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TABLE OF CONTENTS

PLENARY LECTURES

GEOLOGY

THE CHEMICAL COMPOSITION OF Th-BEARING MONAZITES FROM THE JURASSIC SEDIMENTS IN THE PLAVNA AREA, SERBIA

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Abstract

Forty-eight polished section of the lower Jurassic continental sediments with monazites from the Plavna-Sikole region have been analyzed by ore microscopy and electron microprobe. The REEs distribution is subject to important variation, some specimens being particularly rich in Ce, others in La or even in Nd and Pr (the most common member – monazite-Ce). The Ce content is nearly constant (average 24.67 wt% Ce). Substitution of the actinides and Ca for the REE and of Si for P is very limited. The thorium content is high (average 7.74 wt% Th). The content of uranium is below the detection limits of the method (<0.3 wt% U).

***Keywords**: Th-bearing monazite-(Ce), rare earth elements, thorium, sediments, Plavna, Serbia,*

1. INTRODUCTION

Monazite is a rare phosphate mineral with a chemical composition of $(Ce,La,Nd,Th\ldots)PO_4$. It usually occurs in small isolated regular grains, as an accessory mineral in igneous and metamorphic rocks such as granite, pegmatite, schist, and gneiss. These grains are resistant to weathering and become concentrated in soils and sediments downslope from the host rock [1].

Monazite is a primary ore of several rare earth elements most notably thorium, cerium and lanthanum. The lanthanide contraction is responsible for the great geochemical divide that splits the lanthanides into light- and heavy-lanthanide enriched minerals, the latter being almost inevitably associated with and dominated by yttrium. The geochemical divide has put more of the light lanthanides in the Earth's crust, but more of the heavy members in the Earth's mantle. All these metals have various industrial uses and are considered quite valuable. Thorium is a highly radioactive metal and could be used as a replacement for uranium in nuclear power generation. Monazite, therefore, is an extremely important ore mineral [2].

Monazite is known more for where it accumulates instead of where it forms. Monazite is one of the most resistant minerals and becomes concentrated in the weathering debris. The soils and sediments found near a weathering outcrop can have high concentrations of monazite than the source rock. The liberated grains of monazite then begin a journey downslope. Eventually, they are brought to a stream or a dry wash. There, the actions of gravity and running water help heavy grains of monazite and other heavy minerals separate from light minerals. They accumulate behind boulders, on the inside bends of stream channels and work their way down into the lower portions of the sediment deposit. Some are washed to the sea where they accumulate in deltaic, beach, or shallow water sediments [3].

2. GEOLOGICAL SETTINGS

The investigation area of Plavna-Sikole, belonging to the Zaječar region, is situated in North-East Serbia between towns of Majdanpek and Negotin. The area includes terrains of Plavna which were the subject of geological research, in terms of tectonic belongs of Miroč anticlinorium, which made the Cambrian chlorite-sericite and actinolite schists, Cambrian granites and granite-gneisses, Paleozoic gabbros and serpentines, Permian granitoids, rhyodacites and quartz porphyry, andesites and Jurassic and Cretaceous sediments.

The Jurassic sediments cover Paleozoic formations and granitoids. These sediments are represented by a series of conglomerates, quartz and clay sandstones, and shales. The conglomerates are composed of well-rounded fragments of gneiss, quartzite and granitoid. At higher levels (the middle Lias) these sediments turn into brown and yellow quartz sandstones and sandy limestones laying over sediments concordant to lower Lias. Uranium and thorium mineralization are found in the lower levels of Jurassic sediments of the continental facies (conglomerates and sandstones) located between the granite in the basement and sediments of marine facies in the shelf.

In the southern part of the field where thorium anomalies were registered emphasizes the presence of lanthanide - cerium subgroup with contents of Ce and La up to 4,600 and 2,350 ppm, respectively. Apart from these REEs, anomalous values were also registered for dysprosium, erbium, europium, gadolinium, hafnium, holmium, neodymium, promethium, samarium, yttrium and ytterbium [4].

3. MINERALOGY AND CHEMICAL COMPOSITION

Mineral composition of the investigated REE-Th mineralization vary. It is composed mainly of gangue minerals (quartz, silicates), with the distinguished occurrences of Th-bearing monazite-(Ce), zircon, rutile, thorianite, xenotime-(Y), apatite. Pyrite, scheelite, magnetite, limonite-goethite, hydrohematite, leucoxene, secondary minerals of Th and U, also occur but in a less extent [5]. Clastic structures with the appearance of the relatively uniform grains, which have been extensively corroded (up to 10 mm) are characteristic for this mineralization.

Monazite occurs in small isolated long prismatic to tabular crystals up to 100 μm (Figs. 1, 2); luster vitreous to resinous; sometimes weakly radioactive and metamicted [5]. Colors range from yellow, brown, red-brown, to orange. Based on the Electron Micro-Probe analysis (EPMA) its chemistry is very complex, corresponding to Th-bearing monazite-(Ce). According to the twenty-five EPMA the crystallochemical formula of Th-bearing monazite-(Ce) is as follows (min-max): $(Ce_{0.34-0.47},La_{0.16-0.28},Nd_{0.11-0.25},Th_{0.01-0.23},Pr_{0.03-0.06},Ca_{0.01-0.05},Sm_{<0.01-0.04},Gd_{<0.01-0.03})_{0.89-1.03}(P_{0.81-1.05},Si_{<0.01-0.22})_{0.99-1.09}O_{3.99-4.03}$. Besides Ce, La, and Nd, monazite contains large amounts of Th ranging from 0.89 to 21.38 wt%.

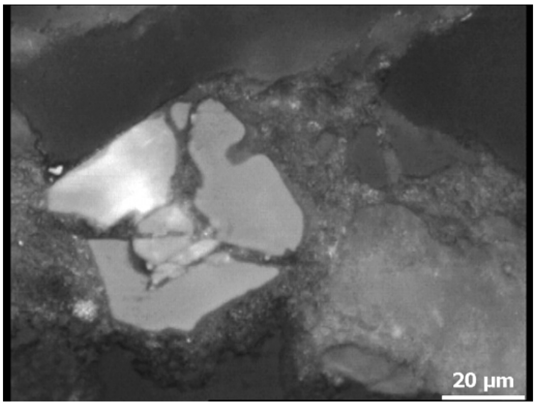

Fig. 1 Cataclased crystal of monazite. Reflected light, in air, II N.

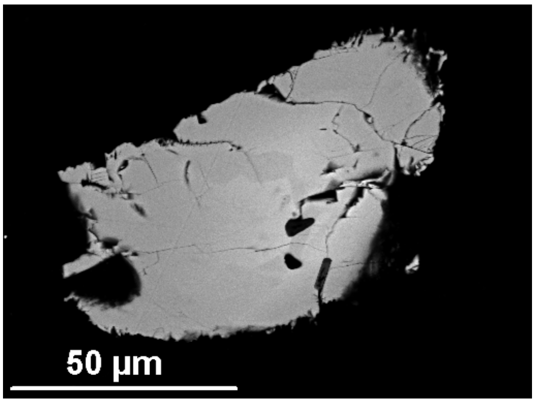

Fig. 2 Cataclased zoned crystal of monazite (bright surface have higher Th). BEI.

The second most abundant mineral is zircon, distinguished by idiomorphic, chunky and commonly zoned crystals with different and regular cross sections (Fig. 3). Based on the EPMA, its chemistry is also complex with increased contents of U and Th. EPMA gave an average crystallochemical formula: $(\mathrm{Zr}_{0.93},\mathrm{Ca}_{0.02},\mathrm{Fe}_{0.02},\mathrm{Sc}_{0.01},\mathrm{Hf}_{0.01},\mathrm{Th}_{0.01},\mathrm{U}_{0.01})_{1.01}(\mathrm{Si}_{0.98},\mathrm{Al}_{0.03})_{1.01}\mathrm{O}_{3.98}$ (6 analyses). Uranium and Th contents range from <0.3 to 11.17 and from <0.3 to 2.16 wt%, respectively.

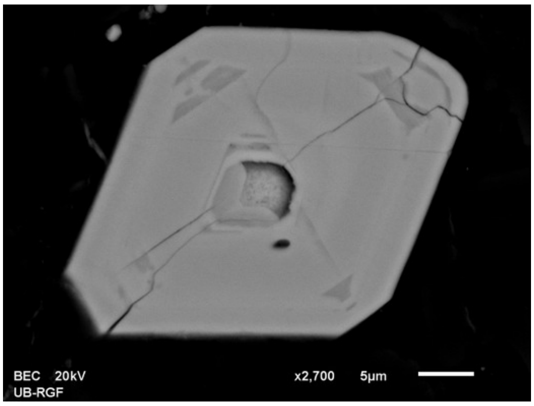

Fig. 3 Regular cross sections a zircon crystal. BEI.

Thorianite was only thorium mineral examined by EPMA. An average crystallochemical formula amounts to this: $(\mathrm{Th}_{0.80},\mathrm{Y}_{0.11})_{0.90}(\mathrm{Si}_{1.01},\mathrm{Al}_{0.03},\mathrm{P}_{0.02})_{1.06}(\mathrm{O}_{3.87},\mathrm{F}_{0.17})_{1.06}$ (3 analyses). Besides thorianite, there are several secondary minerals of Th (27.88 do 52.69 wt%) with U contents ranging from <0.3 to 9.45 wt% (phosphates, carbonates, hydroxides, sulfates…?).

Xenotime-(Y) is less present. EPMA yielded an average crystallochemical formula: $(\mathrm{Y}_{0.74},\mathrm{Dy}_{0.05},\mathrm{Er}_{0.04},\mathrm{Yb}_{0.03},\mathrm{Gd}_{0.03},\mathrm{U}_{0.03},\mathrm{Th}_{0.01},\mathrm{Ca}_{0.01})_{0.95}(\mathrm{P}_{0.94},\mathrm{Si}_{0.10})_{1.04}\mathrm{O}_{4.00}$ (3 analyses).

DISCUSSION

Chemical analyses of REEs of a large number of samples (480) are summarized in Table 1 [4]. These results clearly indicate the perspective of an investigation area which is reflected in the quality of mineralization, i.e., the content of individual REEs in Jurassic sediments (gravel and sands) in the Plavna area.

Table 1

Elements	Min	Max	Average
Y	121	312	182
Zr	29	603	58
La	100	2,270	840
Ce	150	4,460	350
Pr	26	507	220
Nd	90	1,955	480
Sm	20	370	74
Eu	3	7	5
Gd	30	219	47
Tb	10	24	15
Dy	2	91	11
Ho	3	12	7
Er	6	20	9
Tm	0.97	1.75	0.25
Yb	6	7	5
Lu	0.14	0.96	0.25
Hf	2	20	8
Th	100	>1,000	180
U	2	>1,000	16

The presence of monazite is very important in terms of the possibility of its utilization for obtaining REEs, as well as a possible raw material for thorium.

Monazite is an important ore for thorium, lanthanum, and cerium. It is often found in placer deposits. India, Madagascar, and South Africa have large deposits of monazite sands. The deposits in India are particularly rich in monazite. Monazite is radioactive due to the presence of thorium and, less commonly, uranium. Because of its radioactive nature, monazite is a useful for radiometric dating of geological events, such as crystallization, heating, or deformation of the rocks containing monazite [2].

Thorium and its compounds have relatively few uses. The most important thorium compound commercially is thorium dioxide. This compound has the highest melting point of any oxide, about 3,300°C. It is used in high-temperature ceramics. A ceramic is a material made from earthy materials, such as sand or clay. Bricks, tiles, cement, and porcelain are examples of ceramics. Thorium dioxide is also used in the glass industry and as a catalyst. A catalyst is a substance used to speed up or slow down a chemical reaction without undergoing any change itself [6].

Thorium has long been known as a potential source of nuclear fuel to produce electricity. The United States government first built an electricity-only nuclear reactor in Shippingport, Pennsylvania in 1957 as part of President Eisenhower's "Atoms for Peace" initiative. This relatively small reactor ran on thorium from 1977 to 1982. However, thorium is much different than uranium when used as a nuclear fuel. It is not fissile; meaning it cannot go "critical" and generate a nuclear chain reaction. It must undergo neutron bombardment to produce a radionuclide that can sustain a nuclear reaction. A thorium-fueled reactor must be jump-started with a fissile isotope such as uranium (U^{235}) and/or plutonium (Pu^{239}; Pu^{241}). Neutron bombardment of thorium results in this reaction: Th^{232} + Neutron = U^{233} [6].

Thorium as nuclear fuel is clean and safe and offers significant advantages over uranium. The technology for several types of thorium reactors is proven, but still must be developed on a commercial scale. In the opinion of M. Fulp [6] in the world there is at least a decade away from any major commercialization of thorium nuclear reactors and that it is likely to happen in India and China. He also thinks there could be a near-term synergy between a REE producer that processes monazite for its REE content and consigns thorium to a government or private entity seeking a source of thorium for nuclear fuel.

Previous research of the Th mineralization were not interesting for detailed research in terms of energy resource. Besides U, however, the aim of this study is to resume investigation from the aspect of Th and REEs by analogy with similar occurrences and deposits worldwide.

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