Minor amounts of Fe, Ba and Si were identified in the uranium minerals. Supported by XRD investigations, it can be concluded that

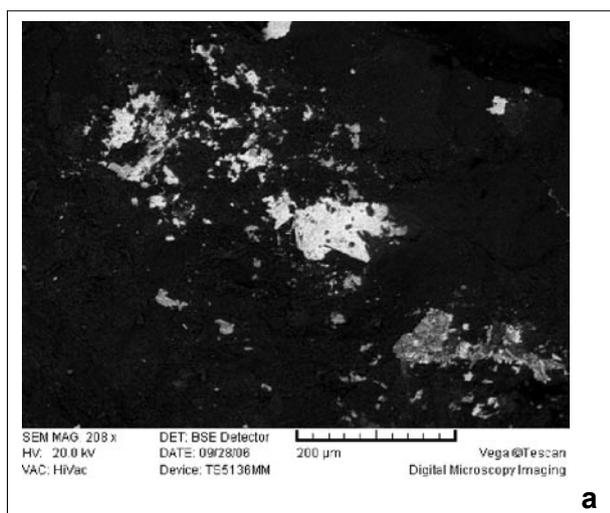
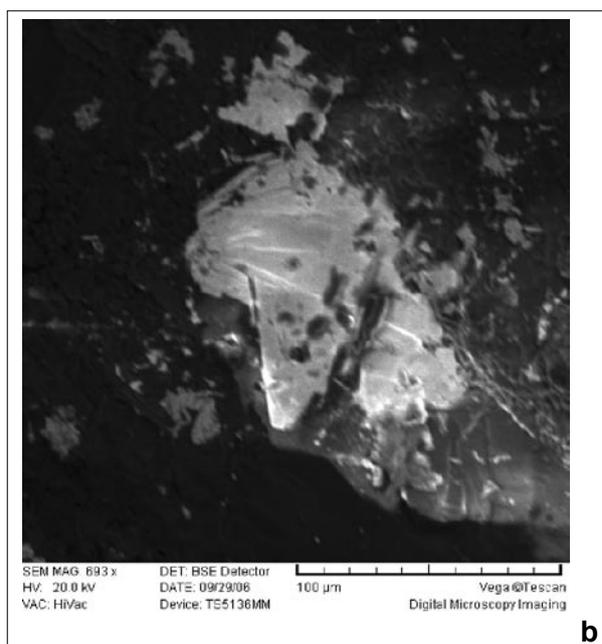


Fig. 2 a) Polished sample RA-4 with visible uranium mineralization (white grains are uranium minerals, grey grains are baryte crystals); b) A more detailed view of Fig. 2a showing meta-zeunerite platelets growing next to baryte.



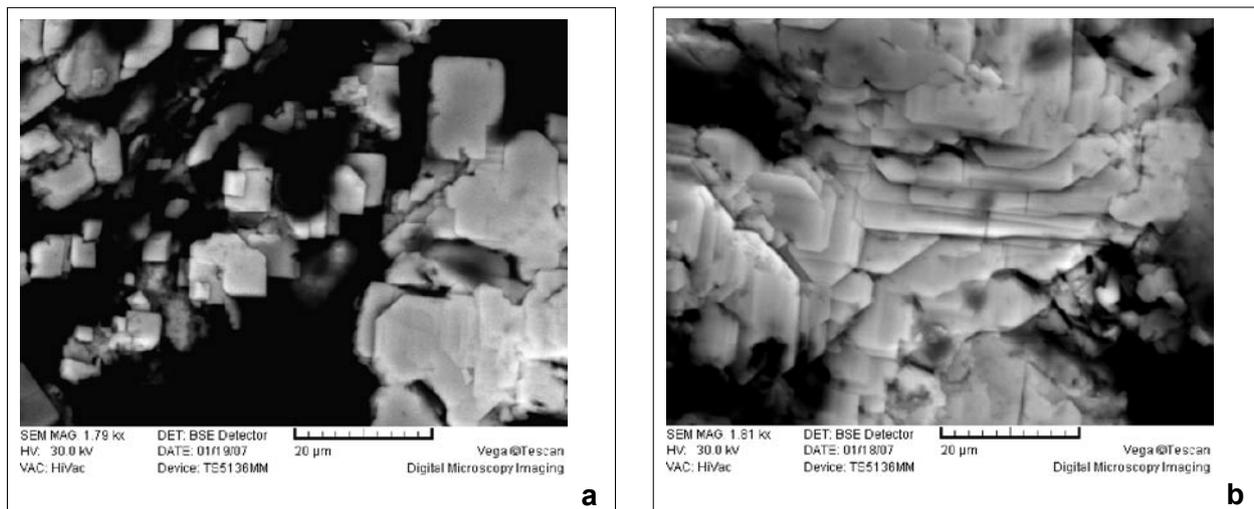


Fig. 3 a) Small crystals of meta-torbernite (2–10 μm) showing rectangular sections; the larger crystals have octagonal sections (sample RA-6); b) Crystals of meta-zeunerite showing similar morphology as meta-uranospinite (sample RA-6).

several uranium minerals are present in the samples – meta-torbernite $[\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2] \cdot 8\text{H}_2\text{O}$, meta-uranospinite $[\text{Ca}(\text{UO}_2)_2(\text{AsO}_4)_2] \cdot 8\text{H}_2\text{O}$, and meta-zeunerite $[\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2] \cdot 8\text{H}_2\text{O}$. The EDX spectra show that the meta-torbernite is a single phase, while there seems to a solid solution series between meta-uranospinite and meta-zeunerite resulting in possible variations in the composition of discrete crystal fragments.

The aggregates of these uranium minerals are partly interspersed with the other rock-forming minerals, resulting in a poikiloblastic texture (porphyroblasts which are riddled with finer grained inclusions of other minerals) of the uranium minerals. Small inclusions of baryte within the uranium minerals are common (Fig. 4a). The baryte fragments have typical morphologies with rhombic sections. They are 2–20 μm in size and formed by several subparallel plates. Individual baryte

crystals associated with other minerals are also represented (Fig. 5), but their incorporation into the uranium minerals is more common (Fig. 4a). Small amounts of silica have been identified in the baryte.

In some samples (i.e. sample ZMAGO-c) a copper oxide phase (most probably cuprite) was observed. It occurs in the form of needle-like crystals up to 200 μm in length, and below 1 μm in thickness (Figs. 6a and b).

The primary form of uranium mineralization has not been identified, but the presence of chalcopyrite was established. This chalcopyrite could have been the primary source of copper for the deposition of cuprite, but also provided copper for meta-torbernite and meta-zeunerite. A fragment of galena, ca. 15 μm in size was observed next to cuprite in one of the samples. A nickel-containing mineral phase was also identified.

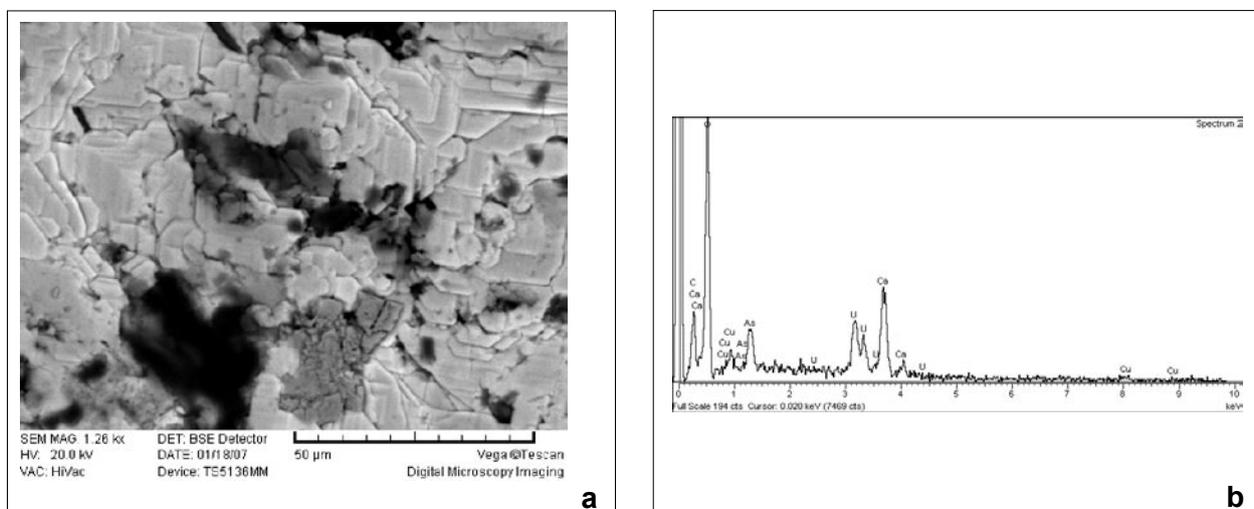


Fig. 4 a) Meta-uranospinite with an incorporated baryte inclusion (sample RA-6). The irregular grey spots are probably areas of dehydration with a partial loss of crystal water. Tetragonal meta-uranospinite crystals have octagonal sections. Different intensities of gray probably indicate Ca–Cu exchange; b) EDX spectrum of the area where meta-uranospinite dominates over meta-zeunerite (sample RA-6).

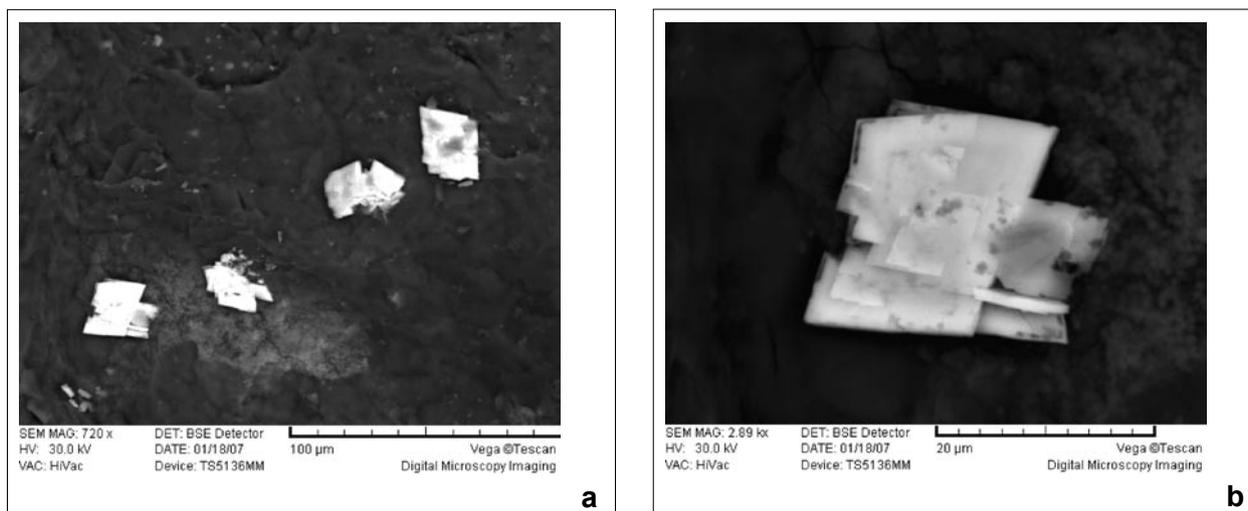


Fig. 5 a) Discrete baryte crystals 10x18 μm in size. The uranium minerals were formed mainly around baryte grains, but baryte crystals also occur separately (sample RA-6). No uranium mineral grains are visible on this image; b) A more detailed view of Fig. 5a.

3.4. Energy dispersive X-ray fluorescence analysis (EDXRF)

Table 1 presents concentrations of the major, minor and trace elements measured in three samples from Radlovac creek. XRF analysis of sample ZMAGO-1 indicated a substantial concentration of uranium at 0.15%. The PIKO sample was characterized by extremely high concentrations of U, Ba, As, and Cu, more than hundred times (U, Cu, Ba) and more than two thousand times (As) higher when compared to normal values that could be obtained in sandstone sediments. Arsenic was also highly enriched in the ZBZ material while U and Ni were elevated approximately 20 and 10 times respec-

tively compared to background values (ZMAGO sample).

Elevated concentrations of K, Ca, Fe, and Ti have also been established in this sample. The presence of all these elements can be related to the formation of uranium minerals, although Ba has only been observed in baryte and not in the uranium mineral phases. Copper forms meta-torbernite and meta-zeunerite, but also cuprite (and the primary chalcopyrite – Figs. 6a and b). The source of titanium is the small, unevenly distributed needles of rutile up to 10 μm in length and less than 1 μm thick (sample ZMAGO-1-4-3a). It is interesting to note that the presence of discrete nickel mineral

Element	Sample					
	PIKO	±	ZBZ	±	ZMAGO	±
K (%)	1.10	0.07	1.37	0.10	1.88	0.06
Ca (%)	1.29	0.07	0.18	0.03	0.34	0.02
Ti (%)	0.060	0.010	0.200	0.02	0.268	0.008
Fe (%)	0.764	0.002	1.644	0.004	1.589	0.001
U (ppm)	1500	200	230	40	16	3
Pb (ppm)	46	1	49	2	12	0.5
Ba (ppm)	3900	300	390	30	630	40
As (ppm)	2200	200	2000	200	n.d.	
Rb (ppm)	6.7	0.7	68.1	1.0	123.8	0.5
Sr (ppm)	170.3	0.9	28.4	0.7	51.0	0.3
Y (ppm)	27.8	0.8	138	2.0	40.4	0.5
Zr (ppm)	131.9	0.7	525.0	2.0	432.2	1.0
Mn (ppm)	320	20	620	40	330	10
Co (ppm)	3.8	0.1	7.1	0.3	5.8	0.1
Ni (ppm)	15	5	140	10	19	3
Cu (ppm)	1550	60	13	2	15.7	0.9
Zn (ppm)	167	3	42	3	39	1

Table 1 Elemental concentrations determined by EDXRF system in three samples from the Radlovac creek.

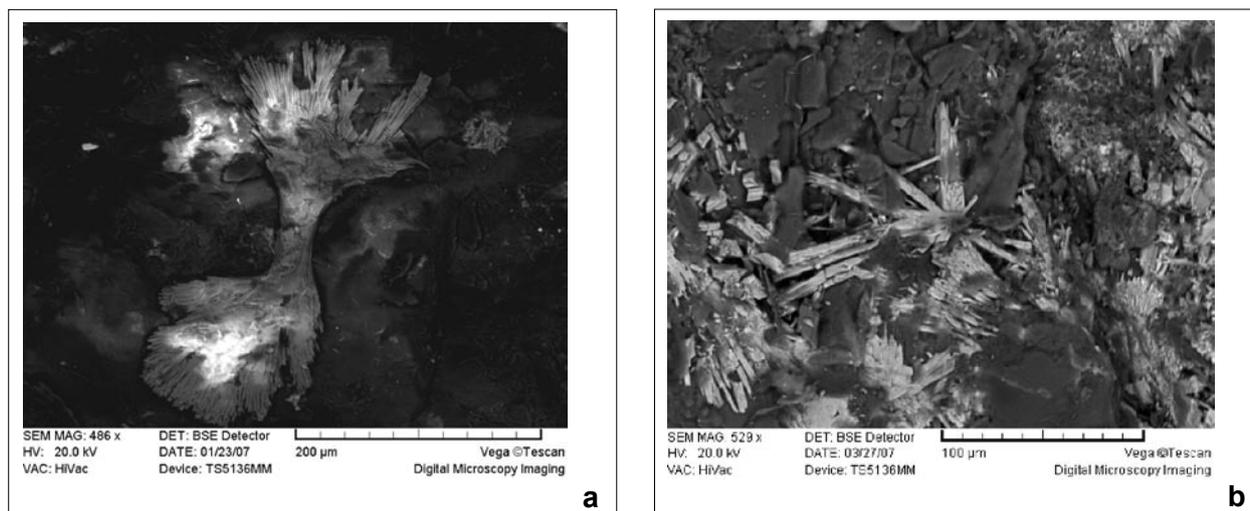


Fig. 6 a) Bundle of needle-like crystals of copper oxide, probably cuprite (sample RA-6); b) Radiating crystal aggregates of copper oxide, probably cuprite (sample Zmago-c).

phases was established, even though the concentration of Ni is rather low.

Apart from its mineralogical significance, the identification of the uranium mineralization in the Mt. Papuk area is also important for a better understanding of the geology and formation of the Radlovac series. Unfortunately, the intricately intergrown uranium mineral fragments cannot be separated without substantial contamination by other phases, so the characteristics and content of structural (crystal) water cannot be measured with sufficient precision. The amount of crystal water in the uranium minerals is variable and changes with dehydration and rehydration, depending on the physico-chemical parameters of the environment in which it was formed, and/or whether it is currently in thermodynamic equilibrium. Apart from the obvious significance of the partial pressure of water vapour, an important parameter of the reaction pathways leading to uranium mineral formation is the redox potential of the environment (BERMANEC et al., 2005). The identification of the oxidation state of uranium and the amount of crystal water in the uranium minerals would be of great importance for a better understanding of the conditions in which the Radlovac series was deposited and the processes which have impacted on the chemical and mineralogical diagenesis of this rock series.

3.5. Gamma spectrometry

The activities of ^{40}K , ^{232}Th , ^{226}Ra and ^{238}U (Bq/kg) as well as the $^{238}\text{U}/^{226}\text{Ra}$ activity ratio are presented in

Table 2. Concentrations of naturally occurring ^{40}K range over an order of magnitude, indicating significant differences in the total potassium content (2.78% of potassium in sample RA-1 against 0.22% of potassium in sample ZMAGO). Similar differences in uranium activities/concentrations were also found. Such differences indicate either compositional variation in the main minerals of the analyzed sandstones and/or intensive weathering processes. This is corroborated by the measured $^{238}\text{U}/^{226}\text{Ra}$ activity ratio, which varies between 0.156 (in sample RA-1) and 1.224 as found in sample ZMAGO.

In their early research of the Radlovac series, BRAUN et al. (1983) maintained that uranium was not in equilibrium with its decay products. A high content of ^{226}Ra (a relatively short lived member of ^{238}U natural decay chain) in comparison with uranium is very probably the result of recent (up to a few hundred thousand years), uranium leaching processes. However, $^{238}\text{U}/^{226}\text{Ra}$ activity of 1,224 units in sample ZMAGO indicates a zone where uranium was recently deposited with uranium enrichment. It seems that the highest uranium content of approximately 150 ppm, in sample RA6, is only 'the remaining' uranium after intensive leaching. On the basis of recent ^{226}Ra activity in that sample, it could be supposed that about 50% of the uranium content was weathered in the last few hundred thousand years.

The uneven distribution of uranium minerals and accessory minerals in the investigated samples indicates that the protolyte was of inhomogenous composi-

Sample	^{40}K	^{232}Th	$^{238}\text{U}/^{226}\text{Ra}$	^{226}Ra	^{238}U
RA1	860.9±13.5	53.3±2.1	0.156	892.2±4.9	139.0±12.3
RA6	276.0±12.7	15.7±2.0	0.487	3 913±11	1 906±30.0
ZMAGO	68.6±6.5	15.4±2.3	1.224	813.4±5.8	995.4±20.0

Table 2 Activities of ^{40}K , ^{232}Th , ^{226}Ra , ^{238}U (Bq/kg) and the $^{238}\text{U}/^{226}\text{Ra}$ activity ratio in the analyzed samples.

tion. This is further corroborated by the fact that several uranium mineral phases have formed, the phases not being fully separate but with variable composition within zoned mineral grains. All such phases appear to be in thermodynamic equilibrium. It was not possible to fully describe the zonations, since the thickness of such grains is very small.

4. CONCLUSIONS

The combination of methods used in this study enabled unambiguous determination of the U-bearing minerals of the Radlovac series as meta-torbernite, meta-uranospinite and meta-zeunerite. These minerals have not been previously identified in Croatia.

Further research will be devoted to identification of the nickel-bearing mineral phases and the determination of the oxidation state of the uranium ion in the uranium minerals – if appropriate samples become available, in which the separation of discrete uranium mineral phases will be possible.

Acknowledgements

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