

KAOLINIZATION OF BAUXITE: A STUDY IN THE VLASENICA BAUXITE AREA, YUGOSLAVIA. I. ALTERATION OF MATRIX¹

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Abstract—The kaolinization of bauxite has generally been thought to be a simple process of epigenetic resilification. A study of the karstic boehmitic bauxites in the Vlasenica region of Yugoslavia, however, shows that kaolinization took place in a rather complex manner, in which the alteration was caused by the percolation of siliceous water descending through the deposit by means of cracks, fissures, etc. The matrix of one such Vlasenica deposit was found to be more highly kaolinized than the oolitic fraction. Based on a mineralogical and geochemical examination of matrix material, the following pattern of zoned alteration was identified: kaolinitic zone–boehmite enrichment zone–original bauxite. In the kaolinitic zone, well-crystallized kaolinite, formed by the reaction of dissolved silica with boehmite, has replaced all other minerals in the matrix. This Si metasomatism was accompanied by an outward migration of Al and resulted in the formation of a transition zone in which new boehmite partly replaces both kaolinite and hematite (Al remobilization). A thermodynamic model of the process has been established on the basis of stability diagrams calculated for the mineral assemblages in the alteration zones and in the deposit as a whole.

Rezime—Opšteprihvaćeno je shvatanje da je kaolinizacija boksita jednostavan proces epigenetske resilifikacije. Proučavanja karsnih bemitskih boksita u regionu Vlasenice u Jugoslaviji pokazala su, međutim, da kaolinizacija predstavlja deo složenijeg procesa alteracije koji nastaje pri perkolaciji voda obogaćenih rastvorenim silicijom kroz pukotine, rasedne zone i sl. u ležištima boksita. Detaljna proučavanja u jednom takvom ležištu u ovom regionu pokazala su da je osnova boksita mnogo jače kaolinisana nego ooliti. Na osnovu mineraloškog i geohemijskog proučavanja osnove boksita identifikovan je sledeći tip zonalne alteracije: kaolinitička zona–bemitska zona–originalni boksit. U kaolinitičkoj zoni dobro iskristalisali kaolinit, obrazovan kroz reakciju silicije iz rastvora sa bemitom, potisnuo je sve minerale u osnovi. Ova Si-metasomatoza je bila udružena sa migracijom Al dublje u boksit, što je dovelo do obrazovanja prelazne zone, u kojoj je neo-bemit delom potisnuo hematit i kaolinit (Al-remobilizacija). Proračunati su i razmotreni dijagrami stabilnosti mineralnih asocijacija u zonama alteracije i u samom ležištu, a na osnovu toga postavljen je i termodinamički model procesa.

Key Words—Aluminum, Bauxite, Boehmite, Kaolinite, Resilification, Silica.

INTRODUCTION

Kaolinite is a common clay mineral in most bauxite deposits and may be residual, syngenetic, or epigenetic in origin. Epigenetic kaolinite, formed by the kaolinization of bauxite, has been reported in laterite- and karst-type bauxites in the United States (Goldman, 1955; Goldman and Tracey, 1964; Keller, 1962; Keller and Clarke, 1984), the Soviet Union (Beneslavsky, 1963, 1968; Bushinsky, 1968), and the Mediterranean region (Valeton, 1972; Bárdossy, 1982). The kaolinization process has been described as a resilification (resilication) of bauxite, and has been thought to be a rather simple metasomatic process (Keller, 1962; Keller and Clarke, 1984; Valeton, 1972; Bárdossy, 1982). The present study reports on the kaolinization of karstic bauxite in the Vlasenica area of Yugoslavia. Here,

kaolinization has occurred in several bauxite deposits, the largest of which, the Braćan deposit, was selected for detailed examination. The mineralogy and geochemistry of matrix material in altered zones of the bauxite were investigated, and a thermodynamic model of the process was established, based on stability diagrams calculated for the relevant minerals.

GEOLOGIC SETTING AND CHARACTERISTICS OF THE BAUXITE DEPOSITS

The Vlasenica bauxite region in eastern Bosnia in the central part of the country is one of the most important aluminum-producing regions of Yugoslavia. The deposits occur in a narrow NW–SE trending belt about 30 km long and 4 km wide (Figure 1). The bauxite bodies are in karstic depressions in Middle Triassic limestones and are covered by Upper Cretaceous limestone and/or sandy-clayey limestone of Upper Cretaceous or Neogene age (Ranković, 1974). Paleozoic schists and sandstone are found beneath the bauxite footwall. In this same region, Jurassic mafic-ultramafic

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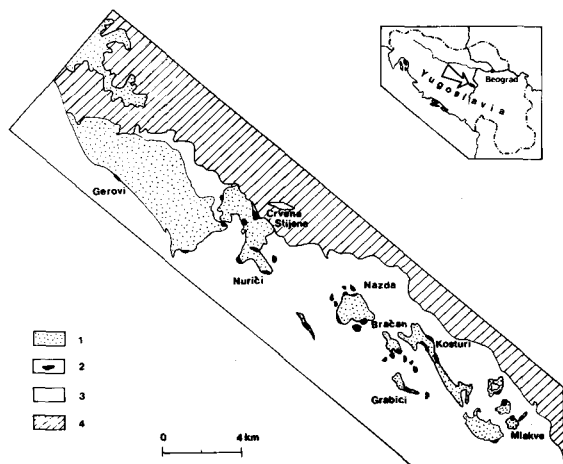


Figure 1. Index and geological map of Vlasenica bauxite area, Yugoslavia. 1 = hanging wall sediments: Albian-Cenomanian limestones and Neogene (?) conglomerates, sands, and clays; 2 = bauxite deposits; 3 = footwall: Middle Triassic limestone; 4 = Paleozoic schists and sandstones.

rocks crop out locally, close to the bauxite deposits. The hanging wall rocks consist mainly of quartz sands, sandstones, and conglomerates; in one limestone bed thin layers and lenses of coal and chert concretions have been found. Pyroclastic materials, related to the Neogene volcanism in the neighboring Srebrenica region, have also been found locally.

The bauxite deposits occur as discontinuous layers, lenses, and pockets within the limestone and are covered by partly or completely eroded hanging wall rocks. The size of the deposits varies from tens of thousands of tons to more than ten million tons of bauxite. The bauxite is boehmitic and has a high iron content. It is characterized by a red matrix and reddish-brown oolite/pisolites. Both boehmite and kaolinite have been recognized and appear to be concentrated in the matrix. Hematite, lepidocrocite, and goethite are primarily concentrated in the oolite/pisolites. Accessory anatase is common; however, other minerals are only locally present (Maksimović *et al.*, 1983).

EXPERIMENTAL

Samples were examined by means of optical microscopy, transmission electron microscopy (TEM), X-ray powder diffractometry (XRD), wet chemical analysis, and spectrochemical analysis. The TEM study was conducted using a Philips EM-300 electron microscope. XRD patterns were obtained on a Philips PW-1050/25 diffractometer equipped with a PW-1730 generator, $\text{CuK}\alpha$ radiation, and a graphite monochromator. A scanning rate of $2^\circ 2\theta/\text{min}$ was used.

Elemental analyses were made by rapid silicate analytical procedures and involved spectrophotometric and atomic absorption techniques. Trace elements were



Figure 2. Vertical cross section, open pit in the Braćan deposit. 1 = hanging wall limestone; 2 = bauxite; 3 = footwall limestone; 4 = footwall boundary; 5 = tentative footwall boundary.

determined using a STE-1 emission spectrograph and corrected against internal standards. Excitation was by means of a vertical dc arc in a controlled Ar-O_2 atmosphere. The precision of this method is estimated to be $\pm 10\%$. Quantitative mineral compositions were calculated from XRD, differential thermal, thermal gravimetric, and chemical analyses.

RESULTS

Zoned alteration of bauxite

Although epigenetic kaolinite has been found as veinlets and fissure fillings in several of the bauxite deposits in the Vlasenica region, it is most prevalent in the Braćan deposit. The Braćan deposit is in the central part of the region and varies in thickness from 10 to 50 m. It is partly covered by both the limestone and sandy-clayey limestone described above, and is well exposed by an open pit (Figure 2). In the lower part of the 130-m thick hanging wall formation, a bedded, marl limestone is present which contains abundant chert concretions. The upper part of the hanging wall limestone is locally as thick as 50 m and is gray to white. The sandy-clayey limestone is gray to white and consists of gray, blue-gray, green, yellow, and red clays, sandy clays, clayey sandstones, quartz sandstones, conglomerates, and clayey limestones.

Small amounts of epigenetic kaolinite are locally present in the bauxite body filling joints or cementing oolites. Extensive kaolinization, however, has taken place in the lower part of the ore, and it was from this zone that most of the samples were collected. Here, the bauxite is kaolinized in and around a 1.5-m wide fissure zone; however, the original bauxite structure has been preserved. Between this zone of kaolinization and surrounding the original bauxite is a 1-m thick transition zone. The original bauxite is compact and consists of black to brown oolites in a red matrix. The main constituent of the matrix is boehmite, although substantial hematite and kaolinite are also present. The oolites are

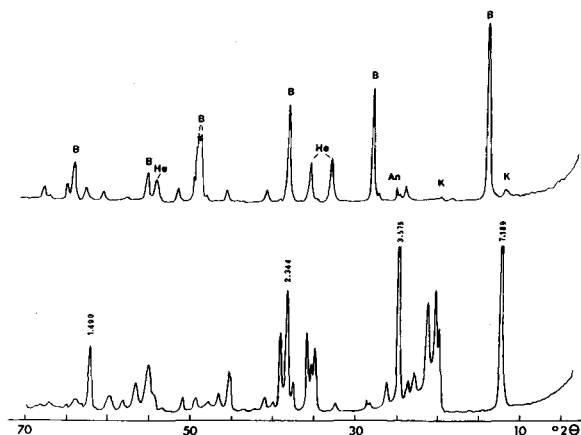


Figure 3. X-ray powder diffraction pattern of matrix from the original bauxite (above) and from the kaolinitic zone (below). B = boehmite; K = kaolinite; H = hematite; An = anatase (CuK α radiation).

mainly hematite, with minor amounts of boehmite and kaolinite. Anatase occurs in both the matrix and the oolites. Highly kaolinized bauxite is characterized by a white matrix, which is composed only of kaolinite (Figure 3), and light brown oolites. The transition zone is characterized by a yellow-pink matrix and brownish oolites. The matrix contains a small amount of kaolinite and substantial boehmite; the boehmite content is greater than that of the original bauxite ore.

On the basis of these mineralogical data, the matrix of the bauxite can be divided into the following alteration zones, outward from the original bauxite: original bauxite, boehmite enrichment zone, and kaolinitic zone (Figure 4).

Mineralogy and geochemistry

Both the mineralogy and chemical composition of the matrix material were changed in the alteration zones, but to different degrees. The matrix was apparently very sensitive to the alteration reactions, and where alteration was most intense, it transformed completely to kaolinite. In the same sample, however, the oolites were only partly affected. The matrix of the original (unaltered) bauxite is red and consists of about 63% boehmite, 20% hematite, 15% kaolinite, and 2–3% anatase. The matrix of the boehmite enrichment zone is yellow-pink and consists of about 76% boehmite, 14% hematite, 4% kaolinite, and about 2% anatase. The matrix of the kaolinitic alteration zone is white and is nearly 100% kaolinite. From XRD and TEM analyses, the kaolinite is well crystallized. Individual grains are euhedral and vary from 1.5 to 4 μm in size. The crystallinity index is high, 1.23 (after Hinckley, 1963). From

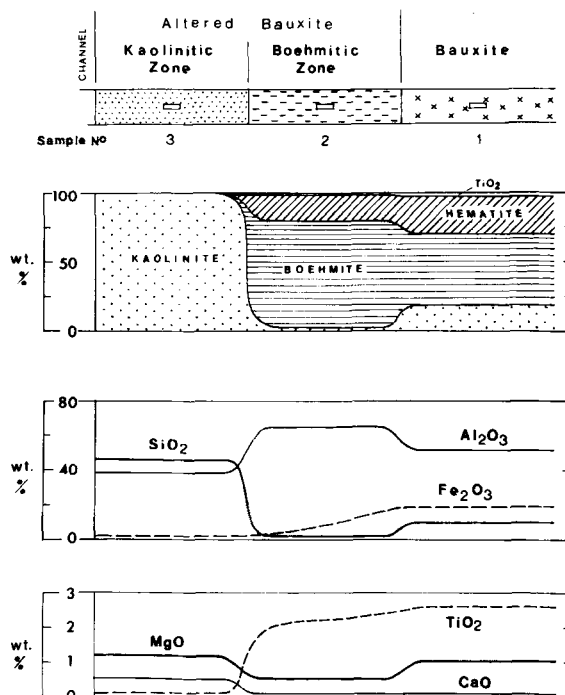
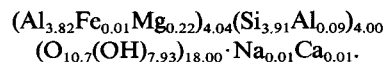


Figure 4. Variation in mineral and chemical composition of the matrix in zoned alteration of bauxite, Bra \acute{c} an deposit.

chemical analyses of the epigenetic kaolinite, the following formula was calculated:



Mg is included in the above kaolinite formula, but it may have been present in the sample as an undetected trace mineral, such as a Mg-containing 7- \AA chlorite. This formula is close to that of an ideal kaolinite.

Compared to the whole, unaltered bauxite ore, the matrix of the unaltered ore contains more alumina (58% vs. 50.2%), slightly more silica (5.9% vs. 4.5%), less ferric oxide (18.3% vs. 29.7%), and about the same amount of TiO_2 (2.6% vs. 2.7%) (Table 1, Figure 3). The matrix of the boehmitic zone is characterized by a higher alumina content (65.7% vs. 58%), and lower silica and ferric iron contents (1.8% vs. 5.9% and 13.5% vs. 18.3%, respectively) than the matrix of the unaltered ore. No significant differences were noted among the minor elements (Table 2). The matrix of the kaolinitic zone differs significantly, on the other hand, from that of both the boehmitic transition zone and the original bauxite material in that it is 7.5 times richer in silica than the matrix of the original bauxite (45.4% vs. 5.9%) and 25 times richer than that of the boehmitic zone (45.4% vs. 1.8%). It is also significantly poorer in alumina and poorer in ferric oxide. Its silica-alumina-water composition is close to that of an ideal kaolinite.

Table 1. Chemical composition (wt. %) of matrix in the original bauxite and alteration zones.

	Altered bauxite		
	Bauxite	Boehmite enrichment zone	Kaolinitic zone
SiO ₂	5.92	1.81	45.35
TiO ₂	2.58	2.24	0.03
Al ₂ O ₃	57.96	65.73	39.11
Cr ₂ O ₃	—	0.03	—
Fe ₂ O ₃	18.31	13.45	0.12
FeO	0.67	—	—
MnO	0.05	0.15	—
NiO	0.06	0.06	0.07
MgO	1.16	0.47	1.03
CaO	0.49	0.08	0.09
Na ₂ O	0.01	0.09	0.13
K ₂ O	—	0.05	0.06
H ₂ O+	10.89	15.20	13.75
H ₂ O-	1.75	0.25	0.30
Total	99.94	99.61	100.04

The trace element content of this material is quite low, and only Ni, Zn, Co, and B are present in the 44–560-ppm range.

DISCUSSION

The changes in mineral and chemical composition of both the matrix materials and the oolites in the altered zones suggest that the kaolinization and the boehmitization of the bauxite were metasomatic processes. The presence of alteration zones emanating from fractures and fissures in the ore suggests that the alteration took place by the reaction of the original bauxite ore with descending silica-rich, conate waters. Although both matrix and oolitic materials were affected by this process, the matrix material was significantly more altered and therefore is the subject of the following discussion. Locally, the matrix material of the ore has been completely altered to kaolinite adjacent to a fissure. Thus, a kaolinitic zone was formed by the diffusion of dissolved silica from a fissure to the bauxite where it reacted with boehmite to form kaolinite which totally replaced boehmite, hematite, and anatase. Excess Al and all of the Fe from the hematite went into solution. A boehmite-enrichment zone exists between the kaolinized zone and the unaltered ore, suggesting that as kaolinite formed, excess Al dissolved and was transported to the unaltered ore where it reacted with the kaolinite there to form boehmite and soluble silica. This latter process was accompanied by the dissolution of both hematite and anatase. The alteration therefore consisted of the transformation first of boehmite to kaolinite and then kaolinite to boehmite and the dissolution of both hematite and anatase.

Hematite and anatase appear to have reacted similarly in the process and therefore can be treated as one phase. A stability diagram was prepared accordingly

Table 2. Trace element content (ppm) of matrix in the original bauxite and alteration zones.

Element	Altered bauxite		
	Bauxite	Boehmite enrichment zone	Kaolinitic zone
B	27	32	44
Ba	—	6	—
Be	10	15	3.5
Co	58	46	64
Cr	425	210	—
Cu	66	22	4
Ga	60	92	—
La	47	74	—
Mn	1100	1150	—
Nb	90	38	—
Ni	540	460	560
Pb	105	130	—
Sc	18	16	11
Sn	—	10	—
Sr	44	70	—
V	225	160	—
Y	90	73	—
Zn	90	185	70
Zr	180	220	15

— = below detection limit. Also below detection limit: Ag, Cd, In, Mo, Sb, W.

for the relevant phases in the system Al₂O₃-SiO₂-Fe₂O₃-FeO-H₂O at 25°C and 1 atm pressure, using thermodynamic data from Garrels and Christ (1965) and Krauskopf (1967) (Figure 6). As indicated in Figure 5, the activity of dissolved silica (H₄SiO₄) is critical in the relationship between boehmite and kaolinite. Boehmite is stable at silica activities < 10^{-7.07}. At higher silica activities, kaolinite is stable to the region of non-crystalline silica saturation at 10^{-2.6}, through the boundary of quartz saturation at 10^{-3.7}. On the other hand, the stability of both boehmite and kaolinite depend not only on the activity of dissolved silica but also on that of Al³⁺ and the pH of the solution.

As seen in Figure 6, the stability fields of boehmite and kaolinite move towards lower pHs with increasing Al³⁺ activity. Thus, boehmite is stable at Al³⁺ activities < 10⁻⁷ at pH > 5. At higher Al³⁺ activities (to 10⁻⁴), the boehmite boundary moves to pH 4. On the other hand, the stability of kaolinite moves towards lower pH as the activities of both Al³⁺ and dissolved silica increase. Thus, if the Al³⁺ and dissolved silica activities are low, e.g., 10⁻⁷, kaolinite is stable at pH > 5, but with an increase in the activity of dissolved silica to 10^{-3.7} (quartz saturation), the kaolinite boundary moves to pH 4.

The stability of hematite depends on the activity of the dissolved iron species at various Eh and pH levels. The geochemical data indicate that the decomposition of hematite was accompanied by the reduction of Fe³⁺ to Fe²⁺. As seen in Figure 6, the stability field of hematite moves towards both lower pH and lower Eh

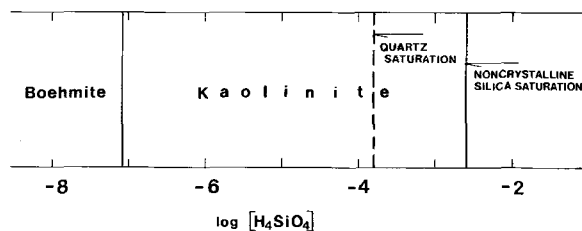


Figure 5. Diagram showing stability of boehmite, kaolinite, quartz and noncrystalline (amorphous) silica as a function of activity of dissolved silica at 25°C and 1 atm total pressure.

with an increase in the Fe^{2+} activity. Thus, at a Fe^{2+} activity as low as 10^{-7} , hematite is stable for pH 4 at Eh 0.43 V, and for pH 5 at Eh 0.26 V. At higher Fe^{2+} activity, e.g., 10^{-4} , the hematite boundary moves for Eh 0.43 V to pH 3, and for Eh 0.26 V to pH 4. The stability diagram in Figure 6 contrasts with that of Norton (1973, p. 357) which represents surface conditions.

A comparative analysis of mineral and chemical transformations in the alteration zones, phase relations in the corresponding water-mineral system, and solubility of both boehmite and hematite provides significant insight into the geochemistry of the alteration process. The activity of dissolved silica in both the fissure and the kaolinitic zone must have been lower than $10^{-3.7}$, as quartz is absent, but higher than $10^{-7.07}$, as boehmite was unstable. The intensity of kaolinitization indicates that the dissolved silica activity was relatively high, probably about 10^{-4} to 10^{-5} . On the other hand, in the boehmite enrichment zone, it must have been lower than $10^{-7.07}$, as kaolinite was unstable. Relics of kaolinite, however, suggest that it was not much lower than this value, probably about 10^{-8} . Further into the bauxite, beyond the boehmitic zone, the dissolved silica activity was about 10^{-9} .

The Al^{3+} activity in the boehmite enrichment zone had to be higher than that produced by the dissolution of boehmite at given pHs, but not much higher, as indicated by the intensity of the boehmitization. The Al^{3+} activity in the kaolinitic zone, from which alumina was only partly remobilized into the boehmite enrichment zone, was either the same as in the boehmite enrichment zone or somewhat higher; however, it must have been substantially higher than in the fissure zone. Because boehmite and kaolinite are in equilibrium at dissolved silica and Al^{3+} activities of $10^{-7.07}$ and $10^{-7.02}$, respectively, the reaction took place at pH 5 to 4–3.5, as seen in Figure 6, and the pH of the solution in the boehmite enrichment zone must have been 4.5–5. The Al^{3+} activities calculated from the solubility of boehmite at pH 5 and 4.5 are 10^{-7} and $10^{-5.5}$, respectively. Thus, an Al^{3+} activity of $10^{-5.5}$ was likely in the boehmite enrichment zone, and the Al^{3+} activity in the surrounding bauxite must have been lower than 10^{-7} , probably about 10^{-8} – 10^{-9} .

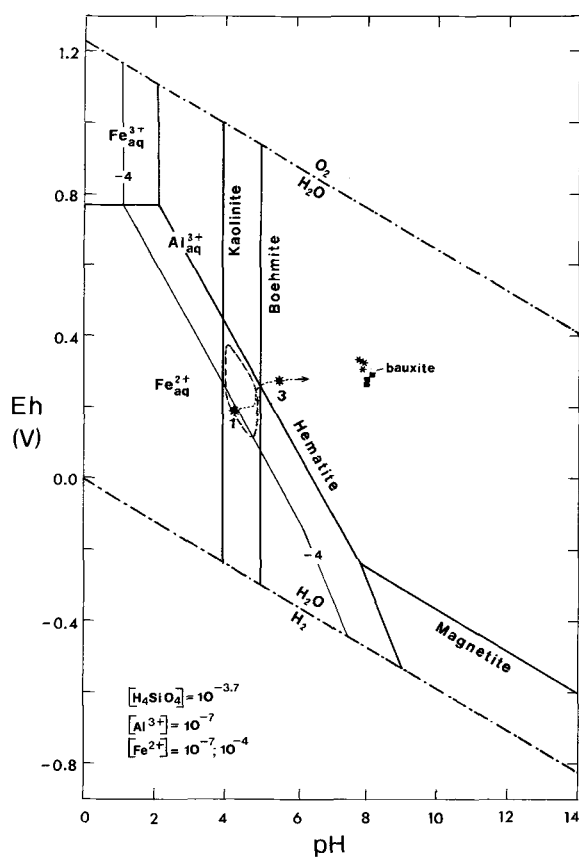


Figure 6. Composite Eh-pH diagram showing stability fields of boehmite, kaolinite, hematite, and magnetite in water at 25°C and 1 atm total pressure. Total dissolved $\text{Al}^{3+} = 10^{-7}$ M, $\text{Fe}^{2+} = 10^{-7}$ M, and $\text{H}_4\text{SiO}_4 = 10^{-3.7}$ M. Light line is stability of hematite at total dissolved $\text{Fe}^{2+} = 10^{-4}$ M. Explanations in text.

The activity of Fe^{2+} in the alteration zones is indicated by the pH of the solution and by the stability (solubility) of hematite. In both alteration zones, the Fe^{2+} activities must have been lower than that in equilibrium with hematite: in the boehmite enrichment zone (where hematite was only partially dissolved), only somewhat lower, but in the kaolinitic zone (where hematite was totally dissolved), much lower. On the other hand, the Fe^{2+} activity in the fissure zone must have been lower than in the alteration zones, because Fe^{2+} diffused towards the fissure zone. Considering that nearly the same number of atoms of Al and Fe were removed from the alteration zones, as suggested by the data in Table 1, the Fe^{2+} activity must have been nearly the same as that of Al^{3+} , about $10^{-5.5}$. Because the solution in the boehmite enrichment zone was somewhat undersaturated with respect to hematite, the equilibrium activity of Fe^{2+} in that zone must have been close to 10^{-5} . Using this value and the solution pH estimated above at about 5–4.5, the Eh of the solution in the boehmite enrichment zone can be calculated

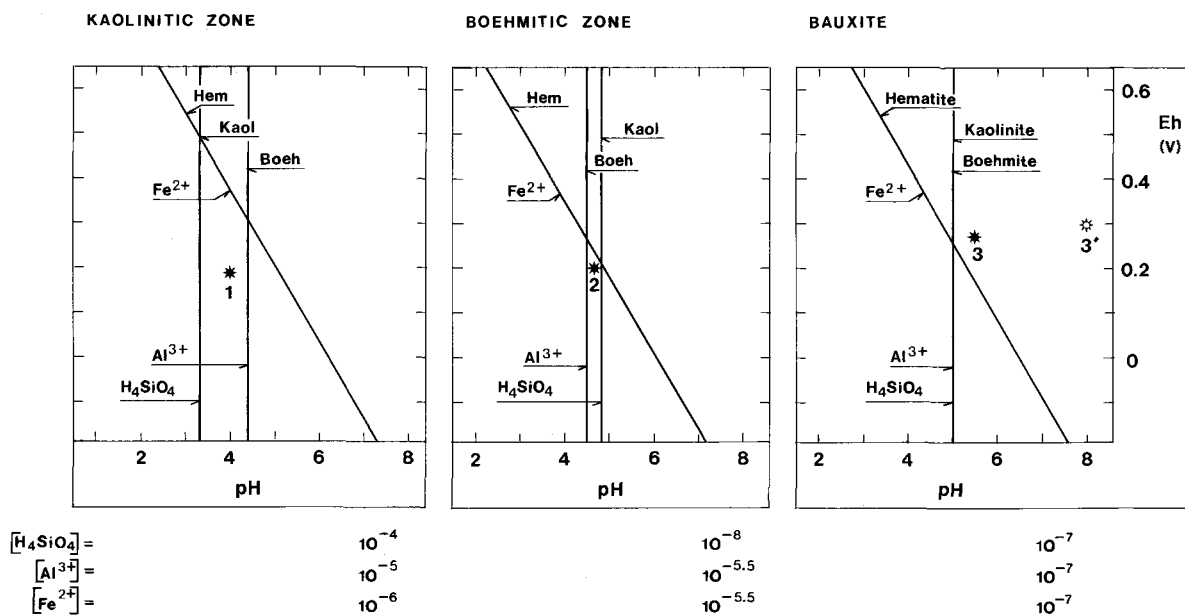


Figure 7. Diagrams showing stability fields of kaolinite, boehmite, and hematite as function of pH, Eh, and activities of silica, Al^{3+} , and Fe^{2+} in water at 25°C and 1 atm total pressure, representing the successive stages in the zoned alteration profile. 1, 2, and 3 are positions of alteration solutions in alteration zones and original bauxite; 3' is "abrasive pH and Eh" of common bauxite. Hem = hematite, Kaol = kaolinite, Boeh = boehmite.

from the solubility of hematite. Thus, for an average pH of 4.7, the Eh of the solution must have been slightly less than 0.19 V. Assuming the same Eh in both zones, the Fe^{2+} activity in equilibrium with hematite in the kaolinitic zone at pH 4 is $10^{-2.8}$. The differences in the Fe^{2+} activities calculated from the experimental data and in equilibrium with hematite at specified conditions well explain the differences in the degree of hematite dissolution in the two alteration zones. The Eh in the unaltered bauxite must have been somewhat higher than in the alteration zones, as evidenced by the position of normal bauxite in Figure 6, and the Fe^{2+} activity must have been somewhat less than 10^{-7} , probably 10^{-8} – 10^{-9} .

Based upon these considerations, stability diagrams showing the relation of boehmite, kaolinite, and hematite and relevant dissolved species in the alteration zones and the unaltered bauxite were calculated (Figure 7). The diagrams representing the alteration zones were calculated for dissolved silica, Al^{3+} , and Fe^{2+} activities of 10^{-4} , 10^{-5} , and 10^{-6} (kaolinitic zone) and 10^{-8} , $10^{-5.5}$, and $10^{-5.5}$ (boehmite enrichment zone), respectively. The diagram representing the unaltered bauxite was calculated for dissolved silica, Al^{3+} , and Fe^{2+} activities of $10^{-7.07}$, $10^{-7.02}$, and 10^{-7} , respectively. The numbers 1, 2, and 3 refer to alteration systems in the kaolinitic, boehmite enrichment, and unaltered bauxite zones, respectively, and 3' refers to water-bauxite reactions in the normal bauxite, far from the alteration system (based on "abrasive pH and Eh").

ALTERATION MODEL

A thermodynamic model of the process leading to the zones of alteration of bauxite, as characterized by the complete kaolinization of the matrix, was developed by considering the observed mineral transformations, the geochemical compositions of the various zones, and the calculated stability diagrams for the systems in question. Spatial relationships and the geochemical compositions suggest that alteration took place after burial of the bauxite by the reaction of the ore with descending waters from the hanging wall through fissure zones. The descending water was characterized by a relatively high dissolved silica activity and a relatively low pH and Eh. The solution diffused laterally from the fissure zones into the bauxite.

The model consists of four stages: a starting stage, which is related to the source of the solution in the hanging wall formation, and three distinct bauxite-alteration stages outward from the fissure zone. Relevant geochemical compositions and mineral transformations are shown in Figures 5–7.

Starting stage

Water from the hanging wall formation descended into the bauxite through fissures (Figure 7). Although the quantity of water was restricted by the permeability of the hanging wall rocks, its descent was slow enough to allow the dissolution of quartz, silicates, and chert in the hanging wall formations, thereby increasing its

dissolved silica activity to a value somewhat less than that of quartz saturation (probably about 10^{-4}). Simultaneously, the oxidation of coal and other organic matter in these formations decreased the pH and Eh of the water to 3.5–4 and <0.2 V, respectively (see stage 1, Figures 6 and 7). The Al^{3+} and Fe^{2+} activities were somewhat less than 10^{-5} and $\leq 10^{-6}$, respectively.

Bauxite alteration stage

The descending solution diffused into the host rock and reacted with the bauxite, primarily with the matrix of the bauxite, resulting in the development of a three-stage alteration process:

(1) At or near the fissure zone, both the hematite and boehmite in the matrix were unstable with respect to kaolinite (see Figure 6, area enclosed by dashed line, and stage 1; Figure 7, stage 1). Kaolinite therefore replaced all other phases in the matrix, and excess Al and all of the Fe (as Fe^{2+}) were removed from the system. The Al^{3+} and Fe^{2+} activities were about 10^{-5} and $10^{-5.5}$, respectively. Thus, a strong kaolinite alteration front diffused away from the fissure zone into the bauxite.

(2) The activity of dissolved silica decreased sharply to $<10^{-7}$ (probably to 10^{-8}), and the pH increased slowly as the solutions diffused into the bauxite from the fissure zone. The Al^{3+} and Fe^{2+} activities were somewhat less ($10^{-5.5}$) and nearly the same ($10^{-5.5}$), respectively, as in the kaolinitic zone. These changes affected the stability of kaolinite with respect to boehmite. For example, at a dissolved silica activity as low as 10^{-8} at pH 4.5–4.8, boehmite is the only stable phase (Figure 7, stage 2). The development of a boehmite alteration front involved the addition of Al (remobilized from the kaolinitic zone) and the removal of part of the silica. In addition, with these changes in pH and at the same Eh (or with a small increase in Eh), the solubility of hematite decreased significantly compared with the preceding zone, and Fe was only partly removed.

(3) Further into the bauxite, the dissolved silica, Al^{3+} , and Fe^{2+} activities of the diffusing solutions decreased, although pH and Eh continued to increase, and all three phases (kaolinite, boehmite, and hematite) became stable (Figure 6, stage 3; Figure 7, boehmite diagram). The dissolved silica, Al^{3+} , and Fe^{2+} activities significantly decreased to $<10^{-7}$, but the pH and Eh of the solution reached 5 and 0.26 V, respectively, and increased further into the unaltered bauxite. As the pH and Eh of the solution rapidly increased, the amount of dissolution of all three phases strongly decreased. For example, at pH 5.5 and Eh 0.27 V (Figure 7, stage 3), the dissolution of boehmite and hematite produces Al^{3+} and Fe^{2+} activities of $10^{-8.5}$ and $10^{-8.7}$, respectively. The dissolution at pH 6 gives a dissolved silica activity of 10^{-9} . Thus, little reaction took place between the solution and the bauxite minerals ahead of the boehmite alteration front.

CONCLUSIONS

Kaolinization of bauxite in the Vlasenica bauxite region of Yugoslavia appears to have taken place not only by simple resilification, but as part of a complex zonal alteration around fissures that was the result of both silica metasomatism and aluminum remobilization. Water from the hanging wall formations descended through fissures and reacted with the bauxite to yield an alteration sequence in the matrix that is characterized by an inward succession of a kaolinitic zone, a boehmite enrichment zone, and unaltered bauxite. A calculated thermodynamic model suggests that as silica was introduced into the bauxite, part of the Al and Fe were moved by diffusion. As the introduced silica was consumed to form kaolinite, excess Al was partly removed into the descending solution in the fissures and partly remobilized into the bauxite, forming new boehmite. Contrary to Al, dissolved Fe from both zones diffused into the descending solutions. Thus, kaolinite and boehmite alteration fronts moved simultaneously into the bauxite.

This alteration pattern suggests that the kaolinitization of bauxite was associated with boehmitization, a process that significantly increased the quality of the bauxite ore.

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REFERENCES

- Bailey, S. W. (1980) Structures of layer silicates: in *Crystal Structures of Clay Minerals and Their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 1–123.
- Bárdossy, G. (1982) *Karst Bauxites—Bauxite Deposits on Carbonate Rocks*: Elsevier, Amsterdam–London–New York, p. 441.
- Beneslavsky, S. I. (1963) *Mineralogy of Bauxites*: Gosgeoltekhizdat, Moscow, p. 170 (in Russian).
- Beneslavsky, S. I. (1968) Basic features of unity of the process of minerogenesis in lateritic and sedimentary bauxites: *Travaux du ICSOBA* No. 5, 4–16 (in Russian with English abstract).
- Bushinsky, G. I. (1968) Case of natural bleaching of bauxites: *Travaux du ICSOBA* No. 5, 17–30 (in Russian with English abstract).
- Dangić, A. (1977) The genesis of primary kaolin deposit Bratunac: in *Proc. 8th Int. Kaolin Symp. and Meeting on Alunite, Madrid-Rome, 1977*, E. Galan, ed., IGCP WG "Genesis of Kaolins," Madrid, K-4, p. 10.
- Garrels, R. M. and Christ, C. L. (1965) *Solutions, Minerals, and Equilibria*: Harper and Row, New York, p. 450.
- Goldman, M. I. (1955) Petrography of bauxite surrounding a core of kaolinized nepheline syenite in Arkansas: *Econ. Geol.* 50th Aniv. Vol., 586–609.
- Goldman, M. I. and Tracey, J. I., Jr. (1964) Relation of bauxite and kaolin in the Arkansas bauxite deposits: *Econ. Geol.* 14, 567–575.

- Hinckley, D. N. (1963) Variability in "crystallinity" values among the kaolin deposits of the coastal plain of Georgia and South Carolina: in *Clays and Clay Minerals, Proc. 11th Natl. Conf., Ottawa, Ontario, 1962*, Ada Swineford, ed., Pergamon Press, New York, 229–235.
- Keller, W. D. (1962) *The Principles of Chemical Weathering*: Lucas Brothers Publ., Columbia, Missouri, p. 111.
- Keller, W. D. and Clarke, O. M., Jr. (1984) Resilication of bauxite at the Alabama Street Mine, Saline County, Arkansas, illustrated by scanning electron micrographs: *Clays & Clay Minerals* 32, 139–146.
- Krauskopf, K. (1967) *Introduction to Geochemistry*: McGraw-Hill, New York, p. 721.
- Maksimović, Z., Dangić, A., and Ranković, M. (1981) Relics of the Upper Cretaceous weathering crust on ultramafic and mafic rocks in the north-west from Zvornik: in *Abstracts, Conference on Fe-Ni Lateritic Ores of Yugoslavia, Kavadarci, 1981*, FENI, Kavadarci, p. 2 (in Serbo-Croatian).
- Maksimović, Z., Šćavničar, B., and Dangić, A. (1983) Sedimentological and geochemical aspects of the origin of karstic bauxites from Vlasenica area (Yugoslavia): in *Abstracts, 4th Int. Assoc. Sedimentologists Regional Meeting, Split, Yugoslavia, 1983*, 101–102.
- Norton, S. A. (1973) Laterite and bauxite formation: *Econ. Geol.* 68, 353–361.
- Ranković, M. (1973) Geology of the bauxite-bearing locality "Bračan" in East Bosnia: *Proc. 2nd Yugosl. Symp. Exploration Exploatac. Bauxite, Tuzla, Yugoslavia, 1973*, Inst. RHTI, Tuzla, A-XII, p. 17 (in Serbo-Croatian with French abstract).
- Valeton, I. (1972) *Bauxites*: Elsevier, Amsterdam–London–New York, p. 226.

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