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AUTHIGENIC MINERALS OF NICKEL AND RARE EARTH ELEMENTS IN KARSTIC BAUXITES AND KARSTIC NICKEL DEPOSITS IN YUGOSLAVIA AND GREECE

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ABSTRACT

The majority of the authigenic minerals of nickel and rare earth elements were found in the karstic bauxites and karstic nickel deposits in Yugoslavia and Greece. The list of these minerals with their structural formulae is given, and conditions of formation are briefly discussed.

INTRODUCTION

The study of nickel and rare earth elements (REE) in the karstic environment is important both from scientific and practical reasons. These elements play an important role in understanding of genesis of karstic bauxites and karstic nickel deposits. Practical reasons are exhibited in the existence of karstic nickel deposits, which may attain the highest nickel content of all nickel deposits of exogenic origin. Rare earth elements (Y, La-Lu) could be very much enriched, as nickel, above the footwall limestones of bauxite deposits. In some cases, these bauxites represent a valuable raw material for chemical separation of the REE. In most cases, the high enrichment of nickel and REE in karstic environment is connected with the occurrence of their authigenic minerals.

In this paper authigenic minerals of nickel and REE, found mainly in the deposits of Yugoslavia and Greece, are briefly presented with new information on this subject.

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NICKEL IN BAUXITES AND IN KARSTIC NICKEL DEPOSITS

In genetic sense there is no difference between karstic bauxites and karstic nickel deposits. Deposits of transitional character exist between these two end types. This is based on the fact that karstic environment is acting as geochemical barrier to descending solutions carrying nickel. If nickel content in these solutions is relatively high, then this element is enriched above the footwall limestone in the form of authigenic nickel clay minerals (Maksimović, 1978). By strong drainage of

Table 1 - Nickel content in some karstic bauxites and karstic nickel deposits

	Average nickel content of the ore (%)	Maximum nickel content (%)*	Form of the nickel occurrence
Bauxite deposits:			
Vlasenica, Yu, N=279	0.03	0.10 (ore)	not known
Les Codouls, France, n=17	0.05	25.13 (mineral)	Takovite
Sideritis, Parnass Mt., Greece, n=4	0.08	0.18 (ore)	Takovite
Mandra 2, Greece, n=7	0.09	0.70 (ore)	Ni-serpentine
Grebnik, Serbia, n=28	0.16	5.10 (mineral)	Ni-chlorite
Marmara, Greece, n=7	0.34	23.30 (mineral)	Brindleyite
Karstic nickel deposits:			
Marmeiko, Greece, n=9	0.80	2,75 (ore)	not known
Neon Kokkinon, Greece, n=16	1.13	4.00 (ore)	Nepouite
Village Ba, Serbia, n=16	2.20	26.29 (mineral)	Nepouite

n=number of samples * in the basal part of the deposit

descending waters, nickel appears in the form of authigenic minerals even with 0.05% Ni in the mean bauxitic mass. That was the case of **takovite** in Les Codouls bauxite deposit in South France (Table 1).

Typical karstic nickel deposits include: a) deposits of Ni-Fe ores in karstic environment, like Neon Kokkinon, Marmeiko, Agios Ioannis in the Central Greece, and b) nickel deposits in limestone, in the village Ba, Serbia (Maksimović, 1973). There are several well-studied deposits of transitional character, between bauxites and karstic nickel deposits, like: Mandra II and Marmara, in the Central Greece (Papastamatiou and Maksimović, 1970; Maksimović, 1979), the bauxite deposit Les Codouls in South France (Maksimović and de Weisse, 1979), and the Grebnik bauxite deposit in South Serbia (Maksimović, 1978). Parts of the Vlasenica bauxite deposits in Bosnia belong also to transitional type (Maksimović et al., 1983).

AUTHIGENIC NICKEL MINERALS

In the karstic environment silica is not as abundant as in the weathering crusts of ultramafic rocks in the Balkan Peninsula. In latter

Table 2 - Authigenic nickel minerals in karstic bauxites and karstic nickel deposits

Mineral	Structural formula
Nepouite [1] :	$(Ni_{2.78}\ Mg_{.22})_{3.00}\ Si_{2.00}\ O_5\ (OH)_4$
Brindleyite [2] :	$(Ni_{1.75}\ Al_{1.00\ \ .25})_{3.00}\ (Si_{1.50}\ Al_{.50})_{2.00}\ O_5\ (OH)_4$
Takovite [3] :	$Ni_6\ Al_2\ (OH)_{16}\ CO_3 \times 4H_2O$

[1] Village Ba (Maksimović, 1973); [2] Marmara deposit, Greece (Maksimović and Bish, 1978); [3] Takovo, Serbia; Australia (Maksimović, 1957, 1973 Bish and Brindley, 1977).

case, **pimelite**, $(Ni,Mg)_3\ Si_4O_{10}\ (OH)_2 \times 2H_2O$, mineral with four Si atoms in the structural formula, has been formed (Maksimović, 1973). In the karstic nickel deposits, silica is less abundant and authigenic nickel mineral is usually **nepouite**, mineral with two atoms of Si in the structural formula (Table 2). The occurrence of this mineral is

especially exhibited in the nickel deposit of this type in the village Ba, in Serbia. In this case, the highest Ni/Mg ratio in this mineral is attained, approaching to pure **nepouite**, the nickel end member of the isomorfous series **nepouite-lizardite**. **Nepouite** has been discovered also in the karstic nickel deposits in Greece, in Lokris area (Kurzweil, 1966; Maksimović, 1973; Rosenberg, 1984).

In the deposits of transitional character, between bauxites and karstic nickel deposits, there is less silica in the weathering solutions and more alumina. Therefore, under these conditions minerals have been formed with less silicium (**brindleyite**), and even without this element (**takovite**). In these minerals aluminium is another dominating element (Table 2). In this way, Ni^{2+} and Al^{3+}, which are usually separated in the lateritization process, form unusual associations in the karstic environment. **Takovite** has been discovered in the village Takovo in Serbia (Maksimović, 1957, 1970), and also in the bauxites of Parnass Mountain in Greece (Bardossy and Mack, 1967), and South France (Nicolas and Kotschoubey, 1972; Maksimović and de Weisse, 1979), as well as in some karstic nickel deposits of the Lokris area in Greece (Rosenberg, 1984). Karstic nickel deposits have been exploited in Greece. Nickel deposit of these type in the village Ba, in Serbia, is of limited extent, but with very rich nickel ore.

REE IN BAUXITES AND IN KARSTIC NICKEL DEPOSITS

First investigation of the REE in karstic bauxites has shown that these elements are also "mobile" as nickel, in the bauxitization process, and are enriched in the lowermost part of the deposit (Maksimović, 1976; Maksimović and Roaldset, 1976). With relatively high REE content in initial bauxitic material (Table 3), and the strong bauxitization process, authigenic REE minerals could be formed in the contact zone between bauxite and the footwall limestone.

Table 3 - Content of the total REE in some karstic bauxite deposits

Deposit	Average REE content (ppm)	Maximum REE* content (%)	Form of REE occurrence
Vlasenica, Yu, n=59	1140	11.3 (mineral)	Nd-goyazite, bastnaesite
Štitovo, Yu, n=9	1320	76.0 (mineral)	Hydroxylbastnaesite-(Nd)
Grebnik, Yu, n=14	1450	52.6 (mineral)	Synchysite-(Nd)
Marmara, Greece, n=6	1582	75.9 (mineral)	Monazite-(Nd), bastnaesite

* in the basal part of the deposit

AUTHIGENIC REE MINERALS

In the karstic nickel deposits in Greece, enrichment of the REE has been observed above footwall limestone (Maksimović, 1978; Rosenberg, 1984; Skarpelis et. al., 1990). In some of these deposits the authigenic REE minerals were discovered in the form of **bastnaesite** (Rosenberg, 1984). These minerals were found in the karstic bauxite deposits of Yugoslavia, Greece, Hungary and Italy, and were described by Maksimović and Pantó (1983). Later, new occurrences have been found, including the new REE mineral from Montenegro, **hydroxylbastaesite-(Nd)** (Maksimović and Pantó, 1985). Apart of that, the new minerals were discovered in the Marmara bauxite deposit in Greece - **monazite-(Nd)**, and in Grebnik bauxite deposit in South Serbia - **synchysite-(Nd)** (Maksimović and Pantó, 1980, 1981). The list of the authigenic REE minerals with structural formulae is presented in Table 4.

The majority of the authigenic REE minerals are fluorocarbonates of the **bastnaesite group**. Authigenic REE phosphates are very rare, and occur in very small amount. Phosphates were discovered in the Marmara bauxite deposit in Greece, together with brindleyite (**monazite-Nd**), in the Jurassic bauxites of Montenegro (**churchite**), and in the form of **Nd-goyazite** in the bauxites of Vlasenica.

Table 4 - Authigenic REE minerals in karstic bauxites

Mineral	Structural formula
Monazite-(Nd) [1]	$(Nd,Ce,La\ ...)_{1.00}\ Ca_{.29}\ (P_{3.84}\ S_{.17})\ O_{3.83}$
Monazite-(La) [2]	$(La,Nd,Ce,Pr\ ...)_{1.00}\ PO_4$
Churchite-(Y) [3]	$(Y_{2.12}\ Dy_{.93}\ Gd_{.28}\ Er_{.24})_{4.11}\ PO_4 x\ 2.8H_2O$
Synchysite-(Nd) [4]	$Ca_{1.05}\ (Nd,La,Y...)_{1.00}\ (CO_3)_{1.9}\ F_{1.04}$
Bastnaesite-(Ce) [5]	$Ca_{.07}\ (Ce,La,Nd...)_{1.00}\ (CO_3)_{1.01}\ F_{.82}$
Hydroxylbastnaesite-(Nd) [6]	$(Nd,La,Pr...)_{.99}\ (CO_3)_{1.03}\ [(OH)_{.56}\ F_{.58}]$
Hydroxylbastnaesite-(La) [7]	$(La.Nd,Pr...)_{1.12}\ (CO_3)_{1.00}[(OH)_{.15}\ F_{.58}]$
Bastnaesite-(Ce) [8]	$(Ce,Nd,La...)_{1.00}\ (CO_3)_{1.02}\ F_{.78}$
Nd-goyazite [9]	$Ca_{.26}Sr_{.46}\ (Nd,Ce,La...)_{.38}\ Al_{3.05}(PO_4)_{1.87}(SO_4)_{.1}(OH)_{8.06}$

[1] Marmara deposit, Greece (Maksimović and Pantó, 1980); [2] Liverovići deposit, Montenegro (Maksimović and Pantó, 1983); [3] Štitovo deposit, Montenegro (Maksimović and Pantó, unpublished results); [4] Grebnik deposit, Serbia (Maksimović and Pantó, 1981); [5] Nagyharsany deposit, Hungary (Maksimović and Pantó, 1983); [6] Zagrad deposit, Montenegro (Maksimović and Pantó, 1985); [7] Liverovići deposit, Montenegro (Maksimović and Pantó, 1983); [8] Vlasenica deposit, Bosnia (Maksimović and Pantó, unpublished results); [9] Vlasenica deposit, Bosnia (Maksimović and Pantó, 1985).

Authigenic REE minerals were found in the Mediterranean region in many bauxite deposits of Cretaceous age, in concentrations visible only by high magnification. The highest REE concentration in the karstic bauxites, found so far in the world, were recorded in the Jurassic bauxites of Montenegro in the form of **hydroxylbastnaesite-(Nd,La)**. This mineral occurs as a typical authigenic mineral in the red boehmitic bauxite, in the lower part of the deposit, following the contact zone

bauxite/footwall limestone, up to 2m in thickness. The highest concentration was observed immediatelly above the footwall, where it forms whitish spots, locally a few millimeters in diameter, which are easily visible by eye in the red bauxitic matrix (Maksimović and Pantó, 1987,1991).

The new investigation of bauxites from the old deposit Zagrad in Montenegro, which were left near the footwall after exploitation, has shown a very high content of REE (Nd,La,Pr), up to 6.66%. The average of three samples, taken up to 1m above the footwall, was 2.80% of Nd, La and Pr (Maksimović and Jović, unpublished data). Extraction of these elements from the samples was easily done. Therefore, the Jurassic bauxites from all deposits in Nikšićka Župa, in Montenegro, represent a valuable raw material for economical exploitation of the REE and production of very expensive alloys.

CONCLUSION

Separation and concentration of the authigenic minerals of nickel and REE near the footwall of karstic deposits was result of several factors: a) content of element in the initial weathering material deposited in karstic depressions; b) intensity of leaching of this material by percolating waters in a karstic environment, and c) influence of footwall limestone as an efficient geochemical barrier. High quality bauxites, with very low silica content, have a very high enrichment coefficient of "mobile" trace elements in the basal part of the deposit. That is the case of the REE concentration in the Jurrasic bauxites of Montenegro. According to the available evidence for the formation of authigenic REE minerals, the average content of total REE in the bauxitic material should be greater than 0.1% (Table 3). In the case of high drainage, nickel occurs in the form of authigenic minerals even with 0.05% of Ni in the average bauxite mass. That is the case of **takovite** in the Les Codouls bauxite deposit in South France (Table 1). With the increase of nickel in the initial material, higher concentration of the authigenic nickel clay minerals occur above the footwall, and karstic bauxites pass gradually into karstic nickel deposits.

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