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GEOCHEMICAL STUDY OF U, Th AND REE MINERALIZATIONS IN JURASSIC SEDIMENTS AND HYDROCHEMICAL CHARACTERIZATION OF GROUNDWATERS IN EASTERN SERBIA – CASE STUDY: PLAVNA AREA

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Abstract: This paper research the newly-discovered U, Th-REE mineralization in Jurassic sediments in Eastern Serbia, Carpatho-Balkanides geotectonic unit - Plavna granitoid. During 2009-2013 research was conducted using a range of geological and hydrogeological methods for geochemical and petrographical analyses of rocks. It was found that uranium mineralization occurs in breccia-conglomerates of continental facies, while Th-REE mineralization is located in quartz sandstones without organic matter (marine facies). Mineralized sediment levels are distinguished according to grain sizes and the presence of organic material, which had an important role in the deposition of uranium. The major uranium minerals were uraninite (pitchblende), coffinite, and urano-organic complexes. Electron microprobe analysis (EMPA) showed that monazite crystals vary in shape and typically are lower than 50 µm in size. The ICP ME-MS81 results of 209 geochemical samples revealed a wide range of U, Th and REE concentrations. The median U concentration was found to be 6 ppm, while maximum concentrations were over 1000 ppm. The median Th concentration was 19 ppm, while maximum was over 1000 ppm. Samples showed REE contents in the range of 14.94 ppm to 10125.86 ppm. Their chondrite-normalized REE patterns are steeply right-inclined with similar slopes, with strong LREE/HREE partitioning [(La/Yb)n=1.35－218.2)], and weak to high Eu depletion (δEu=1.26－0.04). Detailed hydrochemical investigations in the area of the Jurassic sediments have shown that the groundwaters are low-mineralized, with neutral pH values, and redox values between 0.075 V and 0.437 V. A high level of uranium was found in a borehole (48.8 µg/L), while Th concentrations were low in all samples (0.00025 - 0.039 µg/L). The sum of REE concentrations in the groundwater ranged from 10.01 to 308.87 ng/L. Hydrochemical research had aim to determine the chemical composition of groundwater in the study area.

Key words: Jurassic sediments, Uranium, Thorium, Rare Earth Elements, Groundwater, Eastern Serbia

1. INTRODUCTION

Europe is very complex tectonically and sandstone-type uranium deposits or districts occur through European countries. Ages of the host sandstones vary from Ordovician to Quaternary (Finch & Davis, 1985). Exploited deposits of uranium include the occurrences in southeastern Europe, where Carpatho-Balkanides represent one of the largest geotectonic units. From the metallogenic point of view, these are incorporated into the Tethyan-Eurasian Metallogenic Belt. Thus mineral resources of Serbia were formed by complex processes of metallogenic development and in various geological epochs (Pre-Baikalian to Alpine) (Janković, 1997; Jelenković, 2014).

The most important group of metallic mineral resources of Serbia includes Cu, Pb-Zn, Au, Ag, Sn, Mn, U, Mo, Ti, W, Co, Sb and Fe ores (Jelenković et al., 2008). The territory of Serbia is characterized by several uranium deposits and occurrences, and most of them are located in the Carpatho-Balkan metallogenic province (Eastern Serbia).

Research on uranium mineralizations of this area started in the middle of the last century, though subsequently Th and REEs (Rare Earth Elements) mineralizations were discovered (Kovačević & Obrenović, 1996). Geological and hydrochemical data from different investigations conducted by the Geological Survey of Serbia and Faculty of Mining and Geology (Belgrade) were used in this paper. A radiometric survey and other geological examinations in Serbia were carried out from the middle of the 20th century to 2013. Regional metallogenetic prospecting of the entire region indicated significant uranium mineralizations (anomalies of radioactivity), but REEs were not discovered. During the 80s, findings of aero-gamma spectrometry were confirmed by laboratory investigations and elevated concentrations of REEs were registered (Arsenijević & Dromnjak, 1988; Kovačević & Gertik, 1995; Kovačević & Obrenović, 1996). To define a genetic model of U, Th and REE mineralization in the Jurassic sedimentary rocks of Plavna, explorations continued in the period 2009–2014. In this paper we shall present findings about U and the newly-discovered Th and REE mineralizations in Jurassic sedimentary rocks overlying the Carboniferous granitoid of Plavna (Eastern Serbia). The main objective was to understand better the behaviour of U, Th and REE, from weathering of its source rock to accumulation in the sedimentary basin and to determine the chemical composition of groundwater in the study area.

2. STUDY AREA

The Plavna area is located in the Carpathian-Balkanides geotectonic unit, Eastern Serbia (Fig. 1). Different tectonic processes during the Baikalian orogeny, Caledonian and Variscan orogenies, and finally the Alpine orogeny (Anđelković, 1996) controlled the paleogeographic and structural evolution of the region followed by strong plutonic activity. Magmatic processes are probably related to the closure of an ocean during the Cambrian-Ordovician, and the collision of neighbouring blocks, the docking in the early Carboniferous, the subduction during the late Carboniferous, and the post-collisional processes during the Westphalian-Permian (Vasković et al., 2002). The oldest rocks of this area comprise a Proterozoic volcano-sedimentary series metamorphosed under greenschist-facies conditions (Antonijević et al., 1970) intruded by Variscan granitoids (Brnjica, Neresnica, Gornjane, Plavna, Ravno Bučje, Suvodol, Radičevo, Janja) (Fig. 1). Petrographically, these rocks correspond to syenites, syenodiorites, granodiorites and granites. All of them are mainly reported as I-type intrusives formed in the late stage or after amalgamation of the East Serbian terranes (Šarić et al., 2014). The Plavna granitoid occupies an area of around 20 km^2.

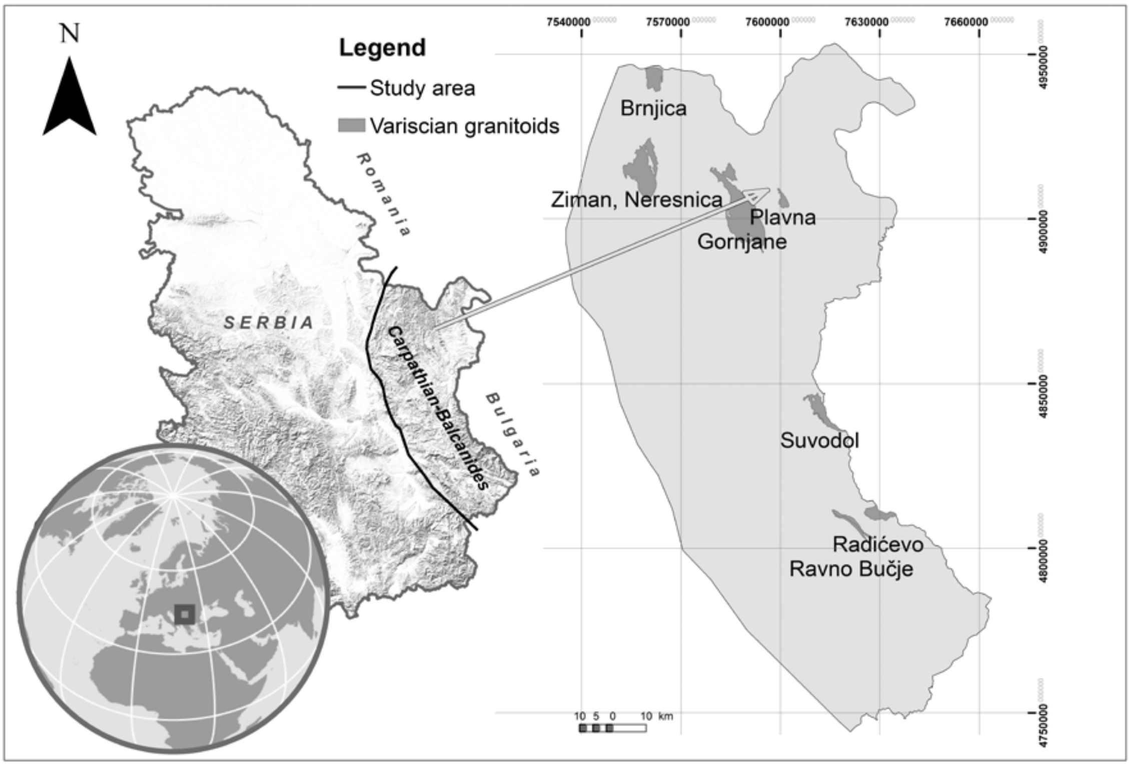

Figure 1. Schematic view of the Carpathian-Balcanides geotectonic unit with Variscan granitoids of eastern Serbia and the study area location.

Plavna granitoid is a grey-reddish colour, holocrystalline and porphyritic structure. Mineral composition of the Plavna granitoid is presented by weight percentages as follows: 30.2% quartz, 45.9% plagioclase, 16.9% alkaline feldspar 6.6% biotite and muscovite and 0.2 % of accessory minerals (zircon, apatite, titanite, allanite, monazite). It is quartz-monzonite rocks originating from magmatic melts that crystallized at a relatively shallow level in the crust. Very steep, almost vertical cracks occur in the massif, which is covered by younger sediments, where Early Jurassic sediments presented with breccia-conglomerates and quartz-sandstones are the most widespread (Antonijević et al., 1976) (Fig. 2).

The sedimentary sequence starts with greyish-green to black Early Jurassic breccia-conglomerates overlying the Carboniferous granitoid of Plavna. Breccia-conglomerates are composed of crushed and weathered granitic material which was subsequently cemented (cemented granite and grus material). Clastic material is made of poorly sorted and briefly transported material. Major minerals in breccia-conglomerates are angular grains of quartz, feldspar, including potassium and plagioclase, biotite and muscovite. The matrix is finer grained sedimentary material, such as limonite, clay and carbonated material with organic substances.

Changes of sedimentation environment have led to deposition of quartz sandstones without fauna.

The thicknesses of these deposits are up to 30 m. At the end of the Early Jurassic, regional transgression occurred resulting in deposition of marine sediments (Anđelković, 1975; Kovačević & Gertik, 1995). The most important episodes for formation of U, Th-REE mineralizations are emplacement and erosion of I-type granites enriched in uraninite, monazite, zircon, biotite, titanite, apatite, rutile and other minerals. During tectonic movements, a descent of granitic blocks of the Plavna massif along a regional fault created the paleodepression with a length of 1400 m and width of 80 m (Kovačević & Gertik, 1995).

3. METHODS

All analyzed rock samples were collected from fresh surface exposures and trenches (Fig. 3). Sampling density was increased in the contact area of granitoid rock of Plavna and Jurassic sediments. Geochemical analyses were performed in an accredited ALS Chemex laboratory - Alba in Romania, where samples were analyzed on 38 elements (palette ME-MS81 by method ICP-MSS), which primarily analyzed radioactive elements and rare-earth elements.

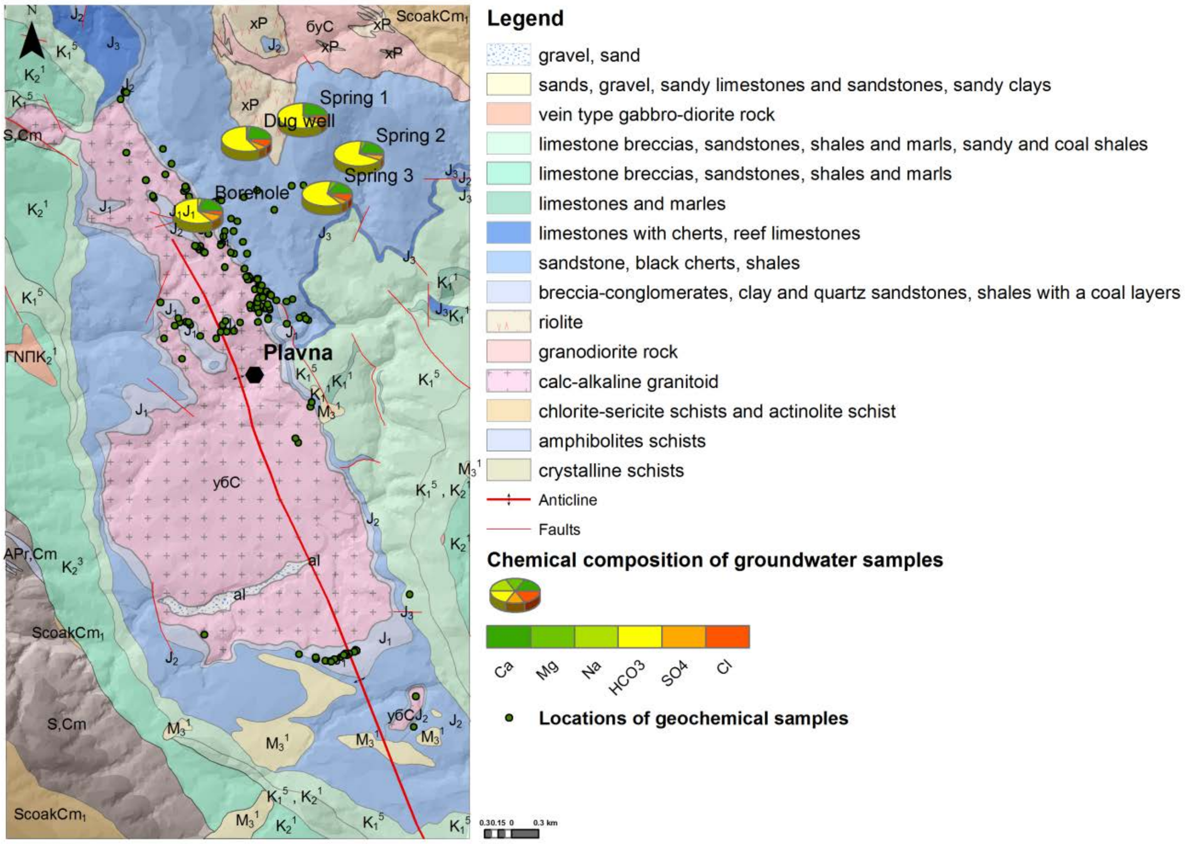

Figure 2. Geological map of the Plavna granitoid with locations of groundwater samples and their chemical composition.

Figure 3. Field measurements and sampling.

A prepared sample (0.200 g) was added to lithium metaborate flux (0.90 g), mixed well and fused in a furnace at 1000 °C. The resulting melt was then cooled and dissolved in 100 mL of 4% HNO_3 / 2% HCl_3 solution.

Petrographic examination and ore-microscopic analyzes were conducted in the laboratory of the Geological Survey of Serbia. Ore microscopic analyses were performed by polarizing microscope Carl-Zeiss, model "JENAPOL-U" equipped with a system for photomicrography. Polished sections were prepared for reflected-light microscopy and electron microprobe analyses (EPMA). EPMA used wavelength dispersive spectrometers to detect the x-ray counts from the sample surface. Analyses obtained using an accelerating voltage of 20 kV and a beam current of 40 nA.

The process of magnetic fractionation was carried out to differentiate between the economic minerals within the resultant subfractions and to facilitate the process of counting economic minerals under the binocular microscope. About 1 kg of 7 river sediment samples was collected from each location from Udubašnica, Medveđa, Zamna and Vrelska River. The fraction of grain size less than 0.5 mm was analyzed, and this was further separated by heavy liquid (2.52 g/cm³) into the light and heavy minerals. These were then fractionated by electro-magnet into: ferromagnetic, +0.25 A, A + 0.5, + 1A, A +1.75, -1.75 A. These fractions were examined under a binocular microscope using xylene as the immersion medium.

Groundwater samples were collected in 2014, one sample from borehole, one from well and 3 samples from natural springs. The oxidation/reduction potential (Eh), pH values, electrical conductivity and water temperatures of the samples were determined in-situ using a portable Field Case (WTW pH 3110 SET 2 and Electrode Sen Tix ORP 100 °C). Major ions: K, Na, SO_4, Cl, Ca and Mg, and alkaline concentrations were determined by atomic absorption spectrometry, ion chromatography, EDTA titration, and acid-based titration, respectively. U, Th and REEs concentrations in the groundwater samples were measured using high resolution inductively-coupled plasma mass spectrometry (HR ICP–MS). Sector ICP/MS using a Finnegan Mat ELEMENT 2 instrument for 57 elements. To test the accuracy and precision of the method, NIST® 1643e “Trace Elements in Water” SRM was analyzed and compared to the certificate values. Geochemist's Workbench (GWB) and Visual Minteq 3.1. software were used for establishing the uranium and REE ionic forms. The results were statistically processed using IBM software SPSS 17.0, and graphically interpreted by ESRI ArcGIS 9.3.

4. RESULTS

4.1. Geochemical results: ICP ME-MS81 results

In the area of Plavna granitoid, 209 rock samples were analyzed: 174 samples of Jurassic sediments and 35 samples of granite rocks. Element concentrations are shown statistically and graphically to identify their ranges (Table 1, Fig. 4).

Significantly higher concentrations of U, Th and REE were determined in samples from Jurassic sediments (Fig. 4)

The median U concentration was found to be 2.85 ppm and maximum value was 110 ppm in granite. In sandstone rocks, the median U concentration was 6.8 ppm while the maximum U concentrations were over 1000 ppm. The median Th concentration in granite was 15.6 ppm and 22.5 ppm in sandstone material, while the maximum values were 45.9 ppm and over 1000 ppm respectively. Comparing the total of light (LREE) and heavy (HREE) rare earth element concentrations between granite and sandstone, significant differences were observed in their maximum concentrations. Sandstones had a higher maximum LREE concentration (9438.51 ppm) and HREE concentration (687.35 ppm) than granite (805.98 ppm and 35.1 ppm). Regarding the medians, slightly higher concentrations were observed in sandstone for both light and heavy rare earths.

4.2. River sediment analyses

Geoenvironmental significance can be attributed to basic components of bottom sediments, including particularly trace elements in bottom sediments of inland water bodies (Filip & Orlandea, 2016) River sediments gave light fraction contents within the range of 40.97% to 99.18%, while the contents of the heavy fractions were in the range 0.82% to 59.03%.

The dominant minerals identified are shown in Table 2. Metallic minerals were present in high percentages of 7.49% to 59.86%, mainly as hematite. Zircon is partially or completely rounded, colourless or rarely reddish. The presence of monazite (up to 6.84 %) is very significant. The microscopic study revealed that the monazite occurs as sub-rounded to rounded grains, reddish or colourless.

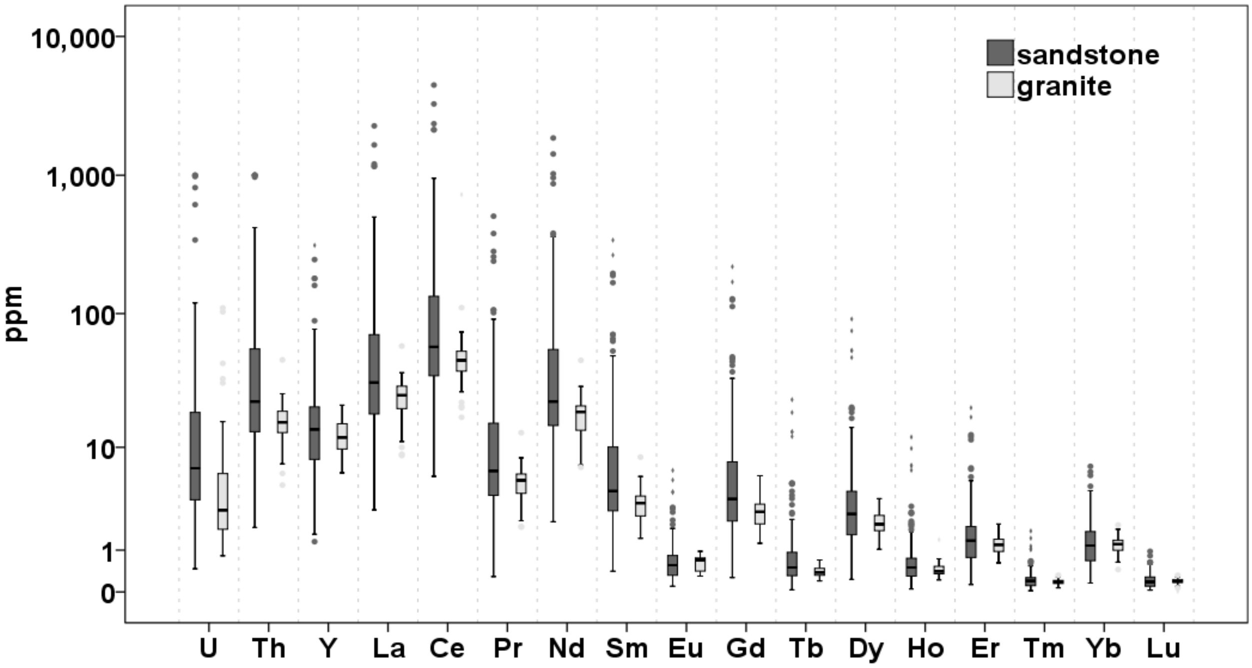

Figure 4. Box-plot of REE, U and Th concentrations.
Table 1. Basic statistics for REE, U and Th in all samples.

	Median (ppm)	Std. Dev.	Min (ppm)	Max (ppm)	25 %	50 %	75 %
La	28.7	244.4	2.9	2270	18.5	28.7	55.2
Ce	54.3	473.5	5.8	4460	35.9	54.3	107.8
Pr	6.1	54.8	0.3	507	4	6.1	12.3
Nd	20.9	200.9	2.2	1855	14.4	20.9	43.1
Sm	4	37.6	0.4	340	2.7	4	8.1
Eu	0.6	0.8	0.1	6.5	0.3	0.6	0.8
Gd	3.4	24.5	0.3	219	2.2	3.4	6.1
Tb	0.5	2.6	0	23.2	0.3	0.5	0.7
Dy	2.4	10.3	0.2	91.3	1.6	2.4	3.7
Ho	0.5	1.4	0.1	12.1	0.3	0.5	0.7
Er	1.3	2.4	0.1	20.2	0.8	1.3	1.9
Tm	0.2	0.2	0	1.8	0.1	0.2	0.3
Yb	1.2	1	0.2	7	0.7	1.2	1.6
Lu	0.2	0.1	0	1	0.1	0.2	0.3
Y	13.3	34.4	1.3	312	8.8	13.3	19.5
U	6	138.2	0.5	1000	2.8	6	17
Th	19	161.4	1.9	1000	13.2	19	41.4

Table 2. Qualitative and quantitative composition of light and heavy fractions of river sediments (“nd“ stands for not detected)

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Light fraction (%)							
quartz	55.44	57.16	57.24	60	35.26	79.84	60.16
feldspar	4.48	8.64	9.53	5	2.88	12.32	15.77
muscovite	1.12	nd	nd	nd	2.16	nd	3.32
rock fragments	29.12	31.41	25.87	28.5	33.12	4.48	20.75
Clay fraction	8.72	6.13	4.87	5.3	5.04	2.24	nd
% light fraction	59.74	94.29	48.4	40.97	85.54	99.18	49.40
Heavy fraction (%)							
magnetite	1.65	0.8	3.92	5.52	5.23	4.76	7.74
metallic minerals	41.5	25.83	18.74	11.35	19.07	59.86	7.49
garnet	4.55	0.8	0.59	3.3	9.89	1.16	2.65
amphibole	nd	1.44	5.58	7.82	0.51	0.58	13.28
pyroxene	0.65	1.44	2.40	9.12	2.85	1.16	nd
Staurolite	nd	0.72	2.40	2.28	2.85	2.32	0.83
epidote / coisit	nd	0.67	2.74	5.54	8.78	9.86	23.88
biotite	2.6	0.8	nd	3.18	4.48	nd	1.68
chlorite	1.3	1.2	16.70	12.22	9.64	1.74	31.71
rock fragments	15.70	31.23	27.48	15.20	8.19	4.64	2.14
tourmaline	nd	1.32	3.15	4.08	2.85	1.16	3.32
apatite	1.95	1.08	1.32	1.54	0.62	4.06	nd
rutile	0.75	nd	0.73	0.66	nd	0.58	nd
zircon	3.9	0.64	2.8	2.64	0.62	6.96	0.55
monazite	1.64	nd	1.20	6.84	nd	0.58	0.83
Fe clay fraction	23.5	33.03	9.52	2	7.6	nd	0.6
% Heavy fractions	40.26	5.71	51.6	59.03	14.46	0.82	50.6

The major uranium minerals are uraninite (pitchblende), coffinite, and urano-organic complexes. The uranium minerals uraninite and coffinite are associated with coalified wood or other organic material. The uranium minerals are commonly very fine grained and locally can replace low-rank coalified wood. In such replacements, the uranium mineral is massive but still very fine grained. In addition, uranium in the deposit occurs as cements of breccias and along fractures in microscopic specimens (Stojanović, 1989).

In certain samples, biotite occurs in a sandstone matrix with accumulated fine-grained crystalline pyrite and organic-graphitic materials with Mn hydroxides and limonite. The largest amounts of pyrite are present as hydrothermal zoned crystal pyrite with pseudomorphosis of limonite.

Monazite grains vary in shape and size and typically are smaller than 50 µm in size. They are compositionally heterogeneous, with grains showing concentric zoning. Crystal chemistry of the monazite can be shown by the following formula: $(Ce_{0.35\text{-}0.46}, La_{0.16\text{-}0.28}, Nd_{0.11\text{-}0.25}, Th_{0.01\text{-}0.13}, Ca_{0.01\text{-}0.05}, Sm_{0.00\text{-}0.04}, Gd_{0.00\text{-}0.03})_{0.89\text{-}0.99}$ $(P_{0.89\text{-}1.02}, Si_{0.00\text{-}0.12})_{0.98\text{-}1.06}$ $O_{4.03\text{-}4.05}$. They commonly have patchy zoning that is typically rich in Th (0.89 to 13.94 %). Zircon is characterized by idiomorphic crystals with regular sections, showing almost regular zones and cataclastic texture. It has a high content of U (<0.3 to 1.74%) and Th (<0.3 to 2.16%), with the following crystalochemical composition: $(Zr_{0.93}, Ca_{0.02}, Fe_{0.02}, Sc_{0.01}, Hf_{0.01}, Th_{0.01}, U_{0.01})_{1.01}(Si_{0.98}, Al_{0.03})_{1:01}O_{3.98}$.

4.3. Hydrochemistry

Temperature, pH, redox, EC, basic chemical compositions and concentrations of U, Th and REE of water samples from the Jurassic sediments are given in Table 3. The pH of the groundwater was found to be neutral, ranging between 7.43 and 7.76. The redox values ranged between 0.075 V and 0.437V. Temperature was found to be between 12.3°C and 15.8°C. The EC of the water ranged from 113µS/cm to 576µS/cm. According to groundwater classification based on dissolved mineral substances, these sandstone aquifers are classified as low-mineralized waters.

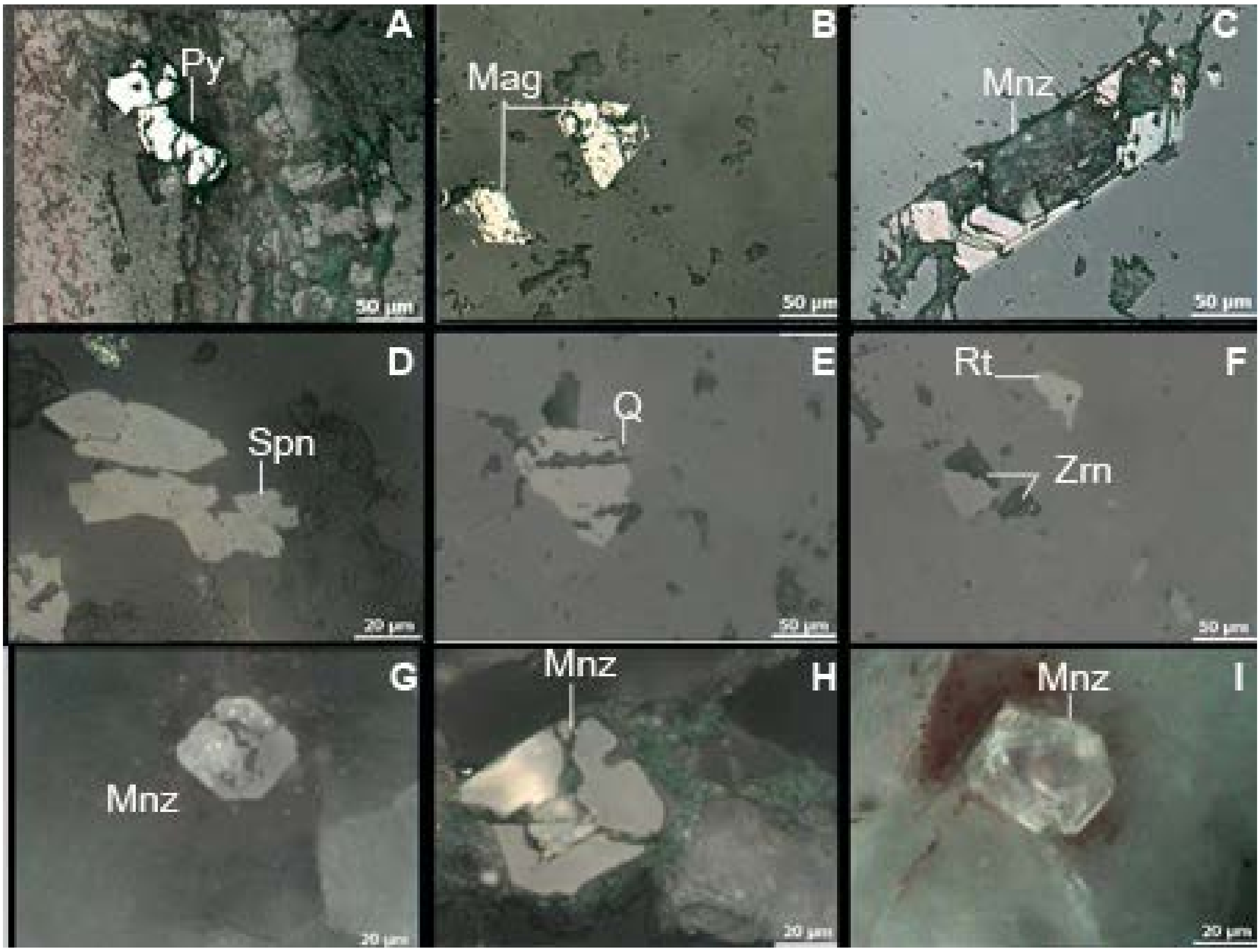

Figure 5. Photomicrographs of selected minerals: A. Pyrite (Py) aggregate in silicate matrix; B. Magnetite (Mag) crystals; C. Crystal of monazite (Mnz); D. Crystal-section of sphene (Spn) in silicated matrix; E. Rutilated quartz (Q); F. Zircon crystals (Zrn) and rutile (Rt) in a quartz matrix; G. Idiomorphic monazite (Mnz) crystal in silicate matrix; H. Cataclastic texture in monazite (Mnz); I. Monazite crystal (Mnz) with reddish submicron effects.

Table 3. Values of physical and chemical parameters of the sampled groundwaters

Water sample	Borehole	Dug well	Spring 1	Spring 2	Spring 3
T(oC)	15.8	15.2	12.3	14.3	15.1
EC (µS/cm)	461	113	409	576	500
pH	7.76	7.75	7.66	7.75	7.43
Eh (V)	0.0785	0.214	0.3404	0.2729	0.4375
Ca (mg/L)	77.2	25.2	86	98.4	78.8
Mg (mg/L)	9.1	3.65	4.86	24	26
Na+K (mg/L)	16.8	1.61	3.22	2.76	0.23
HCO3 (mg/L)	250	73.2	244	378.2	320.8
SO4 (mg/L)	36	7.5	21.4	27.7	24.6
Cl (mg/L)	17	9.92	14.2	8.5	37.3
Th (µg/L)	0.00074	0.0039	0.00066	0.00029	0.00025
U (µg/L)	48.8	0.0079	0.467	0.832	1.32
ΣREE (ng/L)	308.87	80.59	10.01	27.47	51.23

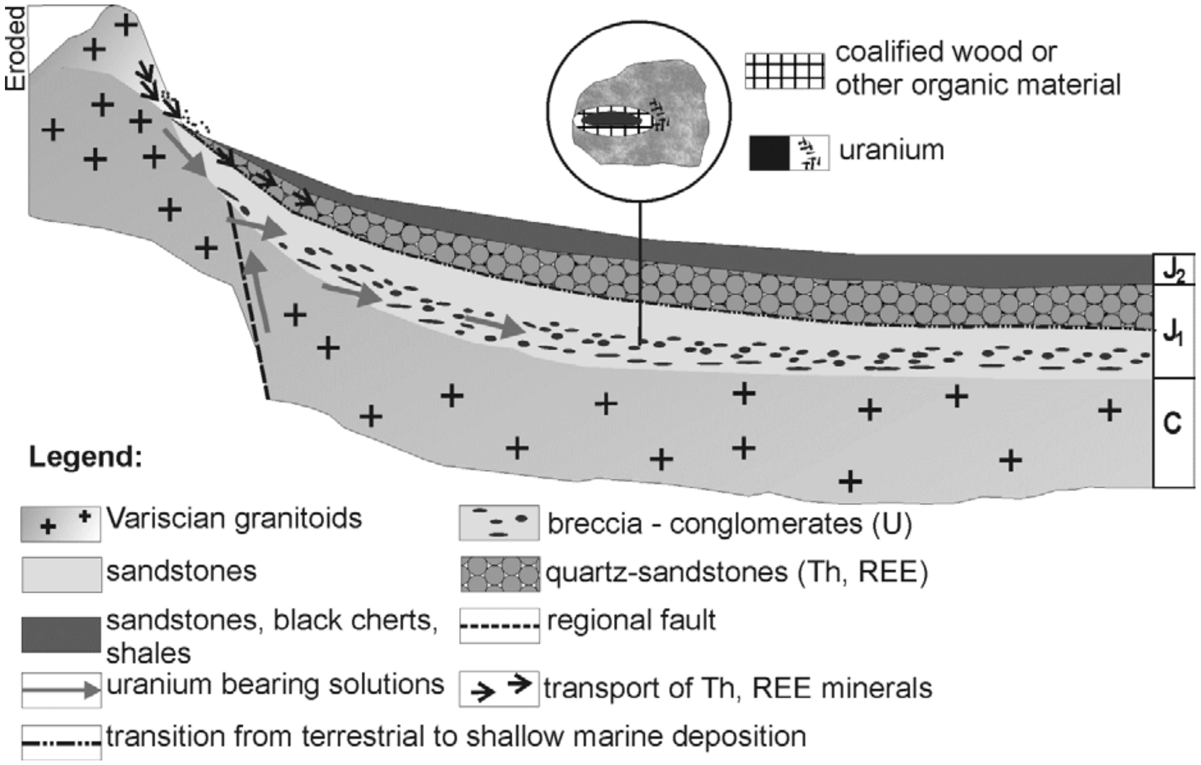

Figure 6. Schematic profile of U, Th – REE mineralizations in Jurassic sediments of the Plavna area

5. DISCUSSION

5.1. U, Th-REE mineralization

Uranium, thorium–REE mineralizations are related to Variscan granites of Eastern Serbia. Carboniferous granites and their metamorphic host rocks provided materials for deposition of Jurassic sediments.

Different sedimentary facies indicated a progressive change from terrestrial to shallow marine deposition. Uranium mineralization occurs in breccia-conglomerates (continental facies), and Th-REE mineralization is located in quartz sandstones without organic matter (marine facies) of Early Jurassic age, while these mineralizations were not registered in younger sediments.

The sedimentary sequence started in the Early Jurassic and had a few important characteristics. Firstly, there are sharp transitions in the sedimentary column, with differences in the grain sizes of sediments and presence of organic matter. These transitions are attributed to rapid changes in depositional conditions from continental to marine.

Plavna uranium mineralization was discovered within continental facies and probably results from leaching magmatic uraninite from granites. Three periods of mineralization genesis can be distinguished in this region: I) U primary mineral formation, II) alteration and mobilization, and III) formation of secondary minerals. The mineralization event is related to weathering processes of primary uranium sources with precipitation of coffinite ($U(SiO_4)$ x nH_2O) and uraninite (UO_2, or powder pitchblende aggregates) that had deposited in the paleo-depression. The presence of organic material in sediments had an important role in the deposition of uranium. The uranium-bearing water in contact with the slightly acidic environment (such as fossil wood remains) decomposed uranium from U-rich complexes and the uranyl ion was absorbed by organic matter (Fig. 6).

Progressive change from terrestrial to shallow marine deposition resulted in formation of a complex of siliciclastic sediments, defined as fine-grained quartz-sandstones. The major characteristic of these sediments is the absence of organic matter and the presence of high Th and REE concentrations. The only established Th, REE-mineral is monazite which is generally stable during sedimentary and diagenetic processes. The angular shape of monazite in the sandstone, weak roundness grains of feldspar, quartz and other minerals indicate a short transportation in the granitoid area.

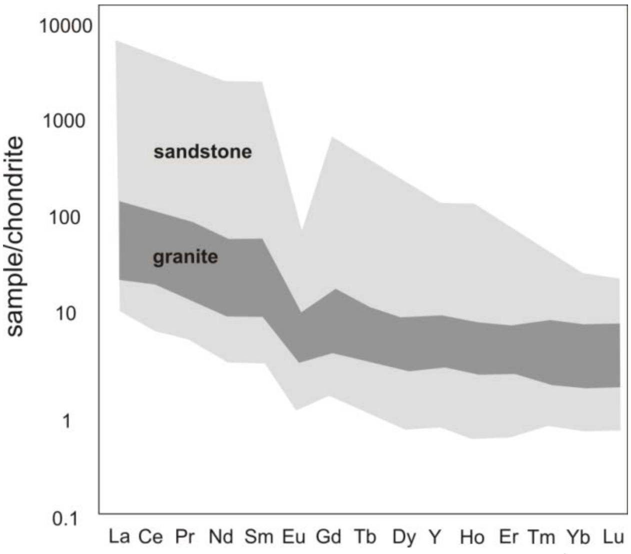

Figure 7. The chondrite-normalized REE patterns of rock samples.

The Jurassic sediment and Plavna granite samples exhibit generally similar rare earth element chondrite-normalized patterns (Fig. 7). They show a pronounced to high enrichment of the LREE over the HREE with $(La/Yb)_{CN}$ values ranging from 1.35 to 218.2, which may result from the preferential incorporation of lighter lanthanides relative to heavier lanthanides in monazite during partial melting. There is no significant fractionation between LREE, but HREE are highly fractionated with $(Gd/Yb)_{CN}$ ranging from 0.62 to 25.24.

Most REE patterns reveal weak to high Eu depletion (δEu=1.26－0.04). The negative Eu anomaly in granitic rocks may be caused by the progressive removal of plagioclase during crystallization.

5.2. Hydrochemistry

There are different aquifer types in the study area, in Jurassic sandstones and granitic rocks. One groundwater sample was taken from a borehole (covering the Jurassic sediments and granitic bedrock with a depth of 67.5 m), one from a well (7 m) and three samples from natural springs from Jurassic sediment. Based on their chemical compositions they are all $Ca\text{-}HCO_3$ water types (Fig 2).

5.2.1. Uranium in groundwater

An Eh–pH diagram was plotted to show uranium species in the water samples (Fig. 8). The Eh–pH diagram shows that well and spring samples are plotted in an oxidizing environment with a pH around neutral, where UO_2OH^{2+} and $(UO_2)_3(OH)_7$ are the dominant species, and the borehole sample is in near reducing Eh values.

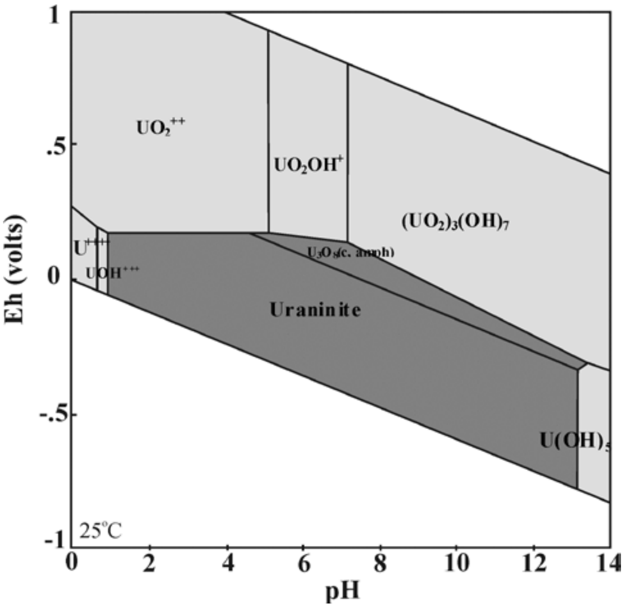

Figure 8. Eh–pH diagram with groundwater occurrences.

These Eh–pH conditions are favourable for the dissolution of uranium in the aquifer material and the surrounding rocks where the water possibly flows during recharge. In the borehole sample, uranium is dissolved at low Eh values (i.e. reducing environments), where reduced U(IV) forms uraninite (UO_2) precipitates. The groundwater becomes increasingly anoxic below the water table with progressive reduction of oxygen, where bacterial respiration and mineralization of organic matter take place. The decrease in the amount of oxygen (reducing Eh) in the aquifer results in uranium precipitating out of solution as uraninite.

This model fits the depositional environment of many uranium ore deposits, especially of the sandstone type. In low Eh environments the stable uranium species is UO_2, so a colloidal form of this material could be the mobile phase. It is possible that the chemical conditions within a deep aquifer do not change abruptly, and that gradual development of reducing conditions would cause UO_2 to form as a colloid which could travel long distances. The highest uranium concentration (48.8 μg/l, borehole) can be explained by a mechanism where the groundwater is progressively gaining uranium from the solid uranium orebody along the flow path. It is most likely that uranium in groundwaters with high uranium concentrations originates from the uranium orebody.

5.2.2. REE in groundwater

The chondrite-normalized REE patterns for water samples are shown in figure 9. All samples have LREE enrichment with $(La/Yb)_N$ in the range of 8.45 to 59.13. The presence of different REE patterns can be explained by the differences in geochemical mobility between LREEs and HREEs during water–rock interaction.

Speciation modeling showed that the HREE occurrences in the water samples were associated with the formation of carbonate complexes, predominantly dicarbonate ion $Ln(CO_3)_2^-$, whereas LREEs are $LnCO_3^+$ dominant. The proportions of $Ln(CO_3)_2^-$ were found to increase from La to Lu, whereas the proportions of $LnCO_3^+$ decrease.

Progressive mixing with shallow groundwater during ascent is most likely responsible for the change towards REE pattern caused by the progressive depletion of HREEs and a slight increase of LREEs. Thus, low concentrations of ΣREEs and REE patterns appear to result from several causes including the dilution of HREEs in concert with a slight enrichment of LREEs by mixing, the removal of REEs likely due to the formation of carbonate precipitates and the co-precipitation and/or adsorption onto Fe and Mn oxides.

The different geochemical behaviours of cerium and europium often lead to positive or negative Ce or Eu anomalies in normalized REE distribution plots. A positive Ce anomaly was noted in three samples from springs. Positive Ce anomalies might be a feature of aerobic, carbonate-rich, low-temperature waters in general, because at high pH and carbonate concentration, the formation and stabilization of carbonatoCe(IV)-complexes in solution leads to enhanced abundances of Ce(IV) in comparison with its trivalent REE neighbours (Möller & Bau, 1993).

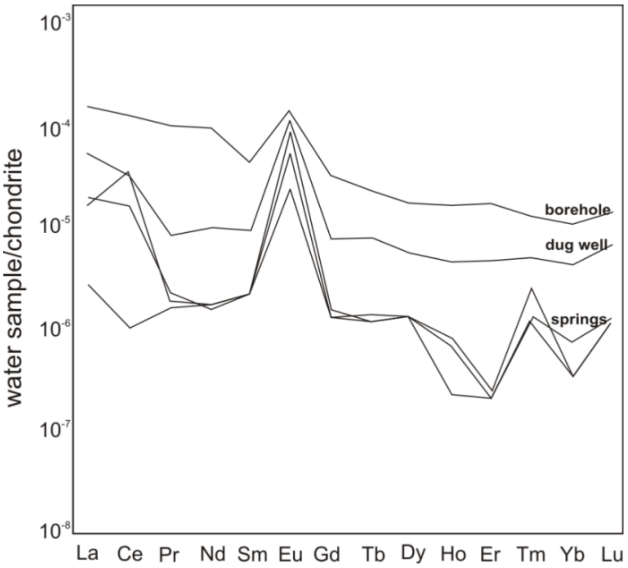

Figure 9. Chondrite-normalized water samples.

All samples have positive Eu anomalies. According to the literature, three hypotheses have been proposed for explaining positive Eu anomalies in groundwaters: (i) positive anomalies in the aquifer sediments through which they flow; (ii) preferential dissolution of Eu–enriched minerals (e.g., plagioclase); and (iii) preferential mobilization of Eu^{2+} during water–mineral interaction compared with the trivalent REE (Banks et al., 1999, Nelson et al., 2004, Leybourne & Johannesson, 2008).

6. CONCLUSION

Chemical weathering of magmatic and metamorphic source rocks due to fluvial and marine processes is an important factor responsible for the enrichment of heavy minerals in Jurassic sediments of Plavna. Early Jurassic sediments consisted of breccia-conglomerates with organic material and quartz-sandstones are the most interesting mineralogical and petrological environment, in terms of the existence of U and Th–REE mineralization. Mineralization genesis of U is related to weathering processes of primary uranium sources, alteration and mobilization of uranium forms, and formation of secondary minerals in sediments (uraninite or powder pitchblende aggregates and coffinite). EPMA and ICP–MS analysis revealed that LREE (La, Ce, Nd and Pr) are enriched and occur predominantly within monazite of quartz sandstones. Monazite crystals vary in shape and typically are lower than 50 µm in size. The maximum U and Th concentrations in Jurassic sediments were found to be over 1000 ppm, while maximum LREE concentration was 9438.51 ppm and HREE concentration was 687.35 ppm. Hydrochemical investigations showed that the groundwater with the highest U concentration (48.8 µg/l in the borehole) progressively gains U from the orebody along the flow path. All groundwater samples had LREE enrichment with $(La/Yb)_{CN}$ in the range of 8.45 to 59.13 and positive Eu anomalies. ΣREE concentrations in groundwater ranged from 10.01 to 308.87 ng/L, and the highest concentrations were measured in the borehole.

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