

## Mineralogical and crystallographic characteristics of bauxites from some Grebnik's (Metohija, Serbia) ore deposits

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### Key words:

*Grebnik, bauxites, mineralogical, crystallographic and chemical characteristics, diaspore, boehmite, Al-hematite.*

**Abstract.** Five typical bauxite samples from three ore deposits from the wider area of Grebnik Mt. (Metohija, Serbia) were examined with the optical microscopic, X-ray powder diffraction (XRPD) and chemical methods. The occurrences in bauxites were studied and described and the presence of major minerals was determined: diaspore, boehmite and hematite; minor minerals: quartz, goethite, rutile, kaolinite and hydro-hematite; as well as anatase, brookite, magnetite and chromite, which occur only sporadically. According to the quantity of main Al-bearers, three types of bauxite ore were recognized: diaspore, boehmite and boehmite-diaspore. Unit cell dimensions of major minerals were determined, mostly with values within reference data. However, all of the studied hematites have smaller  $a_0$  and  $V_0$  values, most probably due to the substitution of  $Fe^{3+}$  by  $Al^{3+}$ . All samples are further classified as iron-rich and ferritic bauxites. It was found that there were changes in origin conditions between major Al-hydroxides minerals and hematite, as well as between the diaspore and boehmite. Determined chemical compositions put this raw material into high-quality raw materials for obtaining the electro corundum and alumina. The synthesis of the obtained data indicate that Grebnik's bauxites have some unique characteristics, more or less different from most of the World's known bauxite ore deposits.

**Апстракт.** Пет типичних узорака боксита из три рудна лежишта са ширег подручја планине Гребник (Метохија, Србија) су проучавани оптичко микроскопским, рендгенском дифракцијом праха (XRPD) и хемијским методама. Проучаване су и описане појаве у бокситима и утврђено је присуство главних минерала: дијаспора, бемита и хематита; минорних минерала: кварца, гетита, рутила, каолинита и хидрохематита; као и анатаса, брукита, магнетита и хромита, који се јављају само спорадично. Према количини главних носилаца алуминијума, утврђена су три типа руде боксита: дијаспорски, бемитски и бемитско-дијаспорски. Израчунате су димензије јединичних ћелија главних минерала, углавном са вредностима које су у оквиру литературних података. Међутим, сви проучавани хематити имају мање вредности  $a_0$  и  $V_0$ , највероватније услед замењивања  $Fe^{3+}$  са  $Al^{3+}$ . Сви узорци су даље класификовани као гвожђем-богати и феритични боксити. Утврђено је да су се догодиле промене у условима постанка између главних минерала Al-хидроксида и хематита, као и између дијаспора и бемита. Одређени хемијски састави стављају ову сировину у високо-квалитетне сировине за добијање електро корунда и глинице. Синтеза добијених података указује на то да Гребнички боксити имају неке јединствене карактеристике, које се мање или више разликују од већине светски познатих лежишта руде боксита.

### Кључне речи:

*Гребник, боксити, минералогске, кристалографске и хемијске карактеристике, дијаспор, бемит, Al-хематит.*

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## Introduction

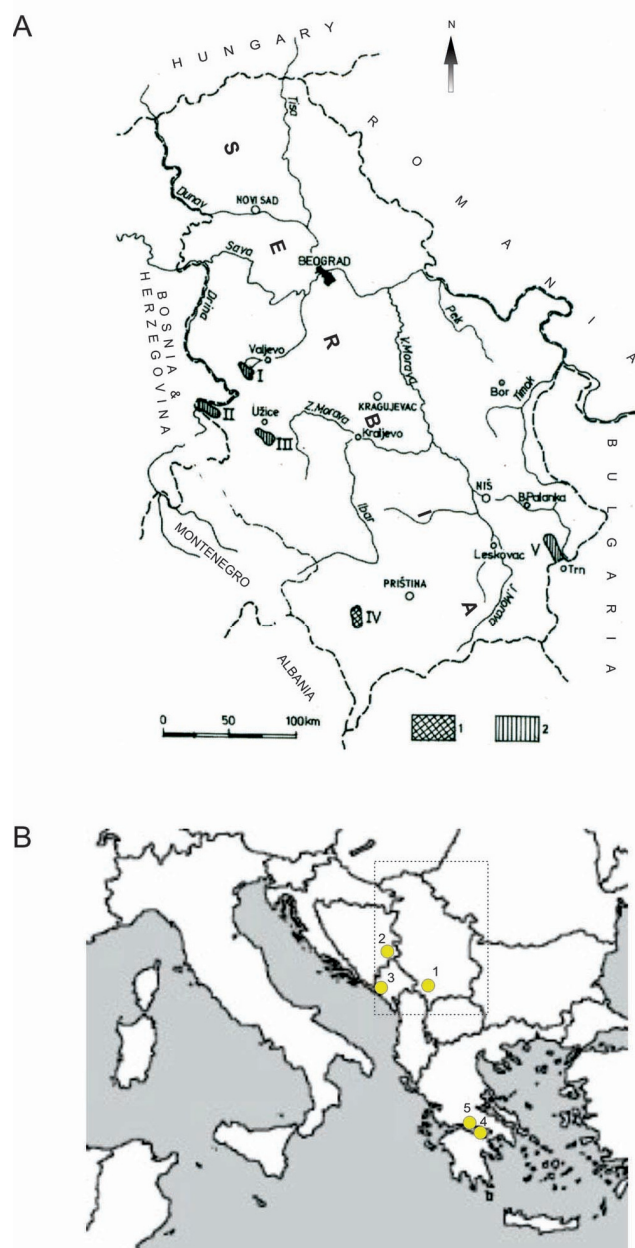
Bauxite resources are the most important ores of aluminium, due to Al-hydroxide minerals, such as gibbsite [Al(OH)<sub>3</sub>], boehmite [γ-AlO(OH)] and diasporite [α-AlO(OH)], together with the iron ore minerals hematite and goethite, kaolinite, quartz and small amounts of rutile and anatase (TiO<sub>2</sub>). Bauxite deposits are commonly classified in three genetic types, i.e. lateritic, karst, and Tikhvin-type, according to mineralogy, chemistry and host-rock lithology (BÁRDOSSY & ALEVA, 1990).

Exploration of the bauxite occurrences and deposits in Serbia started in the early 1950s during the 20th century when Grebnik's karst type bauxites (Metohija, Serbia) were discovered (Fig. 1). The study area belongs to the Inner Dinarides metallogenic province within the Dinaric region, located at the slope of Grebnik Mt. (latitude: N 42° 33' 36", longitude: E 20° 36' 0") in the eastern part of the Metohija basin, 30km east of Peć city within the territory of Klina municipality. Up to now, these bauxites were studied by many authors, and the level of examinations in this area is relatively very high. Although many articles have been published on the geological setting, structure of the ore deposits and occurrences, stratigraphic position, space arrangement, thickness and metallogenic characteristics of the bauxites the mineralogical and especially the crystallographic characteristics of the bauxites has received very little attention.

The oldest data may be found in HISSLEITNER's monograph (1951/52) on the serpentines of the Balkan Peninsula and the Asia Minor which considers the bauxite occurrences in the Grebnik Mt. with typical oolite iron ore deposited in the limestones.

Extensive research was performed during 1954/55 by RIJEVAC (1956), who accomplished the geological map of the Grebnik Mt., diggings and shallows. In this period important occurrences and reserves of the ferrous bauxites from Grebnik were estimated at about 1.500.000 t with remark that they are not suitable for modification with the Bayer's procedure.

The mineralogical features of 14 representative samples from the Grebnik's ore deposit N° 3 were examined, and four types of the mineral raw material, e.g. boehmite, boehmite-diasporite, diasporite-oolite-



**Fig. 1. A)** Overview map of the bauxite location terrains in Serbia (after TIMOTIJEVIĆ, 1997). Roman symbols explanation: (I) Počuta, (II) Tara, (III) Mačkat, (IV) Grebnik and (V) Babušnica. Arabian symbols explanation: (1) Upper Cretaceous and (2) Lower Cretaceous. **B)** Map of south-eastern Europe showing selected bauxite occurrences as mentioned in the text: Grebnik, Serbia (1), Vlasenica, Bosnia and Herzegovina (2), Štitovo, Montenegro (3), Marmara, Greece (4) and Parnassos-Ghiona, Greece (5). Position of Fig. 1A is also marked.

pisolite and diasporite type were distinguished by MISIRLIĆ & MITROVIĆ (1969).

According to ARSIĆ (1973), the bauxites lie in the configuration zone with N-S direction from the Dolac village in the north, across the Grebnik Mt., Labučevo and Okovan villages, to the Zatrići village in the south. The zone length is about 15 km, and width 0.5 to 3.5 km. The western border of the bauxite zone is marked by serpentinites (Orahovac peridotite massif) and "diabase-chert" formation, while the eastern border is represented by the overthrust serpentinites and Cretaceous deposits. Bauxite zone sinks to the north beneath the Pliocene sediments, and to the south near the Zatrići village it tectonically thins between two serpentinite thrust faults. In this zone, about 60 bauxite occurrences and ore deposits, some of them either cropping out or being overlain by other deposits, were found.

MAKSIMOVIĆ & PANTÓ (1991) presented the distribution of the rare earth elements (REE, including La-Lu, Y) along Grebnik's vertical profiles. It was established that the REE content has increased 5.9 times during the weathering and bauxitization in a karstic environment and reveals a high enrichment of these elements in the lowermost part of the deposit. High contents of Cr, Ni, and Co are also characteristic.

Appearances of the "dendrite bauxites with *terra rossa*" were studied by DANGIĆ & PODUNAVAC (1993). During the previous investigations a unit "terra rossa with bauxite fragments" was recognized. In this unit local important bauxite occurrences occur.

TIMOTIJEVIĆ (1997, 2001) concluded that one half of the ore deposit is located at the surface, while the rest were found in boreholes at depths from 20 to 200 m below the overlying rocks. Ore bodies are mostly lenticular-strip, rare with anomalous shapes, with same strike and dip as the Cretaceous series. Bauxites in paleo-karst of the Turonian limestones have very rough substratum and almost always flat hanging wall. Quantity of the ore bodies considerably changes in the range from 1.000 to 2.000.000t, while the bauxite thickness in ore deposits reaches more than 25 m.

The aim of this paper is to present in detail the mineralogical, crystallographic and chemical characteristics of five bauxite samples from three Grebnik's ore deposits. Another goal was to compare obtained results with other bauxite ore deposits from Grebnik Mt., Serbia, Serbia's surroundings, as well as other worldwide bauxite ore deposits.

## Materials and methods

From the three Grebnik's ore deposits (N° 6, N° 21 and N° 22), five typical representative bauxite samples were picked from the surface (labeled as: B-1, B-2, B-3, B-4 and B-5). These samples were further studied by an optical microscopic, X-ray powder diffraction (XRPD) and chemical analysis.

Optical microscopic study has mainly been carried out with reflected light microscope on polished sections. These studies were only sporadically combined with those performed by transmitted light microscope and thin sections, due to a further better and reliable identification of some mineral species. Eight most characteristic occurrences were photographed (Figs. 2 and 3) with the magnification of 50× (A, B, D and E); 100× (C and F; under cedar's oil); and 500× (G and H; under cedar's oil).

The X-ray powder diffraction (XRPD) studies were performed by automatically diffractometer for powder "PHILIPS", model PW-1710. The long-focus (LFF) Cu-anode (U = 40 kV and I = 30 mA) was used, with the monochromatic  $K\alpha_1$  radiation (wave-length  $\lambda = 1.54051 \text{ \AA}$ ) and the Xe proportional counter. Diffraction data were collected in the angle range  $2\theta$  from  $5^\circ$  to  $65^\circ$  with a scanning speed of keeping back with 1 second on every  $0.02^\circ$ . For measurement of the angle positions of diffraction maximums and their belonging intensities the base program PW-1877 was used. Precision of the diffractometer was controlled before and after experiment with the metallic Si powder. Identification of the present mineral phases (qualitative analysis) was done with comparison of the interplanar spacings (d) and relative intensities (I) with the literature data which corresponds card from the ICDD-PDF database. Semi-quantitative analysis was performed by the RIR (relative intensity ratio) method. Calculations of the unit cell dimensions were accomplished with the LSUCRI program for personal computer (GARVEY, 1987).

For determination of the main chemical components in the bauxites:  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and CaO an atomic absorption spectrophotometer method with instrument Perkin-Elmer ICP 6500, hybrid system with optic for AAS-500 and flame technique FAAS were used. Contents of  $\text{H}_2\text{O}^+$  and  $\text{H}_2\text{O}^-$  were determined by gravimetric method.

## Results and discussion

### Optical microscopic study

With macroscopic observations it can be concluded that all of the studied bauxite samples are dark-grimly-red in color. Characteristic shapes and occurrences in the bauxite ores are presented in Figures 2 and 3.

Mineral compositions and appearances of the minerals are not the same in all polished thin sections, mainly depending by the amounts of hematite and limonite. Scattered forms, which appears as gels form the cement of oolites. Dominate form represents combination of the compact mass and oolitic aluminum-hydroxide structures (Figs. 2A and 2C), mostly equally arranged and quantitatively with different contents. Metallic mineral composition in relative quantity is: hematite, hydro-hematite and limonite (Figs. 2B, 2D and 3E-G).

*Hematite* is the most abundant metallic mineral, and it appears in different amounts. Mostly it occurs in mass shapes with different sizes resulted from hydro-hematite transformation (Figs. 3E-G). Also, it occurs as fine disperses particles which penetrate the whole aluminum-hydroxide base and simultaneously pigments it. Furthermore, it is present as oolitic grains, which are either fresh or transformed into limonite. Its smaller crystals are mostly broken, and like this cemented in the bauxite basis (sample B-1). Only locally, it is present in small accumulations, when it is covered with fine disperse limonite, so it looks like honey-comb and vein structure (sample B-2).

*Hydro-hematite* is mostly present as bespattered and oolite grains with different dimensions. At certain cases dimension of the oolite-pisolite is 0.2–0.5 cm (samples B-2, B-3 and B-4). Oolites and pisolites are impressed, and in the same time also cemented in the Al-hydroxide basis. At the surface of the oolite shapes, it is clearly evident the separation from hematite according to different anisotropy characteristics. Appart the fresh hydro-hematite grains, the grains transformed into limonite through different stages are also present (Fig. 3E). In some oolites is evident zonal alteration of hydro-hematite with limonite, and somewhere it is present zonal separation of hematite in the

hydro-hematite's large oolite grains (Figs. 3F-G). Macroscopically visible large oolites are composed of numerous little oolites of hydro-hematite and hematite. Fractures of these big oolites are filled by Al-hydroxides. At some places, large hydro-hematite grains were completely transformed into limonite (sample B-5).

*Limonitization* is mostly observed in the central parts of the oolites. Small parts of it occur as mass shapes of different sizes, which most often resulted from transformation of hematite.

*Titanium minerals* were established in minor content in all of the samples mainly as rutile, and only sporadically as anatase and brookite. Rutile appears as small prismatic, mostly broken grains, with light-grimly to dark-red color (Fig. 3H).

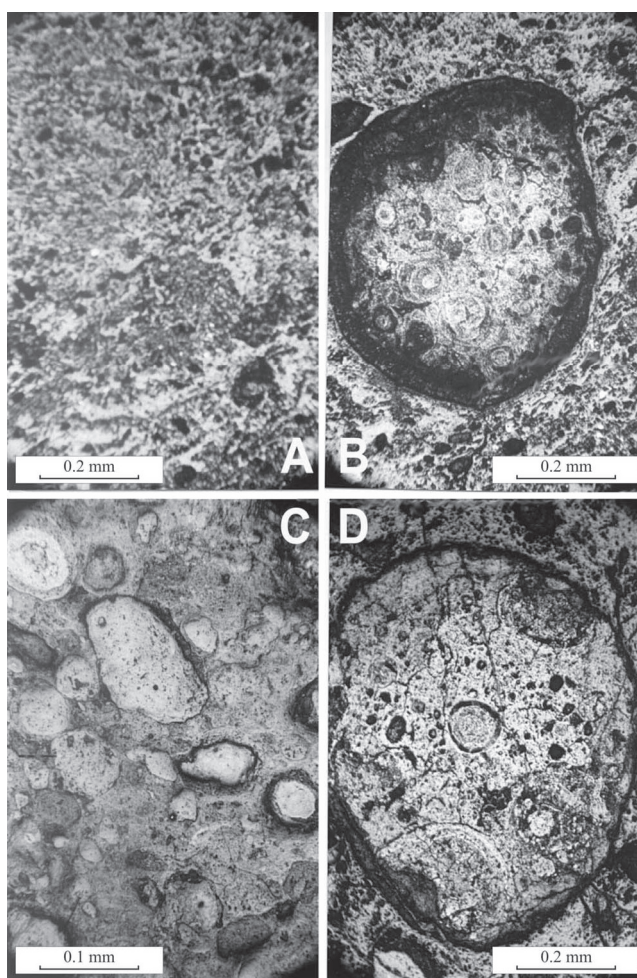
*Magnetite* occurs very rarely with grains of irregular shapes, individually arranged in the base.

Microscopic study highlights different kinds of structure, mostly oolitic and oolitic-pysolithic (Figs. 2 and 3). Besides metallic oolites occurrences of pisolites and nonmetallic oolites of different size are present. Common characteristics of the bauxites from three studied ore deposits are massive rocks, compact, somewhere with conchoidal fracture with clear visible oolites and pisolites with size of 0.5–0.8 cm (Figs. 2A and 2C). Besides oolites, there were noticed plenty of small angular fragments of clay material, and insignificant content of biggest fragments of the sedimentary bauxites, which have the similar structure as main rock, but with somewhat brightness color. By this study it was noticed that the non-metallic oolites are much more abundant than the metallic. The metallic oolites-pisolites are completely formed by metallic mineral, and often are bigger than nonmetallic. Nonmetallic oolites exhibit different characteristics and forms; e.g. they are mostly with or without concentric structure, with small metallic mineral in its nucleus.

It is need to point out that kind of appearance of the described minerals is more-less the same in all of the preparations, with some differences. Namely, in the sample B-1 there is a lack of hydro-hematite, whereas the presence of magnetite is only observed in the sample B-2.

It should be emphasized that minerals of the basis mass of bauxites, which are otherwise dominant in all studied samples, could not be determined by



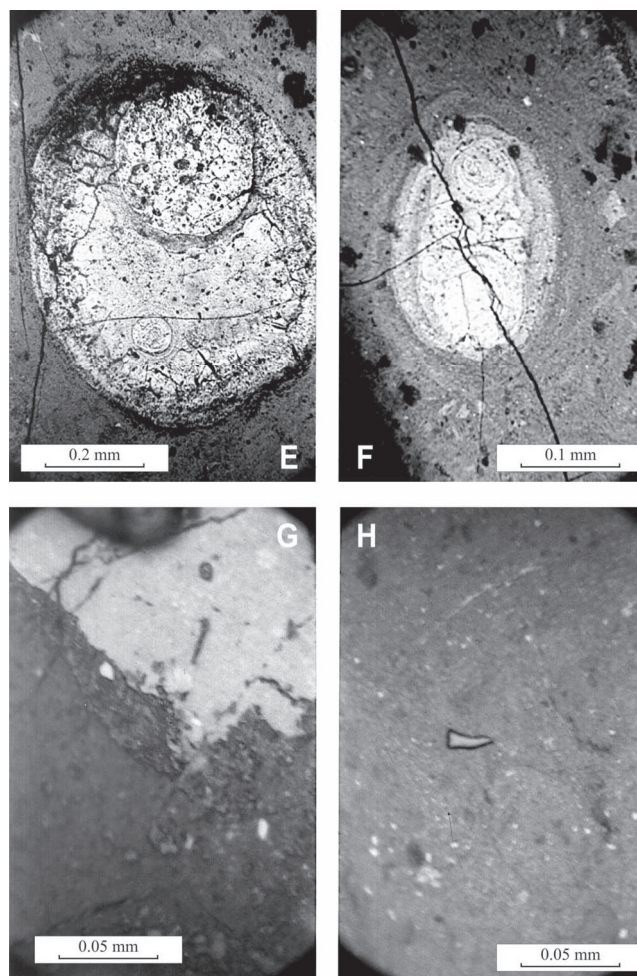


**Fig. 2.** Characteristic shapes and occurrences in the bauxite ores: **A)** compact basis of the bauxite; **B)** bigger oolite contained of more smaller oolites; **C)** oolite basis of the bauxite; and **D)** zonal oolite: Fe-hydroxide, Fe-oxide and nonmetallic part are exchanging.

microscopic methods due to objective reasons, as well as limonite and clay minerals. With further XRPD study (next Chapter) it was established that these are Al-hydroxides, e.g. diasporite and boehmite; limonite phase is specified as goethite; whereas clay minerals were identified only as kaolinite.

### XRPD-crystallographic study

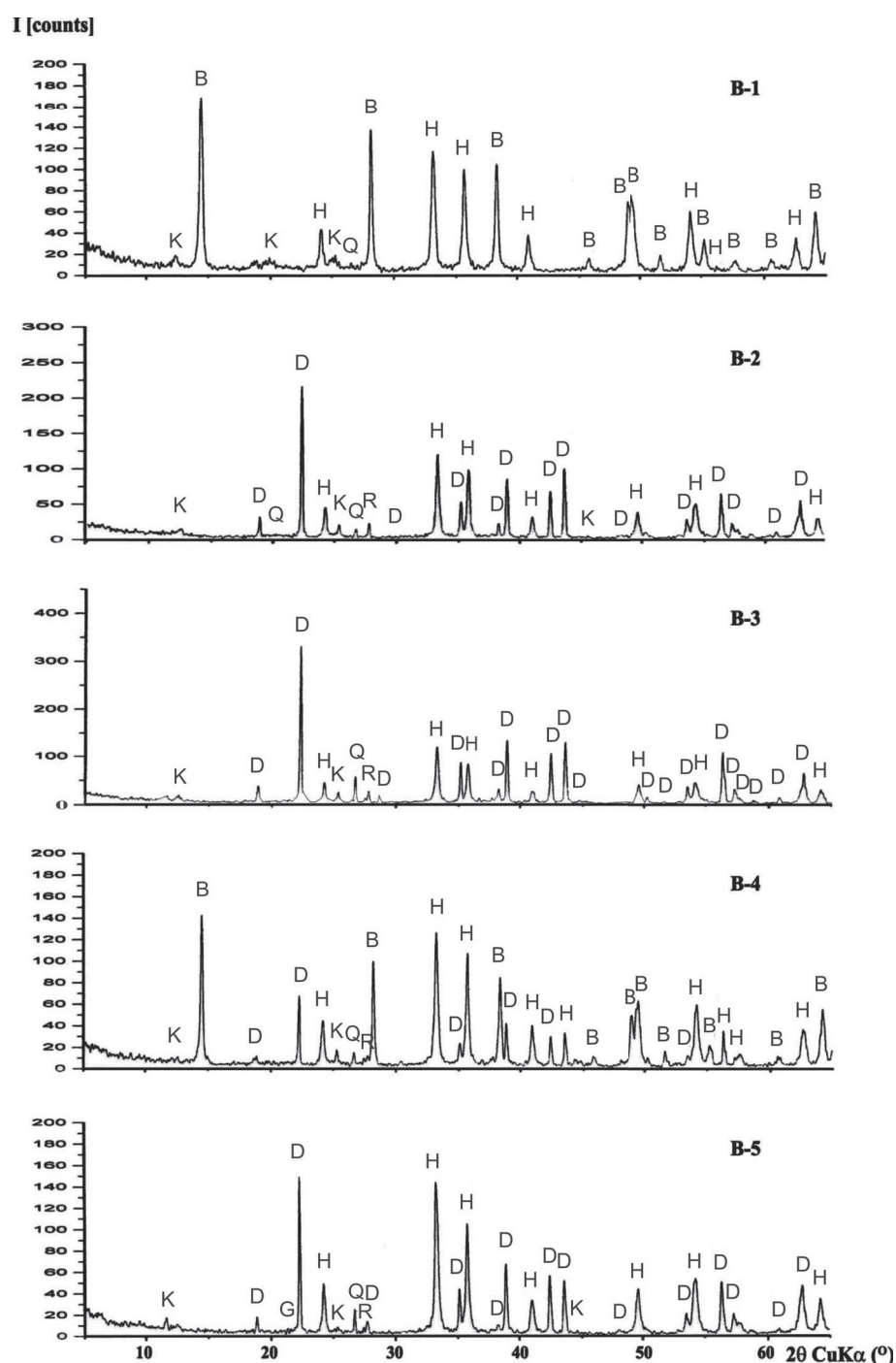
Identified mineral compositions within XRPD studies of the bauxite samples, are presented in Figure 4 and Table 1. It should be mentioned that at places where peak overlapping intensively occur, only main mineral species were presented, due to a



**Fig. 3.** Characteristic shapes and occurrences in the bauxite ores: **E)** included smaller oolite within bigger; change of the grain is comprised by transformation of hematite into hydro-hematite, and further of hydro-hematite into limonite from the end of the grain towards its center; **F)** oolites consisting of hematite and hydro-hematite; their different anisotropy characteristics are clearly visible; **G)** hematite relict remains within hydro-hematite grain; and **H)** broken grain of chromite and few rutile grains cemented in bauxite basis.

better view. The observed peaks are relatively sharp, indicating good crystallinity of the compounds.

By their approximate quantity there were determined following qualitative compositions of the studied bauxite samples: *B-1*: boehmite (~62%), hematite (~29%), kaolinite (~5%) and quartz (~4%). There is almost double quantity of boehmite than hematite; *B-2*: diasporite (~62%), hematite (~31%), quartz (~3%), rutile (~2%) and kaolinite (~2%).



**Fig. 4.** XRPD patterns of the studied bauxite samples with the observed main identified minerals. Marks: **D** - diaspore; **B** - boehmite; **H** - hematite; **Q** - quartz; **G** - goethite; **R** - rutile and **K** - kaolinite.

There is almost double quantity of diaspore than hematite; *B-3*: diaspore (~70 %), hematite (~24 %), quartz (~2 %), rutile (~2 %) and kaolinite (~2 %). There is almost three times quantity of diaspore than

hematite; *B-4*: boehmite (~43 %), hematite (~33 %), diaspore (~21 %), quartz (~1 %), rutile (~1 %) and kaolinite (~1 %). Quantity of boehmite is something higher than hematite, and double than diaspore; and *B-5*: diaspore (~45 %), hematite (~40 %), quartz (~6 %), goethite (~3 %), rutile (~3 %) and kaolinite (~3 %). There is something more diaspore than hematite.

From previous, it is obvious that in the samples where diaspore, boehmite and hematite occurred, their quantities are considerable. These varies from about 45 to 70 % (average 61 %) for Al-hydroxides (either as mono mineral; or in total sum of two phases), and from about 24 to 40 % (average 31 %) for hematite. Therefore, they were considered as major minerals. On the other hand, in all of the samples quantities of quartz, goethite, rutile and kaolinite are relatively very small, i.e. from about 1 to 6 % (average 2.5 %), and they were consequently considered as minor minerals.

According to the quantity of the main Al-bearers, following bauxite types were determined: 1. diaspore type (samples *B-2*, *B-3* and *B-5*), 2. boehmite type (sample *B-1*), and 3. boehmite-diaspore type (sample *B-4*). Diaspore bauxite type is the most

dominant with frequency of occurrence of about 60 %, which is in excellent agreement with data for Grebnik Mt. given by BÁRDOSSY (1982). Taking into account previously observed quantities of Fe, (Al + Ti),



**Table 1.** XRPD data of the studied bauxite samples with their observed intensities ( $I_{\text{obs}}$ , in %); observed interplanar spacings ( $d_{\text{obs}}$ , in Å); and main identified minerals, marked as: D-diaspore; B-boehmite; H-hematite; Q-quartz; G-goethite; R-rutile and K-kaolinite.

B-1			B-2			B-3			B-4			B-5		
$I_{\text{obs}}$	$d_{\text{obs}}$	min.	$I_{\text{obs}}$	$d_{\text{obs}}$	min.	$I_{\text{obs}}$	$d_{\text{obs}}$	min.	$I_{\text{obs}}$	$d_{\text{obs}}$	min.	$I_{\text{obs}}$	$d_{\text{obs}}$	min.
6	7.1296	K	4	7.1583	K	3	7.0195	K	7	7.0931	K	6	7.0860	K
100	6.0581	B	12	4.7039	D	11	4.6805	D	100	6.1080	B	10	4.6990	D
6	4.4736	K	5	4.2480	Q	100	3.9706	D	7	4.7301	D	6	4.1623	G
22	3.6599	H	100	3.9816	D	12	3.6671	H	49	3.9843	D	100	3.9737	D
6	3.5188	K	19	3.6755	H	5	3.4997	K	27	3.6770	H	27	3.6606	H
6	3.3434	Q	8	3.5093	K	3	3.3341	Q	7	3.5181	K	6	3.5120	K
75	3.1510	B	5	3.3410	Q	3	3.2461	R	7	3.3373	Q	16	3.3281	Q
59	2.6912	H	4	3.2478	R	9	3.2079	D	7	3.2420	R	6	3.2437	R
49	2.5086	H	8	3.2145	D	35	2.6917	H	64	3.1620	B	7	3.2060	D
46	2.3432	B	54	2.6943	H	24	2.5527	D	79	2.6987	H	89	2.6924	H,G
49	2.3391	B	23	2.5574	D	27	2.5119	H	79	2.6924	H	27	2.5528	D
15	2.2024	H	45	2.5140	H	7	2.3497	D	13	2.5567	D	62	2.5045	H, G, R
7	1.9763	B	8	2.3562	D	39	2.3131	D	69	2.5130	H	6	2.3494	D
32	1.8591	B	6	2.3391	D	9	2.2018	H	56	2.3455	B	44	2.3128	D
41	1.8452	B, H	42	2.3162	D	35	2.1277	D	29	2.3165	D	19	2.1988	H, G, R
9	1.7652	B	12	2.2039	H, R	40	2.0747	D, H	26	2.2037	H	35	2.1294	D
24	1.6907	H	39	2.1308	D	3	1.8944	D	21	2.1313	D	33	2.0742	D, H
14	1.6586	B	45	2.0772	D, H	10	1.8394	H	23	2.0776	H, D	6	2.0300	K, R
6	1.5953	H	10	2.0270	K, R	4	1.8110	D	7	1.9792	B	6	1.8972	D
6	1.5337	B	4	1.8955	D	3	1.7310	D	33	1.8611	B	25	1.8354	H
6	1.5268	B	16	1.8389	H	9	1.7099	D	39	1.8390	B, H	11	1.7105	D
15	1.4835	H	13	1.7123	D	16	1.6928	H	10	1.7676	B	30	1.6925	H
26	1.4515	B, H	22	1.6934	H	29	1.6331	D, H	7	1.7376	D	32	1.6879	H, R
21	1.4475	B, H	36	1.6329	D, H	9	1.6087	D, H	37	1.6914	H	30	1.6322	D, H
			12	1.6087	D, H	7	1.6026	D, H	13	1.6606	B	10	1.6074	D, H
			4	1.5217	D	3	1.5699	D	24	1.6333	H, D	6	1.5721	D, H
			30	1.4800	D, H	6	1.5226	D	7	1.6085	H, D	28	1.4793	D, H
			12	1.4516	H	21	1.4794	D, H	7	1.5979	H, D	20	1.4493	H
			11	1.4500	H	9	1.4512	H	7	1.5254	B, D			
									21	1.4844	H, D			
									36	1.4515	B, H			

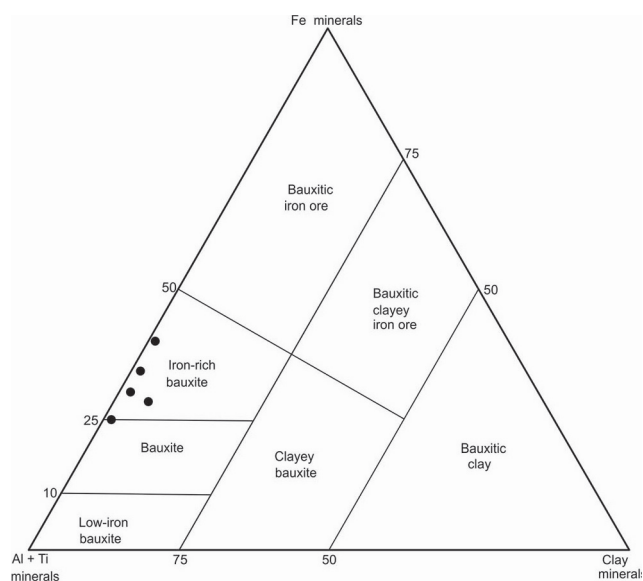
and clay minerals, these samples were classified as iron-rich bauxites (Fig. 5).

Calculated ( $d_{\text{calc}}$ ) and observed ( $d_{\text{obs}}$ ) interplanar spacings, as well as calculated unit cell dimensions of major minerals diaspore, boehmite and hematite, are presented in Tables 2–4.

From these results, it is obvious that studied diaspore and boehmite have values of the unit cell dimensions which are mostly within reference data (Tables 2 and 3). However, all of the studied hematites have smaller  $a_0$  and  $V_0$  values (Table 4). These were certainly not caused by previously microscopically identified hydro-hematite  $[\text{Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}]$  transfor-

mations, because hydroxyl groups can only slightly expand the unit cell dimensions (STANJEK & SCHWERTMANN, 1992). There is also theoretical possibility that  $\text{Fe}^{3+}$  ion could be substituted by  $\text{Ti}^{4+}$  ion. However, despite that  $\text{Ti}^{4+}$  ion is smaller than  $\text{Fe}^{3+}$  ion at octahedral position (0.605 Å vs. 0.645 Å, respectively; SHANNON & PREWITT, 1969), it seems that such substitution even slightly expand the hematite unit cell dimensions (NIKOLIĆ et al., 2013). Furthermore, decrease of  $a_0$  and increase of  $c_0$  values with increasing of Ti content were determined by ZHAO et al. (2011).

On the other hand, most probably cause for such phenomenon is due to the substitution of  $\text{Fe}^{3+}$  by  $\text{Al}^{3+}$



**Fig. 5.** Ternary plot for the system of Fe, (Al + Ti), and clay minerals (after BÁRDOSSY, 1982) showing the positions of the studied Grebnik Mt. bauxite samples data points.

**Table 2.** Values of the calculated ( $d_{calc}$ ) and observed ( $d_{obs}$ ) interplanar spacings (in Å); as well as calculated unit cell dimensions of diaspore.

ICDD-PDF 5-0355	B-2		B-3		B-4		B-5		
h k l	d	$d_{calc}$	$d_{obs}$	$d_{calc}$	$d_{obs}$	$d_{calc}$	$d_{obs}$	$d_{calc}$	$d_{obs}$
0 2 0	4.7100	4.7121	4.7039	4.7051	4.6805	4.7262	4.7301	4.7093	4.6990
1 1 0	3.9900	3.9873	3.9816	3.9840	3.9706	3.9848	3.9843	3.9832	3.9737
1 2 0	3.2140	3.2162	3.2145	3.2128	3.2079	/	/	3.2134	3.2060
1 3 0	2.5580	2.5568	2.5574	2.5537	2.5527	2.5606	2.5567	2.5548	2.5528
0 4 0 $\alpha_1$	2.3560	2.3560	2.3562	2.3526	2.3497	/	/	2.3547	2.3494
0 4 0 $\alpha_2$	2.3560	2.3560	2.3391*	/	/	/	/	/	/
1 1 1	2.3170	2.3161	2.3162	2.3134	2.3131	2.3190	2.3165	2.3137	2.3128
1 2 1	2.1310	2.1310	2.1308	2.1285	2.1277	2.1343	2.1313	2.1290	2.1294
1 4 0	2.0770	2.0771	2.0772	2.0744	2.0747	2.0813	2.0776	2.0756	2.0742
1 3 1	1.9010	1.9018	1.8955	1.8994	1.8944	/	/	1.9001	1.8972
0 4 1	1.8150	/	/	1.8121	1.8110	/	/	/	/
1 5 0	1.7330	/	/	1.7302	1.7310	1.7366	1.7376	/	/
2 1 1	1.7120	1.7116	1.7123	1.7100	1.7099	/	/	1.7098	1.7105
2 2 1	1.6330	1.6327	1.6329	1.6311	1.6331	1.6332	1.6333	1.6311	1.6322
2 4 0 $\alpha_1$	1.6080	1.6081	1.6087	1.6064	1.6087	1.6091	1.6085	1.6067	1.6074
2 4 0 $\alpha_2$	1.6080	/	/	1.6064	1.6026	1.6091	1.5979*	/	/
0 6 0	1.5700	/	/	1.5684	1.5699	/	/	1.5698	1.5721
2 3 1	1.5220	1.5225	1.5217	1.5209	1.5226	1.5235	1.5254	/	/
1 5 1	1.4800	1.4798	1.4800	1.4778	1.4794	1.4832	1.4844	1.4787	1.4793
$a_0$ (Å)	4.396	4.401(2)		4.398(5)		4.394(6)		4.396(5)	
$b_0$ (Å)	9.426	9.424(3)		9.410(6)		9.452(8)		9.419(6)	
$c_0$ (Å)	2.844	2.845(2)		2.842(4)		2.852(4)		2.842(4)	
$V_0$ (Å <sup>3</sup> )	117.85	118.00(5)		117.6(1)		118.4(1)		117.7(1)	

\*-rejected from the calculations

(STANJEK & SCHWERTMANN, 1992; RUAN & GILKES, 1995), and forming Al-hematite. Namely, at octahedral position  $Fe^{3+}$  ion has ionic radii of 0.645 Å, whereas  $Al^{3+}$  ion has considerable smaller ionic radii of 0.535 Å (SHANNON & PREWITT, 1969). Such substitutions and their influence to the M-O distances and consequently to the interplanar spacings and unit cell dimensions are well known and previously studied, discussed and explained elsewhere in our papers for various solid-solution systems (TANČIĆ, 2005; TANČIĆ et al., 2012a, b).

In present study, contents of  $Fe^{3+}$  by  $Al^{3+}$  substitutions by  $a_0$  and  $V_0$  correlations were calculated from about 2.5 at. % in B-4 sample to about 6.0 at. % in B-5 sample (Table 4). From these, it can be seen that excellent results were obtained for all of the samples, except partially for the B-3 sample, in which content of hematite is the lowest. Therefore, such crystallographic calculations are promising to be useful for similar studies in the future similar bauxite explorations,

especially since MONGELLI (2002) established that the ferruginous concretions, which are geochemical recorders of the environment of formation, have a large core of Al-hematite surrounded by a cortex of alternating Al-hematite and boehmite. Boehmite forms instead of Al-hematite at lower water activity values.

Nevertheless, such smaller  $a_0$  and  $V_0$  values for hematite are already found in nature, and almost identical with those studied in present paper were observed for specularite, a variety of hematite (i.e.  $a_0 = 5.022(3)$  Å and  $V_0 = 300.1(4)$  Å<sup>3</sup>; TANČIĆ et al., 2007).

### Chemical study

Obtained results of the main chemical components are presented at Table 5.

In all of the bauxite samples main bearers of the most



**Table 3.** Values of the calculated ( $d_{\text{calc}}$ ) and observed ( $d_{\text{obs}}$ ) interplanar spacings (in Å); as well as calculated unit cell dimensions of boehmite.

ICDD-PDF 5-0190		B-1		B-4	
h k l	d	$d_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$d_{\text{obs}}$
0 2 0	6.1100	6.1183	6.0581	6.1025	6.1080
0 2 1	3.1640	3.1593	3.1510	3.1602	3.1620
1 3 0 $\alpha_1$	2.3460	2.3410	2.3432	2.3458	2.3455
1 3 0 $\alpha_2$	2.3460	2.3410	2.3391	/	/
1 3 1	1.9800	1.9766	1.9763	1.9803	1.9792
1 5 0	1.8600	1.8591	1.8591	1.8597	1.8611
0 0 2	1.8500	1.8446	1.8452	/	/
0 2 2	1.7700	1.7661	1.7652	1.7679	1.7676
1 5 1	1.6620	1.6602	1.6586	1.6611	1.6606
0 8 0 $\alpha_1$	1.5270	1.5296	1.5337	1.5256	1.5254
0 8 0 $\alpha_2$	1.5270	1.5296	1.5268	/	/
1 3 2 $\alpha_1$	1.4530	1.4488	1.4515	1.4512	1.4515
1 3 2 $\alpha_2$	1.4530	1.4888	1.4415	/	/
$a_0$ (Å)	2.868	2.859(6)		2.871(2)	
$b_0$ (Å)	12.22	12.24(1)		12.205(4)	
$c_0$ (Å)	3.700	3.689(4)		3.694(1)	
$V_0$ (Å <sup>3</sup> )	129.75	129.0(2)		129.45(6)	

important  $\text{Al}_2\text{O}_3$  component are major minerals diaspore (in B-2, B-3, B-4 and B-5) and boehmite (in B-1 and B-4), as well as partly kaolinite, which is minor in all of the samples. These contents are from 45.35 % (in B-5) to 57.60 % (in B-3), with average value of 50.03 %.

Content of silica component  $\text{SiO}_2$ , which is of great importance for the bauxite application, is relatively small. It ranges from 1.98 % (in B-5) to 4.43 % (in B-2). Somewhat higher concentration appears in the sample B-1 (8.40 %). Its average value is 3.95 %. Bearers of the silica component are minor minerals quartz and kaolinite.

For all of the present bauxite mineral raw material it is also important  $\text{Fe}_2\text{O}_3$  contents, which ranges from 23.10 % (in B-3) to 39.60 % (in B-5), and with average value of 30.72 %. Main bearers of iron are major hematite, and minor hydro-hematite and goethite.

Contents of  $\text{TiO}_2$  in all samples are almost equal: from 3.84 % (in B-1) to 4.61 % (in B-2), with average value of 4.21 %. Bearers of this component are minor

**Table 4.** Values of the calculated ( $d_{\text{calc}}$ ) and observed ( $d_{\text{obs}}$ ) interplanar spacings (in Å); as well as calculated unit cell dimensions of hematite. The contents of  $\text{Fe}^{3+}$  by  $\text{Al}^{3+}$  substitutions (in at. %), calculated by  $a_0$ ,  $V_0$  and their average values, are also presented.

ICDD-PDF 33-0664		B-1		B-2		B-3		B-4		B-5	
h k l	d	$d_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$d_{\text{obs}}$
0 1 2	3.6840	3.6730	3.6599	3.6773	3.6755	3.6780	3.6671	3.6774	3.6770	3.6770	3.6606
1 0 4 $\alpha_1$	2.7000	2.6930	2.6912	2.6971	2.6943	2.6996	2.6917	2.6963	2.6987	2.6916	2.6924
1 0 4 $\alpha_2$	2.7000	/	/	/	/	/	/	2.6963	2.6924	/	/
1 1 0	2.5190	2.5109	2.5086	2.5132	2.5140	2.5120	2.5119	2.5139	2.5130	2.5090	2.5045
1 1 3	2.2070	2.2009	2.2024	2.2034	2.2039	2.2036	2.2018	2.2036	2.2037	2.1995	2.1988
2 0 2	2.0779	/	/	2.0749	2.0772	2.0744	2.0747	2.0753	2.0776	2.0714	2.0742
0 2 4	1.8406	1.8365	1.8452*	1.8387	1.8389	1.8390	1.8394	1.8387	1.8390	1.8353	1.8354
1 1 6 $\alpha_1$	1.6941	1.6906	1.6907	1.6930	1.6934	1.6943	1.6928	1.6926	1.6914	1.6896	1.6925
1 1 6 $\alpha_2$	1.6941	/	/	/	/	/	/	/	/	1.6896	1.6879
2 1 1	1.6367	/	/	1.6336	1.6329	1.6329	1.6331	1.6341	1.6333	1.6309	1.6322
1 2 2	1.6033	/	/	1.6000	1.6087*	1.5995	1.6087*	1.6004	1.6085*	1.5974	1.6074*
0 1 8	1.5992	1.5953	1.5953	/	/	1.6005	1.6026	1.5973	1.5979	1.5946	1.5721*
2 1 4	1.4859	1.4823	1.4835	1.4839	1.4800*	1.4839	1.4794*	1.4841	1.4844	1.4813	1.4793
3 0 0 $\alpha_1$	1.4538	1.4496	1.4515	1.4510	1.4516	1.4503	1.4512	1.4514	1.4515	1.4485	1.4493
3 0 0 $\alpha_2$	1.4538	1.4496	1.4475	1.4510	0.4500	/	/	/	/	/	/
$a_0$ (Å)	5.035	5.022(3)		5.026(1)		5.024(2)		5.028(1)		5.018(3)	
$c_0$ (Å)	13.74	13.72(1)		13.74(1)		13.77(1)		13.736(6)		13.71(2)	
$V_0$ (Å <sup>3</sup> )	301.93	299.6(4)		300.7(2)		301.0(3)		300.7(2)		299.0(4)	
substituted $\text{Fe}^{3+}$ by $\text{Al}^{3+}$ (in at. %)	$a_0$	4.6		3.2		3.9		2.5		6.0	
	$V_0$	4.8		2.5		1.9		2.5		6.0	
	average	4.7		2.8		2.9		2.5		6.0	

\*-rejected from the calculations

minerals: rutile, and sporadically anatase and brookite.

**Table 5.** Chemical analysis of the studied bauxite samples (in wt. %); ratios  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  and  $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ ; and calculated coefficients  $K_i$  (by equation presented by BÁRDOSSY, 1982). The average values from all of the samples are also calculated and presented.

	B-1	B-2	B-3	B-4	B-5	Average
$\text{Al}_2\text{O}_3$	49.00	49.60	57.60	48.60	45.35	50.03
$\text{SiO}_2$	8.40	4.43	2.95	2.00	1.98	3.95
$\text{Fe}_2\text{O}_3$	26.45	29.65	23.10	34.80	39.60	30.72
$\text{TiO}_2$	3.84	4.61	4.21	4.45	3.93	4.21
$\text{CaO}$	0.14	0.26	0.07	0.10	0.19	0.15
$\text{H}_2\text{O}^-$	0.42	0.34	0.06	0.12	0.12	0.21
$\text{H}_2\text{O}^+$	9.94	9.68	10.78	8.86	8.42	9.54
$\Sigma$	<b>98.19</b>	<b>98.57</b>	<b>98.77</b>	<b>98.93</b>	<b>99.59</b>	<b>98.81</b>
$\text{Al}_2\text{O}_3 : \text{SiO}_2$	5.83	11.20	19.52	24.30	22.90	16.75
$\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$	1.85	1.67	2.49	1.40	1.14	1.71
$K_i$	0.29	0.15	0.09	0.07	0.07	0.13

Low contents of  $\text{CaO}$ , i.e. from 0.07 to 0.26 % (average 0.15 %) are primary due to a lack of any of the carbonate minerals or their groups.

Contents of loss of ignition (LOI,  $\text{H}_2\text{O}^+$ ) are from 8.42 % (in B-5) to 10.78 % (in B-3), with average value of 9.54 %. Its main mineral bearers are major Al-hydroxides and minor kaolinite, hydro-hematite and goethite.

Ratios  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  are highest in the samples B-3, B-4 and B-5, primarily due to their lowest  $\text{SiO}_2$  contents. The lowest ratio is in the sample B-1, primarily due to its highest  $\text{SiO}_2$  content. These vary from 5.83 to 24.20, with average value of 16.75. Ratios  $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$  are different in present types of the bauxite mineral raw material. Highest ratio with value of 2.49 is in the sample B-3 where it was established that there is diaspore almost three times than hematite. The lowest ratios with values of 1.40 and 1.14 are in the samples B-4 and B-5 where it was established the most quantity of hematite. Its average value is 1.71.

High content of  $\text{Al}_2\text{O}_3$ , low content of  $\text{SiO}_2$ , and high ratios of  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  put this raw material into the high-quality raw materials for obtaining the electro corundum and alumina. The  $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$  ternary diagram of SCHELLMANN (1986) suggests that

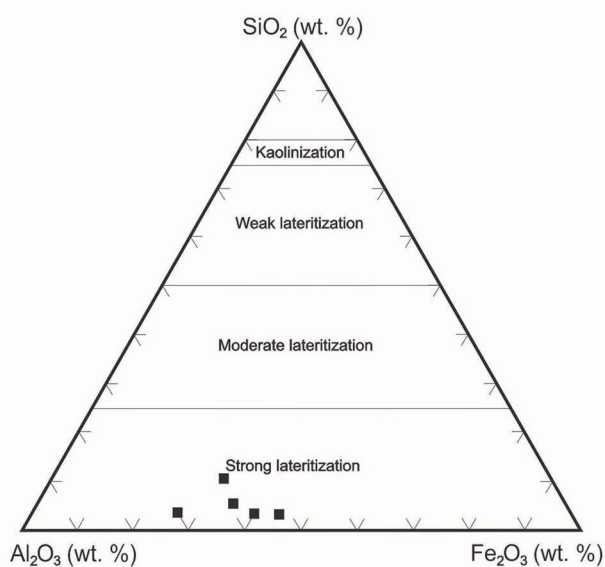
chemical variation can be explained by strong lateritization (Fig. 6). Calculated  $K_i$  coefficients of 0.07-0.29 (average: 0.13) strongly indicate that all of these studied samples should be classified as bauxites by nomenclature given by BÁRDOSSY (1982). On the other hand, these samples were further more specifically classified as ferritic bauxites (Fig. 7), according to the quantity of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  contents (Table 5).

### Comparison of the obtained results and its implications

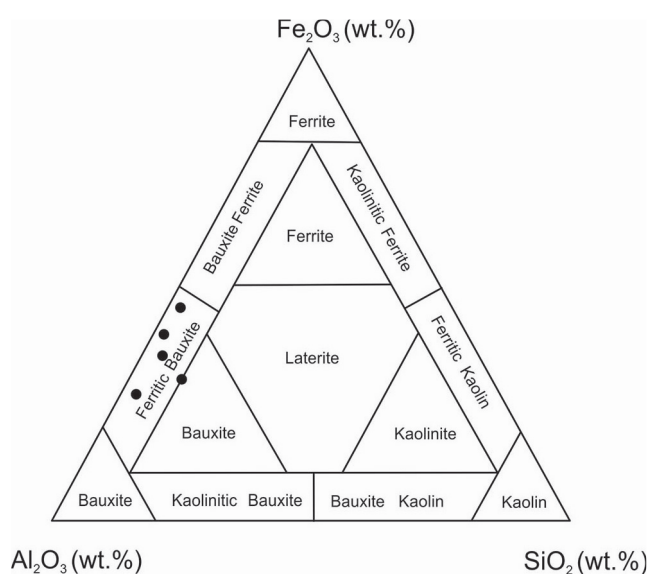
Approximate semi quantitative relations of major minerals by their amounts obtained with the XRPD analysis are in a very good agreement with the chemical analysis. It is particularly for the sum of the  $\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}^+$  contents relating to the  $\text{Fe}_2\text{O}_3$  contents, i.e. which is adequate to the relation between diaspore and/or boehmite to hematite. Therefore, it can be seen that: a). most of the  $\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}^+$  and least of the  $\text{Fe}_2\text{O}_3$  are in the sample B-3, in which was determined that there is three times diaspore than hematite; and b). most of the  $\text{Fe}_2\text{O}_3$  and least of the  $\text{Al}_2\text{O}_3$  and  $\text{H}_2\text{O}^+$  are in the samples B-4 and B-5, in which were determined that there is most hematite.

On the other hand, some of the approximate semi quantitative contents of some minor minerals by their amounts obtained by the XRPD analysis, such as: Ti-minerals, quartz and kaolinite, slightly disagree with the results of the chemical analysis, particularly for  $\text{TiO}_2$  and  $\text{SiO}_2$ . Possible factors for these discrepancies could be very various, such as: their small quantity, preferred sample orientation, peak overlapping, mineral inclusions, ion substitutions (as it was, for example, established for hematite, Table 4), microstructural parameters, presence of other minor phases with quantities under the XRPD detection limit range of about 2–3 % (such as anatase and brookite determined by an optical microscopic method), etc.

The obtained results allow us also to study correlations between the main chemical components, e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  (Figs. 8 and 9). At such way there was established as following: linear correlation for  $\text{Al}_2\text{O}_3$  vs.  $\text{H}_2\text{O}$ ; inverse correlations for  $\text{Fe}_2\text{O}_3$  vs.  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  vs.  $\text{H}_2\text{O}$ ; and no correlations for  $\text{SiO}_2$  vs.  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  vs.  $\text{Al}_2\text{O}_3$ .



**Fig. 6.** Ternary plot for the system  $Al_2O_3$ - $SiO_2$ - $Fe_2O_3$  (after SCHELLMANN, 1986) showing the positions of the studied Grebnik Mt. bauxite samples data points and degree of lateritization.



**Fig. 7.** Ternary plot for the system of  $Fe_2O_3$ ,  $Al_2O_3$  and  $SiO_2$  contents (after ALEVA, 1994) showing the positions of the studied Grebnik Mt. bauxite samples data points.

Such correlations further confirm the mineralogical-crystallographic study. Namely, high inverse correlations for  $Fe_2O_3$  vs.  $Al_2O_3$  (Fig. 8a) indicate that Al-hydroxides and hematite, as a main bearers of these oxides are inversely correlated, i.e. that increase of hematite content is related to the decrease of Al-hydroxides content, and vice versa. Something lower "r" factor of -0.8390 value, suggests that  $Al_2O_3$  and  $Fe_2O_3$  are also constituents of other minerals which appear in minor contents, i.e. kaolinite, goethite and hydro-hematite.

Very high inverse correlation for  $Fe_2O_3$  vs.  $H_2O$  (Fig. 8b;  $r = -0.9859$ ) and high linear correlation for  $Al_2O_3$  vs.  $H_2O$  (Fig. 8c;  $r = 0.89884$ ), confirm that the vast majority of water enters into diaspore and boehmite, and only partially into minor kaolinite, goethite and hydro-hematite.

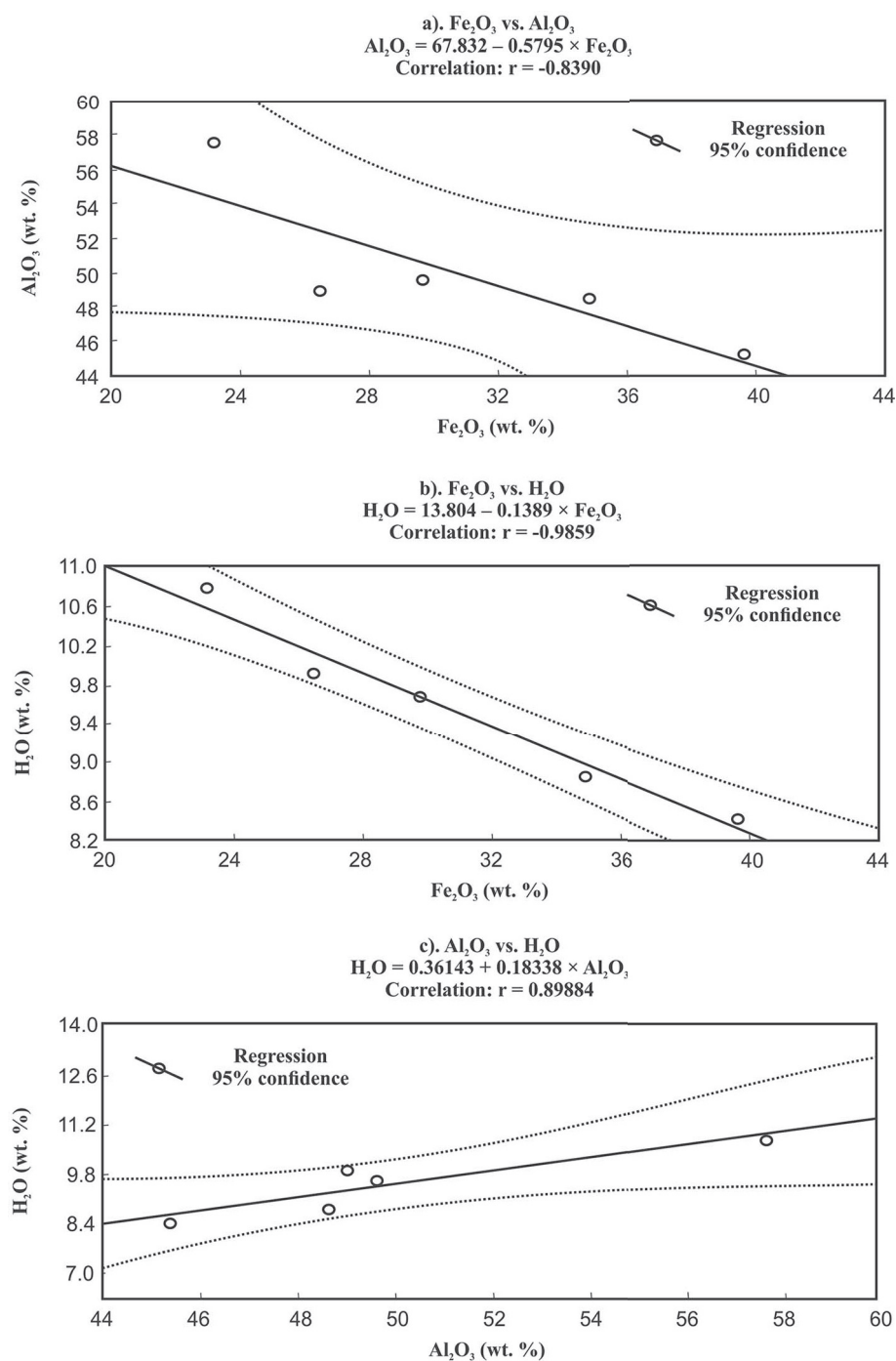
Finally, very low correlations for  $SiO_2$  vs.  $Al_2O_3$  (Fig. 9a;  $r = -0.0072$ ) and  $TiO_2$  vs.  $Al_2O_3$  (Fig. 9b;  $r = 0.19684$ ) are also expected, because they are confirming minor contents of kaolinite, quartz and Ti-minerals. Positive r value between  $TiO_2$  and  $Al_2O_3$  could also indirectly indicate to a possible entering of Ti-ion into the structure of Al-hydroxide minerals and simultaneously explained small excess of  $TiO_2$

obtained by chemical analysis in comparison with the XRPD results. Such substitution (as well as substitution by  $SiO_2$ , FeO and other) in diaspore was observed by LIU et al. (2012). But, this matter is beyond of the scope of this paper and additional study is necessary to confirm such hypothesis.

Studied and presented mineralogical and chemical compositions, as well as their correlations, further strongly indicate that conditional variations occurred in origin mainly between Al-hydroxides and hematite. Most probably, the conditional variations in origin between diaspore and boehmite also occurred, which are, from the crystallographic aspect of view, two mineral polymorphs of the same substance, but different in structural relationship by the packing of the oxygens. Due to the fact that quartz, goethite, rutile and kaolinite appear in relatively small quantities, their influence to the origin should be considered as minor.

As DANGIĆ (1988) argued, the stability and conditions of formation of boehmite and diaspore and their genetic relationship to one another and to kaolinite are only poorly understood, despite to many studies on these subjects. However, observed variations in mineral and chemical compositions





**Fig. 8.** Correlations: **a).**  $Fe_2O_3$  vs.  $Al_2O_3$ ; **b).**  $Fe_2O_3$  vs.  $H_2O$ ; and **c).**  $Al_2O_3$  vs.  $H_2O$ . All of the regressions were done at basis of 95 % confidence.

could be most probably mainly influenced by changing of some or many of the following parameters, such as: temperature, pressure, humidity, pH, Eh, crystallite size, inversely correlated  $Al^{3+}$ - $Fe^{3+}$  distribution, activities of  $Al^{3+}$  and  $Fe^{3+}$ , reducing-oxidizing condi-

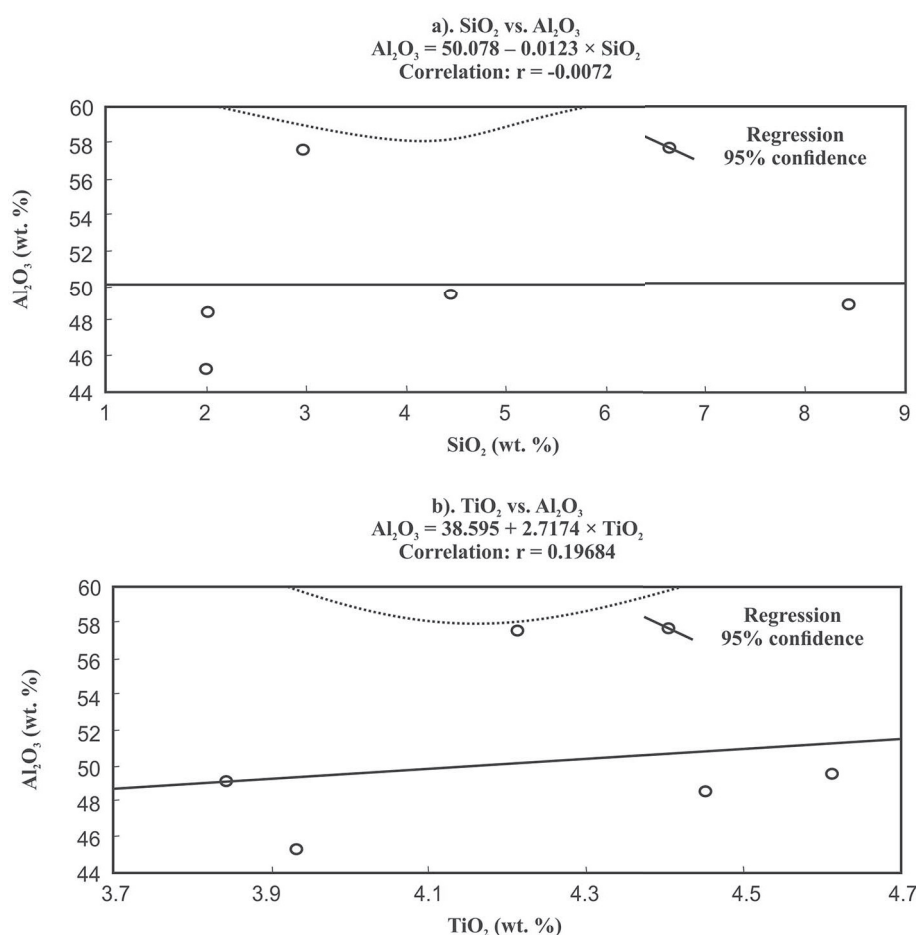
tions, etc. This problematic is also beyond of the scope of this paper, and complex additional study is necessary to resolve it.

sits derived *in situ* and by direct lateritization (autochthonous) of aluminosilicate rocks lying beneath the surface. These represent the predominant global source of bauxite of about 88 % (BÁRDOSY, 1982). Therefore, although determined

tions, etc. This problematic is also beyond of the scope of this paper, and complex additional study is necessary to resolve it.

### Comparison with some other bauxite ore deposits

Because bauxite consists of a mixture of minerals, it does not have specific, or predictable, chemical composition. Also, due to the fact that there are many different bauxite ore deposits in the World, which characterization was done more or less in detail, comparison of the Grebnik's bauxites with them could be done only briefly, but using several most important and relevant parameters of crucial interest. For example, according to the classification given by BÁRDOSY (1982), Grebnik's Upper Cretaceous bauxites geographically belong to the middle part of the Mediterranean Sea province, which are within 18 % of total World's bauxite deposits, and they are stratigraphically among 23 % of total World's bauxite deposits of the karst type. On the other hand, the lateritic-type bauxites that contain gibbsite as main hydrated aluminium oxide, are generally residual depo-



**Fig. 9.** Correlations: **a).**  $\text{SiO}_2$  vs.  $\text{Al}_2\text{O}_3$ ; and **b).**  $\text{TiO}_2$  vs.  $\text{Al}_2\text{O}_3$ . All of the regressions were done at basis of 95 % confidence.

minerals in this paper are common bauxite constituents, for comparison with other ore deposits the following important factors should be considered: a). determined mineral composition and their quantity, i.e. determined major and minor minerals; b). presence or lack of diaspore, boehmite, gibbsite, hematite, kaolinite, quartz, carbonates or some other main constituents; c). bauxite chemical compositions; d). bauxite genetic characteristics, e.g. primarily are they lateritic, Tikhvin or karst-type; and e). bauxite stratigraphic origin, e.g. according to their geological age.

Using these parameters, it could be observed as following:

1. Presented results in this paper are, as expected, in a very good agreement with other studies of Grebnik's bauxite ore deposits (MISIRLIĆ & MITROVIĆ,

1969; ARSIĆ, 1973; TIMOTIJEVIĆ, 1997 and 2001; MAKSIMOVIĆ, 2003). Only slight difference is that  $\text{TiO}_2$  contents are something higher in the studied ore deposits (Table 5). Also, there are no adequate arguments for specifically further separation of bauxite's fourth type, i.e. diaspore-oolite-pisolite as MISIRLIĆ & MITROVIĆ (1969) done for the Grebnik's ore deposit N° 3. That is mainly due to the fact that all of the studied samples already have oolitic and/or oolitic-pisolitic characteristics. Therefore, in this paper it was separated only three main bauxite types, e.g. diaspore, boehmite and boehmite-diaspore.

2. On the contrary, all the other bauxite ore deposits in wider vicinity of Grebnik Mt. differ primarily by their mainly boehmite composition and different stratigraphic position. These are: Počuta, Tara and Mačkat (Western Serbia, Lower Cretaceous, TIMOTIJEVIĆ, 1995, 1997 and 2001) and Babušnica (eastern Serbia, Lower Cretaceous, ARSIĆ, 1984) presented at Fig. 1A, and Vlasenica (Eastern Bosnia and Herzegovina, Lower Cretaceous, DANGIĆ, 1988; MAKSIMOVIĆ & PANTÓ, 1991), Štitovo (Montenegro, Jurassic, MAKSIMOVIĆ & PANTÓ, 1991), Marmara (Greece, Lower Cretaceous, MAKSIMOVIĆ & PANTÓ, 1991) and Parnassos-Ghiona (Greece, Lower Cretaceous, GAMALETOS et al., 2007) presented at Fig. 1B, as well as some others (BÁRDOSSY, 1982).

3. Also, many bauxite ore deposits in the World are different from Grebnik's primarily due to their major gibbsite composition, with or without diaspore and boehmite constituents as major or minor (BÁRDOSSY, 1982; ZARASVANDI et al., 2008; MESHAM & RANDIVE, 2011; JADHAVI et al., 2012; YUSTE et al., 2015; TORRÓ et al., 2017).

4. Furthermore, many bauxite ore deposits with mainly boehmite and/or diasporite composition differs from Grebnik's bauxite ore deposits either by: a). lack or minor of boehmite component (BÁRDOSSY, 1982; TEMUR & KANSUN, 2006; GAMALETSOS et al., 2007; ESMAEILI, 2010; LIU et al., 2010, 2012 and 2017; MOLLAI, 2011; AHMADNEJAD et al., 2017); b). lack or minor of diasporite component (BÁRDOSSY, 1982; MONGELLI et al., 2017); c). lack or minor of hematite component (BÁRDOSSY, 1982; GU et al., 2013); d). presence of major kaolinite and/or quartz and/or carbonates and/or some other constituents (BÁRDOSSY, 1982; ZARASVANDI et al., 2012; ZAMANIAN et al., 2016); and/or e). different stratigraphic origin (BÁRDOSSY, 1982; ABEDINI et al., 2008; LING et al., 2017; ZHANG et al., 2017).

5. MAKSIMOVIĆ & PANTÓ (1991) argued that a unique example of the relationship between source rocks and karst-bauxites was found in the Grebnik Mt. relics of the Cretaceous weathering crust on shales and on ultramafic rocks which occur at a few hundred meters distance from the Grebnik bauxite deposits. According to the geological setting and mineralogical and geochemical studies, it was proved that the products originating from the weathered shale and ultramafic rocks present the source material for the formation of Grebnik bauxites.

According to previously obtained results, the synthesis of all the presented data indicate that Grebnik's bauxites have some unique characteristics, more or less different from most of the World's known bauxite ore deposits. For our best knowledge, it has partially similar characteristics only with some Upper Cretaceous pisolitic bauxite samples from Mandan bauxite ore deposit (Zagros Mt., Iran, ZARASVANDI et al., 2012).

## Conclusion

For bauxite studies, from three ore deposits from Grebnik Mt. five representative samples were taken. Their mineralogical, crystallographic and chemical characteristics were examined by the microscopic, XRPD and chemical analysis. The occurrences in the bauxites were studied and described and established the presence of major and minor minerals, as well those which occur only sporadically. Three ore types

were recognized: diasporite, boehmite and boehmite-diasporite. All of them were classified as bauxites and more specifically as ferritic bauxites.

Unit cell dimensions of diasporite, boehmite and hematite were determined, mostly with values within reference data, except for hematite samples which have smaller  $a_0$  and  $V_0$  values, most probably due to the substitution of  $Fe^{3+}$  by  $Al^{3+}$ . Such crystallographic calculations are promising to be useful for similar studies in the future bauxite explorations.

Linear correlation exists between  $Al_2O_3$  vs.  $H_2O$ ; inverse correlations exist between  $Fe_2O_3$  vs.  $Al_2O_3$  and  $Fe_2O_3$  vs.  $H_2O$ ; whereas there is no correlation between  $SiO_2$  vs.  $Al_2O_3$  and  $TiO_2$  vs.  $Al_2O_3$ . High content of  $Al_2O_3$ , low content of  $SiO_2$  and high ratios of  $Al_2O_3:SiO_2$  put this raw material into the high-quality raw materials for obtaining the electro corundum and alumina.

It was shown that Grebnik's bauxites have some unique characteristics; more or less different from most of the World's known bauxite ore deposits.

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## Резиме

### Минералогске и кристалографске карактеристике боксита из неких рудних лежишта Гребника (Метохија, Србија)

Лежишта боксита су најважнији извори за добијање алуминијума. Њиховим проучавањима су се бавили многи аутори. То се углавном односи на геолошко окружење, структуру рудних лежишта и појаве, стратиграфски положај, распоред и дебљину боксита, итд. Међутим, у српској литератури постоји релативно мали број радова који су проучавали боксите са минералогске, а посебно са кристалографске тачке гледишта.

Пет типичних узорака боксита (В-1, В-2, В-3, В-4 и В-5) из три рудна лежишта (6, 21 и 22) са ширег подручја планине Гребник (Метохија, Србија, Слика 1) су проучавани оптичко микроскопским, рендгенским и хемијским методама.

Оптичком микроскопијом (Слике 2 и 3) утврђена је присутност металичних минерала гвожђа (хематит, хидрохематит, лимонит и магнетит) и Тi (углавном рутил, и спорадично анатас и брукит), а детаљно су описане њихове трансформације.

Рендгенским проучавањима (Слика 4 и Табела 1) утврђено је присуство главних минерала:

дијаспора, бемита и хематита, као и минорних минерала: кварца, гетита, рутила и каолинита. Према количини главних носилаца алуминијума, утврђена су три типа руде боксита: дијаспорски (узорци В-2, В-3 и В-5), бемитски (узорак В-1) и бемитско-дијаспорски (узорак В-4). На основу садржаја минерала, ови узорци су класификовани као гвожђем-богати боксити (Слика 5). Израчунате су и димензије јединичних ћелија главних минерала (Табеле 2–4), углавном са вредностима које су у оквиру литературних података. Међутим, сви проучавани хематити имају мање вредности  $a_0$  и  $V_0$ , највероватније услед замењивања Fe<sup>3+</sup> са Al<sup>3+</sup>, и то у количинама од око 2,5 до 6,0 at. %.

Одређени хемијски састави (Табела 5) стављају ову сировину у високо-квалитетне сировине за добијање електро корунда и глинице. Хемијски састави указују и на јаку латеритизацију (Слика 6), а због високог садржаја Fe, ови боксити су класификовани као феритични (Слика 7). Утврђена је линеарна корелација за Al<sub>2</sub>O<sub>3</sub> vs. H<sub>2</sub>O; инверзна корелација за Fe<sub>2</sub>O<sub>3</sub> vs. Al<sub>2</sub>O<sub>3</sub> и Fe<sub>2</sub>O<sub>3</sub> vs. H<sub>2</sub>O; а без корелације за SiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub> и TiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub> (Слике 8 и 9).

Синтеза добијених података указује на то да су Гребнички боксити специфични, јер имају неке јединствене карактеристике које се мање или више разликују од већине светски познатих лежишта руде боксита. Тренутно, због немогућности приступа овим лежиштима, детаљнија истраживања и експлоатација су одложена на неодређено време.

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