

KAOLINIZATION OF BAUXITE: A STUDY OF THE VLASENICA BAUXITE AREA, YUGOSLAVIA. II. ALTERATION OF OOLITES

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Abstract—During the epigenetic alteration of boehmitic karstic bauxite in the Vlasenica region of Yugoslavia, which was caused by siliceous water descending through the deposit by means of cracks, fissures, etc., oolites were less altered compared with the coexisting matrix material, which was intensely kaolinized. The following zonal alteration pattern of the oolites was identified: a diasporite enrichment zone, followed by a diasporite-boehmite enrichment zone, and then the original bauxite. Considering this alteration pattern and that determined previously for the matrix material, the following overall pattern of alteration was established: a kaolinite-diasporite zone, followed by a boehmite-diasporite zone, and then the original bauxite. The alteration solutions reacted with the bauxite to form solution-matrix and solution-oolite subsystems, which were characterized by different types of diffusion and geochemistry.

In the kaolinite-diasporite zone Si-metasomatism kaolinized the matrix, and excess Al partly migrated into the oolites, forming diasporite, and outward into the bauxite. The latter Al-remobilization resulted in a transition zone, in which new boehmite was formed in both the matrix and the oolites, and diasporite only in the oolites. Thermodynamic models of oolites and whole bauxite alterations were established, on the basis of stability diagrams calculated for the mineral assemblages of both the oolites and the matrix, in the alteration zones and in the deposit as a whole. Based on these models, the genesis of the diasporite and the relationship of diasporite-boehmite-kaolinite assemblages in natural systems at low temperature and low pressure can be described.

Key Words—Aluminum, Bauxite, Boehmite, Diasporite, Kaolinization, Oolites.

Rezime—Tokom epigenetske alteracije bemitskih karsnih boksita u području Vlasenice, izazvane perkolacijom voda obogaćenih rastvorenom silicijom koje su ponirale kroz pukotine, rasedne zone i sl., ooliti su slabije alterisani u poredjenju sa koegzistentnom osnovom koja je intenzivno kaolinisana. Identifikovan je sledeći tip zonalne alteracije za oolite: zona obogaćenja dijasporom, iza koje slede zona obogaćenja dijasporom i bemitom i zatim originalni boksit. Na osnovu razmatranja ovog tipa alteracije i tipa alteracije za materijal osnove, ustanovljen je sledeći tip alteracije boksita kao celine: kaolinitsko-dijasporiska zona, iza koje slede bemitsko-dijasporiska zona i zatim originalni boksit. Alteracioni rastvor je reagovao sa boksitom obrazujući kompleksan sistem, koji se sastojao od dva podsistema: rastvor-materijal osnove i rastvor-ooliti, koji su se medju sobom razlikovali kako po modelima difuzije tako i po geohemijskim karakteristikama.

U kaolinitsko-dijasporiskoj zoni Si-metasomatizam je doveo do kaolinizacije materijala osnove, a višak Al je delom migrirao kako u koegzistentne oolite, obrazujući u njima dijaspor, tako i dublje u boksit. Remobilizacija Al dublje u boksit dovela je do obrazovanja prelazne zone, u kojoj se obrazovao bemit i u osnovi i u oolitima, i dijaspor samo u oolitima. Postavljeni su termodinamički modeli za alteraciju oolita i boksita kao celine, a na osnovu dijagrama stabilnosti proračunatih za mineralne asocijacije i oolita i osnove, u zonama alteracije i u samom ležištu. Na osnovu svega ovoga razmotreni su tačnije i pouzdanije geneza dijaspora i odnos dijaspor-bemit-kaolinit u prirodnim sistemima na niskim temperaturama i niskim pritiscima.

INTRODUCTION

Aluminum monohydrate minerals are present in most bauxite deposits, some clay deposits, and some soils and commonly coexist with kaolinite. The stability and conditions of formation of boehmite and diasporite and their genetic relationship to one another and to kaolinite are only poorly understood, despite the many studies on these subjects. Diasporite itself has been reported in both metamorphosed and unmetamorphosed karst- and laterite-type bauxite deposits (Fox, 1932; Beneslavsky, 1963; Valetton, 1972; Bárdossy, 1982), but in contrast to earlier ideas that it formed only under metamorphic conditions (Gorecky *et al.*, 1949; Ervin

and Osborn, 1951), experimental studies and field observations now indicate that diasporite may also form in the near-surface environment (Kennedy, 1959; Keller, 1962; Keller and Stevens, 1983; Valetton, 1964; Kittrick, 1969; Nia, 1968; Bárdossy, 1982; Özlü, 1985). Many uncertainties remain, however, concerning the exact processes of formation of this mineral and its genetic relationship to coexisting phases in nonmetamorphic deposits (Bárdossy, 1982; Maynard, 1983).

The alteration of karst- and laterite-type bauxites to kaolinite (Goldman, 1955; Goldman and Tracey, 1964; Keller, 1962; Beneslavsky, 1963, 1968; Bushinsky, 1968; Valetton, 1972; Bárdossy, 1982) has been thought

to be a relatively simple process of metasomatic resilicification (Keller, 1962; Keller and Clarke, 1984; Valetton, 1972; Bárdossy, 1982). Dangić (1985a), however, showed that for bauxite in the Vlasenica region of Yugoslavia, kaolinization of the matrix material took place in a complex manner, involving both Si-metasomatism and Al-remobilization. He found that the original bauxite altered progressively to various assemblages of syngenetic and/or epigenetic boehmite, diaspore, and kaolinite, thereby illustrating the complexity of the process (Dangić, 1983, 1985a, 1985b). The present study involves the mineralogy and geochemistry of the oolites in the alteration profile of the Braćan deposit in the Vlasenica bauxite region. Based on the thermodynamic model calculated earlier for the matrix material (Dangić, 1985a) and a stability diagram developed in this study for the principal minerals in the oolites, a thermodynamic model for the alteration process as a whole is proposed.

GEOLOGIC SETTING AND CHARACTERISTICS OF THE BAUXITE DEPOSITS

The Vlasenica bauxite region in eastern Bosnia is one of the most important bauxite-producing regions of Yugoslavia. The deposits occur in a narrow belt about 30 km long and 4 km wide. The relevant geology and mineralogy of the deposits were described by Dangić (1985a). Briefly, the bauxite bodies are in karstic depressions in Middle Triassic limestones and are covered by Upper Cretaceous limestones and/or sandy-clayey limestones of Upper Cretaceous or Neogene age. The ore bodies occur as discontinuous layers, lenses, and pockets within limestone and are overlain by partly or completely eroded hanging wall rocks.

The deposits range in size from tens of thousands 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 oolites/pisolites. Mineralogically, the bauxite consists chiefly of boehmite, hematite, kaolinite, and TiO_2 minerals (anatase and rutile). Boehmite and kaolinite appear to be concentrated in the matrix, and hematite is most abundant in the oolites/pisolites. Epigenetic kaolinite, boehmite, and diaspore are only locally present (Bárdossy, 1982; Dangić, 1983, 1985a, 1985b).

Kaolinized bauxite is locally present in several of the deposits of the region, but it is most prevalent in the Braćan deposit in and around a fissure zone (Dangić, 1983, 1985a). The Braćan ore body is the largest in the region and is well exposed in an open pit. The ore ranges in thickness from 10 to 50 m and is partly covered by both limestone and sandy-clayey limestone formations (locally as thick as 150 m and 50 m, respectively). Kaolinized bauxite, 1.5 m thick, occurs in and around a fissure zone and is separated from the original bauxite by a 1-m transition zone. Although

the bauxite is highly kaolinized, the oolitic structure was preserved.

The original bauxite is compact and consists of black to brown oolites and a red matrix. The oolites are chiefly hematite, but substantial boehmite and minor kaolinite are also present. The matrix of the original bauxite is chiefly boehmite with substantial hematite and kaolinite. Minor anatase and rutile are also present in both the oolites and the matrix. Highly kaolinized bauxite is characterized by a white matrix, composed of kaolinite only, and light-brown oolites. The transition zone is characterized by a yellow-pink matrix, enriched in boehmite, and brown oolites. Dangić (1985a) reported the following pattern of matrix alteration inwards from the fissures: kaolinitic zone → boehmitic zone → original bauxite.

EXPERIMENTAL

Samples were examined by means of optical microscopy, transmission electron microscopic (TEM), X-ray powder diffraction (XRD), differential thermal gravimetric (DTG), wet chemical, and spectrochemical analyses. The oolitic material used for TEM, XRD, DTG, and chemical and spectrochemical analyses was carefully hand picked from the bauxite ore. A Philips EM-300 transition electron microscope was used; XRD patterns were obtained using $\text{CuK}\alpha$ radiation at a scanning rate of $2^\circ 2\theta/\text{min}$ and a graphite monochromator; DTG curves were obtained using a Pt-Pt/Rh thermocouple on a Lindsey apparatus.

Elemental analyses were made by rapid silicate analytical procedures and involved spectrophotometric and atomic absorption techniques. Trace elements were determined using an STE-1 emission spectrograph and corrected against both internal standards and international reference samples. Excitation was by means of a vertical d.c. arc in a controlled Ar- O_2 atmosphere. The precision of the method is estimated to be $\pm 10\%$.

Quantitative mineral composition was calculated from the XRD, DTG, and chemical analyses.

RESULTS

X-ray powder diffraction results

The alteration of the oolites in the altered bauxite was by the replacement of original minerals and by the filling of cracks by boehmite, diaspore, and probably trace amounts of chlorite. As seen from the XRD patterns (Figure 1), oolites in the highly kaolinized bauxite are characterized by an increased amount of diaspore and a decreased amount of all other primary minerals, compared with the original bauxite. The oolites in the transition zone are characterized by the presence of diaspore and an enrichment of boehmite. The boehmite content is greater and the content of all other primary minerals is smaller than those of the original bauxite ore. On the basis of these data, the oolites of

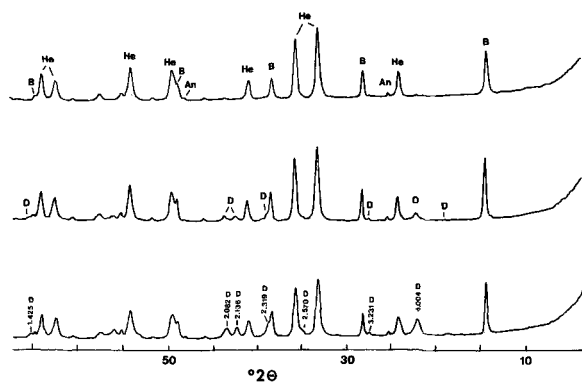


Figure 1. X-ray powder diffraction pattern of oolites from unaltered bauxite (above) and diaspore-boehmite and diaspore zones (middle and below, respectively). B = boehmite; D = diaspore; K = kaolinite; H = hematite; An = anatase (CuK α radiation; values indicated in Å).

the bauxite can be divided into the following alteration zones, outwards from the original bauxite: original bauxite \rightarrow diaspore-boehmite zone \rightarrow diaspore zone (see Figure 2).

Mineralogy and geochemistry

Oolitic material in the alteration zones differs from that in the original bauxite both mineralogically and chemically, but to different degrees. In general, the oolites are less intensely altered than coexisting matrix material, especially in the zone of most intense alteration. Oolites in the original bauxite are black or brown and consist of about 55–60% hematite, 30–35% boehmite, 3–4% kaolinite, 3–4% TiO₂ minerals (anatase + rutile), and about 4% other minerals. The oolites in the transition zone (diaspore-boehmite) are brown and consist of about 50% hematite, 35–40% boehmite, 6–7% diaspore, 2–3% kaolinite, 2–3% TiO₂ minerals (anatase + rutile), and about 2% other minerals. Oolites in the most intensely altered zone (diaspore) are light brown and consist of about 40–45% hematite, 25–30% boehmite, 20–25% diaspore, 4–5% kaolinite + chlorite, 2–3% TiO₂ minerals (anatase + rutile), and about 1% other minerals; a Mg-containing 7-Å chlorite mineral is probably present, as indicated by the increase of MgO in this zone.

Chemical and spectrochemical analyses of oolites from the original bauxite, the transition zone, and the most intensely altered zone are listed in Tables 1 and 2, respectively. Compared with the whole ore (oolites + matrix), oolites in the unaltered, original bauxite contain more ferric oxide (55.1 vs. 29.7%), less alumina (28.84 vs. 50.2%), less silica (1.6 vs. 4.5%), and slightly more titania (3.13 vs. 2.7%). They are also characterized by a relatively high water content (8.4%) and low contents of ferrous oxide (0.86%), magnesia (0.5%), and lime (0.3%) and a trace of Na₂O. The more abundant trace elements in oolites from the original

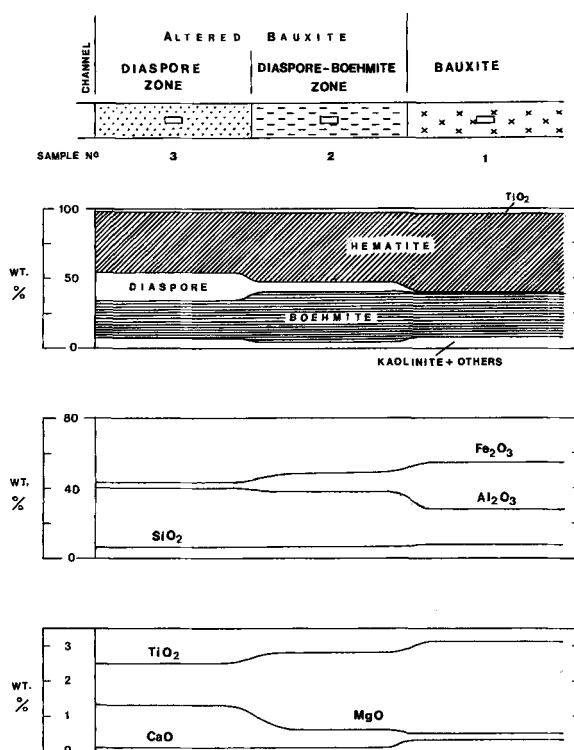


Figure 2. Variation in mineral and chemical composition of the oolites in zoned alteration of bauxite, Braćan deposit.

bauxite are Zr, Mn, V, Cr (450–880-ppm range) and Pb, Nb, Y, Ni, and Zn (100–250-ppm range), and compared with the whole ore, the oolites contain more Zr, V, and Pb (see Table 2).

Oolites in the transition zone contain more alumina (37.7 vs. 28.8%) and less ferric oxide (48.0 vs. 55.1%), silica (1.15 vs. 1.6%), and titania (2.9 vs. 3.1%) than those in the original bauxite. No significant differences were noted among the minor elements—only a few decreased (Zr, Y, V, Nb) or increased (Be, Ga) by as much as a factor of 2–2.5 (see Table 2). Oolites in the most intensely altered zone (diaspore zone) are characterized by higher alumina (39.8 vs. 37.7%), higher magnesia (1.33 vs. 0.59%), lower ferric oxide (43.6 vs. 48%), and lower titania (2.5 vs. 2.9%) contents than those in the transition zone. No significant differences were noted among the minor elements—only a few decreased (Ba, Mn) or increased (Nb, Ni, Y, Zn, Zr) by as much as a factor of 1.5–2 (see Table 2).

DISCUSSION

The alteration of oolites in the bauxite was much less severe than that of the matrix material (see Dangić, 1985a). Oolites in the original, unaltered bauxite are mineralogically similar to the matrix material and consist of boehmite, hematite, kaolinite, and TiO₂ minerals, but the relative abundance of these minerals in the two materials differs significantly. Hematite and

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

	Original bauxite (matrix + oolites)	Oolites		
		Original bauxite	Diaspore- boehmite zone	Diaspore zone
SiO ₂	4.54	1.60	1.15	1.14
TiO ₂	2.69	3.13	2.85	2.50
Al ₂ O ₃	50.19	28.84	37.65	39.80
Cr ₂ O ₃	0.07	0.06	0.05	0.06
Fe ₂ O ₃	29.65	55.10	48.02	43.55
FeO	0.64	0.86	0.70	0.63
MnO	0.06	0.09	0.12	0.07
NiO	0.04	0.01	0.02	0.03
MgO	0.93	0.46	0.59	1.33
CaO	0.45	0.30	0.12	0.11
Na ₂ O	0.01	0.02	0.13	0.05
K ₂ O	—	—	0.06	0.05
H ₂ O+	10.22	8.35	8.51	10.17
H ₂ O-	0.80	0.73	0.60	0.54
Total	100.29	99.55	100.48	100.03

boehmite are the predominant phases in both materials; however, hematite is the most abundant phase in the oolites, and boehmite is the most abundant phase in the matrix material. Kaolinite is abundant only in the matrix material.

The oolites and matrix material in the two alteration zones differ in both the nature of the minerals present and in their abundance. As reported by Dangić (1985a), matrix material adjacent to fissures has been altered almost completely to kaolinite, whereas in the transition zone, only small amounts of boehmite have been formed. Oolites coexisting with completely kaolinized matrix material have been only partly altered; diaspore appears to be the only new phase to have formed. In the transition zone, alteration was apparently even less severe, and only diaspore and second generation boehmite were formed. The alteration pattern of the oolites, therefore, appears to have been the transformation of kaolinite to diaspore + boehmite and of boehmite to diaspore accompanied by the formation of diaspore and new boehmite and the dissolution of hematite and TiO₂ minerals. The alteration pattern can be represented outwards from fissures as: diaspore zone → diaspore-boehmite zone → original bauxite.

The overall alteration of the original bauxite therefore consisted of the formation of kaolinite and boehmite in the matrix material, the formation of diaspore and boehmite in the oolites, and the dissolution of hematite and TiO₂ minerals in both. The composite alteration can be represented outwards from the fissures by: kaolinite-diaspore zone → boehmite-diaspore zone → original bauxite. The relationships between the principal minerals and the chemical composition of the oolites and coexisting matrix in the original bauxite and the two alteration zones are depicted in the triangular diagram of Figure 3. The path 123 indicates an intense mass transfer during matrix alteration, with

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

	Original bauxite (matrix + oolites)	Oolites		
		Original bauxite	Diaspore- boehmite zone	Diaspore zone
B	56	35	32	40
Ba	18	8	12	8
Be	10	7	18	15
Co	52	30	28	40
Cr	450	450	370	430
Cu	72	66	43	33
Ga	50	28	74	78
La	75	70	40	32
Mn	870	870	980	580
Nb	145	130	50	113
Pb	180	250	183	155
Sc	48	58	32	50
Sn	—	—	13	—
Sr	52	15	15	20
V	270	520	270	285
Y	170	120	60	185
Zn	150	100	150	230
Zr	620	880	340	430

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

an enrichment of alumina-Al-monohydrate minerals in the boehmite-diaspore zone, and a silica-kaolinite strong enrichment in the kaolinite-diaspore zone. On the other hand, the path 1'2'3' indicates a less intense mass transfer during oolite alteration, with a progressive alumina-Al-monohydrate minerals enrichment in alteration zones. Iron (hematite) was progressively removed in both paths. Differences in the matrix and oolite alteration paths, as well as formation of diaspore and boehmite only in oolites and in both oolite and matrix alteration, respectively, indicate that alteration of bauxite as a whole (matrix + oolites) appears to have been a rather complex geochemical process.

The genesis of diaspore has been considered in many papers. The hypothesis that diaspore forms not only under metamorphic or hydrothermal conditions but under surface conditions as well is based on both field observations and the experimental studies. Kennedy (1959) found in an experimental study of the system Al₂O₃-H₂O that diaspore is the only stable aluminum oxyhydroxide at low temperature. Kittrick (1969) came to this same conclusion and suggested aging transition in the sequence: noncrystalline Al hydroxide-gibbsite-boehmite-diaspore. Inasmuch as diaspore has been identified as a syngenetic, diagenetic, or epigenetic mineral in various unmetamorphosed bauxites, laterites, and clays, numerous hypotheses have been put forward for its genesis. The presence of diaspore in some bauxites and laterites was explained by Gladkovsky and Ushatinsky (1964) and Bárdossy (1982) as the result of the dehydration of gibbsite during the dry season in hot climate.

Keller (1962) suggested that diaspore in the Missouri clays was formed under reducing conditions by the slow removal of silica during kaolinite hydrolysis or dialysis. Studies of bauxites, especially karst bauxites, suggest that the reducing conditions and/or water percolation are important factors in the formation of diaspore. For example, Valeton (1965) suggested that stagnant ground water under reducing conditions favors the formation of diaspore instead of boehmite or gibbsite, and Combes (1969) found that diaspore and/or boehmite can form during *in situ* bauxitization under reducing conditions. Kiskyras *et al.* (1978) reported that diaspore coexisting with chamosite and magnetite in some Greek bauxites formed under reducing conditions, and that the drainage regime was not the controlling factor between diaspore and boehmite formation. On the other hand, Nia (1968) concluded that diaspore formed during diagenesis by transformation of both boehmite and kaolinite, and that intense ground-water percolation, rather than reducing conditions, enabled the process. Valeton (1965) and Combes (1969) indicated an Eh near or less than zero. Komlóssy (1976) also reported that diaspore could be formed at these Eh conditions, but also under neutral or slightly alkaline conditions. Under more reducing and more alkaline conditions chamosite would form. Kiskyras *et al.* (1978) reported that diaspore and magnetite formed syngenetically in the oolites of bauxite, but that some of boehmite, mainly in the bauxite matrix, changed to diaspore during diagenesis. Özlü (1985) reported that in some boehmitic karst bauxites of Turkey diaspore is syngenetic (mainly in pisolites), syndiagenetic (coexisting with pyrite), and epigenetic (in veinlets, coexisting with secondary calcite). He concluded that mineral assemblages containing syndiagenetic diaspore suggest reducing, probably alkaline conditions.

From studies of matrix alteration, Dangić (1985a) concluded that bauxite kaolinization in the Vlasenica region was an epigenetic process. From studies of diaspore occurrences in the same region, he (1985b) concluded that diasporization of oolites took place simultaneously with kaolinization of coexisting matrix, i.e., as an epigenetic process.

Thus, during the epigenetic alteration of bauxite around fissures in the Vlasenica region, the alteration solution appears to have reacted with both the matrix and the coexisting oolites, but in different ways. The alteration solution-bauxite system probably consisted of two coexisting systems: water-matrix and water-oolite, formed by diffusion of water from the fissure into matrix material and from the matrix into individual oolite, respectively. The water-oolite system, as constituted by many individual water-oolite systems, was related to the water-matrix system as the dispersion phase was related to the dispersion medium in a dispersion system. On this basis, these complex alteration

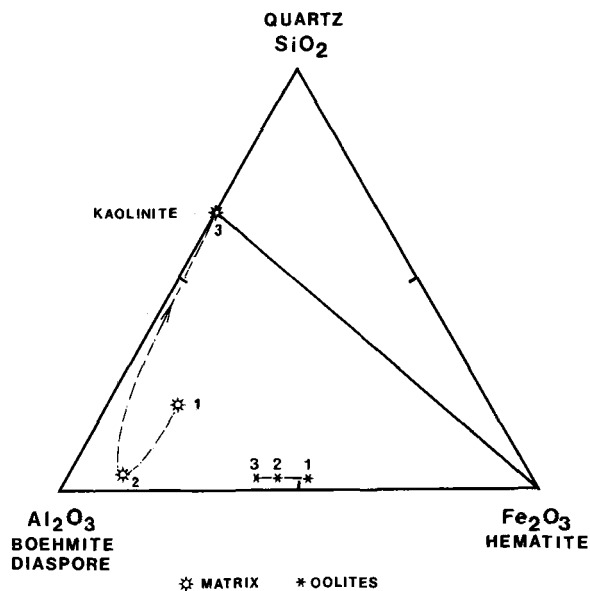
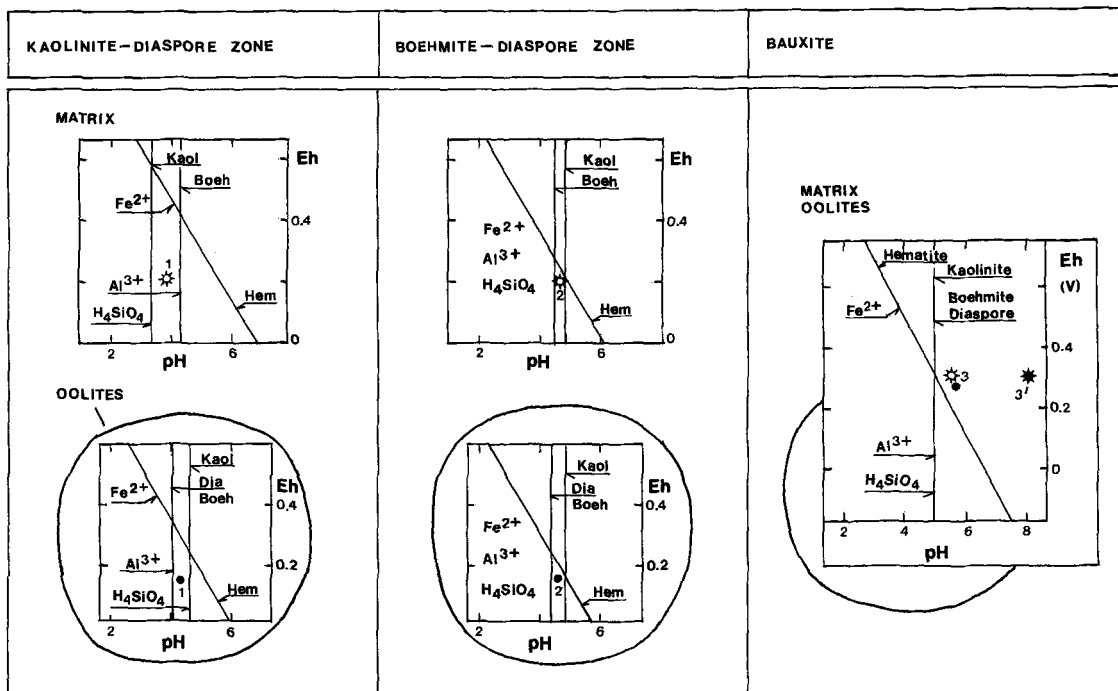


Figure 3. Some stability relations in the system $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$, at 25°C and 1 atm total pressure (water present). Dashed and heavy lines 1-2-3 show effects of alteration of matrix and oolites, respectively, in zoned alteration of bauxite, Braćan deposit. 1, 2, and 3 indicate composition in original bauxite, boehmite-diaspore zone, and kaolinite-diaspore zone, respectively.

systems can be termed the dispersion alteration system, the main alteration system, and the alteration subsystem, respectively.

Diaspore was present only in the water-oolite system, but boehmite, kaolinite, hematite, and TiO_2 minerals appear to have been important phases in both systems. Inasmuch as hematite and TiO_2 minerals appear to have reacted similarly in the process, they are treated here as a single phase. Accordingly, the previously prepared stability diagram for kaolinite, boehmite, and hematite in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3\text{-FeO-H}_2\text{O}$ at 25°C and 1 atm pressure (Figure 6, Dangić, 1985a) was complemented with diaspore (Figure 4). Because the standard free energies of diaspore and boehmite (Garrels and Christ, 1965; Naumov *et al.*, 1974; Hemingway *et al.*, 1978; Perkins *et al.*, 1979) are very close, the stability fields of diaspore and boehmite are practically coincidence in this diagram. The same coincidence appears in the diagram showing the relation of diaspore, boehmite, kaolinite, quartz, and noncrystalline silica with respect to dissolved silica activity (diagram with boehmite was given as Figure 5 in Dangić, 1985a). Both diagrams indicate that the diaspore-boehmite relation is a function of physicochemical or geochemical factors other than the simple activities of dissolved alumina or silica species or the pH of solution.

A comparative analysis of mineral and chemical transformations of the oolites in the alteration zones,



	Matrix	Oolites	Matrix	Oolites	
$[H_4SiO_4]$ =	10^{-4}	$10^{-7.5}$	10^{-8}	$10^{-7.5}$	10^{-7}
$[Al^{3+}]$ =	10^{-5}	$10^{-5.5}$	$10^{-5.5}$	10^{-6}	10^{-7}
$[Fe^{2+}]$ =	10^{-6}	$10^{-5.5}$	$10^{-5.5}$	10^{-5}	10^{-7}

Figure 4. Stability fields of kaolinite, boehmite, diaspore, 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 successive stages of alteration of bauxite matrix (diagrams from Dangić, 1985a) and oolites in zoned alteration profile. 1, 2, and 3 are positions in alteration zones and original bauxite; 3' is "abrasive pH and Eh" of common bauxite. Hem = hematite; Kaol = kaolinite; Boeh = boehmite; Dia = diaspore.

the phase relations in the corresponding water-mineral system, the solubility of diaspore, boehmite, and hematite, as well as the relation to the surrounding water-matrix system, provides significant insight into the process of oolite alteration.

From studies of matrix alteration, Dangić (1985a) concluded that the water-matrix system was characterized (1) in the kaolinite-diaspore zone, by activities of Al^{3+} , Fe^{2+} , and dissolved silica of about 10^{-4} , 10^{-5} , and $10^{-5.5}$, respectively, a pH of 4, an Eh of 0.19 V, and near equilibrium conditions; (2) in the boehmite-diaspore zone, by activities of Al^{3+} , Fe^{2+} , and dissolved silica of about $10^{-5.5}$, $10^{-5.5}$, and 10^{-8} , respectively, a pH of 4.7, an Eh of 0.19 V, and nonequilibrium conditions; and (3) in original bauxite, by activities of Al^{3+} , Fe^{2+} , and dissolved silica of about 10^{-8} – 10^{-9} , 10^{-8} – 10^{-9} , and 10^{-9} , respectively, a pH of 5.5, and an Eh of 0.27 V.

The activity of dissolved silica in the water-oolite system in both alteration zones must have been $<10^{-7.07}$, because boehmite and/or diaspore were stable in the oolites, but not much less than this value, because kaolinite was relatively slightly unstable. On the other hand, in the boehmite-diaspore zone it must

have been $>10^{-8}$, probably about $10^{-7.5}$, because some silica was diffused from the oolites into the surrounding water-matrix system; for the kaolinite-diaspore zone, the same activity is suggested by the diaspore-kaolinite relation. In the bauxite beyond the boehmite-diaspore zone, the activity of silica was about 10^{-9} , as in the surrounding water-matrix system.

The Al^{3+} activity in the water-oolite system in both alteration zones had to be greater than that produced by the dissolution of boehmite and/or diaspore at a given pH, but not much greater, as indicated by the intensity of boehmitization and/or diasporization of the oolites. On the other hand, it had to be somewhat less than that in the surrounding water-matrix system, because some of the alumina was remobilized from matrix material into the oolites. Accordingly, the Al^{3+} activity in the boehmite-diaspore and kaolinite-diaspore zones must have been $<10^{-5}$, probably about $10^{-5.5}$, and $<10^{-5.5}$, probably about 10^{-6} , respectively. In the bauxite beyond the boehmite-diaspore zone, the Al^{3+} activity was probably about 10^{-8} – 10^{-9} , as in the surrounding water-matrix system.

The Fe^{2+} activity in the water-oolite system is indicated by the pH of the solution and the stability

(solubility) of hematite. The Fe^{2+} activity in both alteration zones must have been only somewhat less than that in equilibrium with hematite, inasmuch as hematite was only partly dissolved. On the other hand, it must have been greater than that in the surrounding water-matrix system, because some Fe was removed from the oolites. Accordingly, in the kaolinite-diaspore and boehmite-diaspore zones, the Fe^{2+} activity was $>10^{-6}$, probably about $10^{-5.5}$, and $>10^{-5.5}$, probably about 10^{-5} , respectively. The Eh and pHs in this system were probably the same or slightly greater than the surrounding water-matrix system, as indicated by the experimental study of the $\text{FeO-Fe}_2\text{O}_3\text{-H}_2\text{O}$ system (Dangić, 1984). The Fe^{2+} activities calculated to be in equilibrium with hematite in the water-oolite system at pH 4, $10^{-2.8}$ or slightly greater, and at pH 4.7, 10^{-5} or slightly greater, respectively, in the kaolinite-diaspore and boehmite-diaspore zones. The differences in the Fe^{2+} activities calculated as actual and as in equilibrium with hematite well explain the differences in hematite dissolution rates in the oolites in the alteration zones. The Fe^{2+} activity, pH, and Eh of the water-oolite system in the bauxite beyond the boehmite-diaspore zone were 10^{-7} , ~ 5 , and 0.26 V, respectively, i.e., the same as in the surrounding water-matrix system.

Based upon these considerations, stability diagrams showing the relation of diaspore, boehmite, kaolinite, and hematite and the relevant dissolved species in the water-oolite system in the alteration zones in the unaltered bauxite were calculated (Figure 4). The diagrams were calculated for dissolved silica, Al^{3+} , and Fe^{2+} activities of $10^{-7.5}$, $10^{-5.5}$, and $10^{-5.5}$ (kaolinite-diaspore zone), $10^{-7.5}$, 10^{-6} , and 10^{-5} (boehmite-diaspore zone), and $10^{-7.07}$, $10^{-7.02}$, and 10^{-7} (unaltered bauxite), respectively. The diagram for the unaltered bauxite is practically the same as the diagram for the water-matrix system, but it is complicated by the presence of a diaspore stability field. Figure 4, as shown here, and the diagrams representing the water-matrix system (from Dangić, 1985a) represent the whole bauxite alteration.

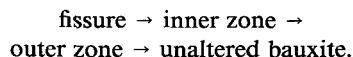
ALTERATION MODEL

A thermodynamic model of the process leading to the alteration of the oolites in the zoned alteration of the bauxite and a complex model of whole bauxite alteration, based on this and the previously established model for the matrix alteration (Dangić, 1985a), follow.

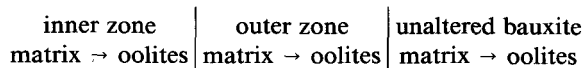
The model of the oolites alteration was based on a consideration of the observed mineral transformations, the calculated stability diagrams for the system in question, and the relation to alteration of the matrix. Dangić's (1985a) model of matrix alteration suggests that epigenetic bauxite alteration in the Vlasenica region took place after burial of the bauxite. Three dis-

tinct bauxite-alteration stages and a starting stage were postulated, related to the water-bauxite system around fissure and the source water in hanging wall formation. By comparing the oolite and matrix alteration patterns, however, a water-matrix and a water-oolite system had to coexist, differing in geochemical characteristics. The latter system must have consisted of many individual (isolated) water-oolite systems dispersed in the former. During alteration, two complex alteration fronts were successively formed and migrated, from fissures towards unaltered bauxite, each composed of a matrix and an oolite alteration front: boehmite (matrix) \rightarrow boehmite-diaspore (oolites) as the outer front, and kaolinite (matrix) \rightarrow diaspore (oolites) as the inner front, giving rise to corresponding alteration zones.

The matrix alteration fronts were a result of continuous fissure-unaltered bauxite diffusion and can be characterized by the following diffusion model:



On the other hand, the oolite alteration fronts were a result of a local matrix \rightarrow oolite diffusion in each zone and can be characterized by the following diffusion model:



indicating the water-matrix and the water-oolite systems as the principal system and a subsystem, respectively. Thus, the oolite alteration appears to have been similar to that of the matrix inasmuch as the alteration solution of the matrix system was probably the source solution for the oolite alteration. The above relationships and the matrix alteration model developed by Dangić (1985a) have led to the present model for the alteration of the bauxite as a whole. Relevant geochemical compositions and mineral transformations are shown in Figure 4.

Starting stage

Water from the hanging wall formation descended into the bauxite through fissures. Due to the small quantity of the water, its slow descent, and its interaction with quartz, silicates, and chert, as well as the oxidation of coal and other organic matter, the dissolved silica activity increased to about 10^{-4} (somewhat less than quartz saturation), the Al^{3+} and Fe^{2+} activities increased to somewhat less than 10^{-5} and 10^{-6} , respectively, and the pH and Eh decreased to 3.5–4 and <0.2 V, respectively.

Bauxite alteration stages

The descending solution diffused through fissures into the host bauxite and reacted with both the matrix material and oolites, forming a complex alteration system which consisted of two alteration fronts, each com-

posed of a matrix and an oolitic front. A three-stage alteration process appears to have been operative:

(1) At or near the fissure zone, a kaolinitic and a diasporic alteration front were developed in the matrix and in the oolites, respectively (Figure 4, stages 1 and 1'). In the matrix alteration system, hematite and boehmite were unstable with respect to kaolinite, and kaolinite replaced all other phases. The excess Al^{3+} and all of the Fe (as Fe^{2+}) were removed from the system, and the Al^{3+} and Fe^{2+} activities were about 10^{-5} and $10^{-5.5}$, respectively. On the other hand, in the oolite alteration subsystem, all three phases (i.e., hematite, boehmite, and kaolinite) were unstable with respect to diasporite, which formed as a new phase. The process was slower than in the matrix system, and therefore diasporite only partly replaced the primary phases. Compared with the matrix alteration system, the activities of dissolved silica and Al^{3+} were lower, the activity of Fe^{2+} was higher, and the pH and Eh were slightly greater. The diasporic front was formed by the addition of Al, remobilized from the matrix system, and was accompanied by the removal of part of the Fe and silica. The concentrations of dissolved silica, Al^{3+} , and Fe^{2+} were about $10^{-7.5}$, $10^{-5.5}$, and $10^{-5.5}$, respectively.

(2) Ahead of the kaolinite-diasporite alteration front, the changes of the activities of dissolved species of the diffusing solution affected the stability of some of the primary minerals and a boehmitic and a diasporite-boehmite alteration front were formed in the matrix and the oolites, respectively (Figure 4, stages 2 and 2'). In the matrix alteration system, the activity of dissolved silica decreased sharply to about 10^{-8} , the Al^{3+} and Fe^{2+} activities were about $10^{-5.5}$, somewhat less and higher, respectively, than in the matrix system of the previous zone, and the pH (4.5–4.8) and Eh increased slowly. Boehmite apparently was the only stable phase and partly replaced other phases. The boehmitic alteration front was formed by the addition of Al, remobilized from the previous zone, which was accompanied by the removal of part of the silica and Fe.

In the oolite alteration subsystem, however, both the hematite and kaolinite were unstable with respect to boehmite and diasporite, which partly replaced the primary phases, but more slowly compared with the process of mineral replacement in the surrounding matrix. The diasporite-boehmite alteration front was formed by the addition of Al remobilized from the matrix system and was accompanied by the removal of part of the silica and Fe. The activities of the dissolved silica and Fe^{2+} were somewhat greater, the activity of Al^{3+} somewhat lower, and the pH and Eh were slightly greater, compared with the matrix alteration system. Dissolved silica, Al^{3+} , and Fe^{2+} activities were about $10^{-7.5}$, 10^{-6} , and 10^{-5} , respectively.

(3) Farther into the bauxite, ahead of the boehmite-diasporite front, the dissolved silica activity remained

low, the activities of the Al^{3+} and Fe^{2+} decreased, and the pH and Eh significantly increased in both the matrix and the oolites systems. All three phases (kaolinite, boehmite, and hematite) became stable in the system as a whole (Figure 4, stages 3 and 3'). Dissolved silica, Al^{3+} , and Fe^{2+} activities were $<10^{-7}$, and the pH and Eh were about 5 and 0.26 V, respectively. Some reaction took place between the solution and the bauxite minerals, because the pH and Eh of solution rapidly increased.

CONCLUSIONS

Kaolinization of the bauxite matrix around fissures in the Vlasenica bauxite area was accompanied by a slight diasporization of the oolites in a complex zonal alteration of boehmitic bauxite. Alteration was the result of a Si-metasomatism and an Al-remobilization in the matrix and in both the matrix and oolites, respectively. Water from the hanging wall formation descended through fissures and reacted with bauxite to yield a two-zone alteration, which is characterized (1) for oolites, by an inward succession of a diasporite enrichment zone, a diasporite-boehmite enrichment zone, and then the original bauxite; and (2) for the matrix, an inward succession of a kaolinite zone, followed by a boehmite enrichment zone, and then the original bauxite. The data suggest that during alteration solution-matrix and solution-oolite systems coexisted, which were characterized by an overall, continual diffusion from the fissures toward unaltered bauxite, and a local diffusion between individual oolites and the surrounding matrix system, respectively. Calculated thermodynamic models representing both alteration of matrix and oolites suggest that as silica was introduced into the bauxite, part of the Al and Fe diffused. As the introduced silica was consumed in the matrix to form kaolinite, excess Al partly entered the descending solution, partly remobilized into coexisting oolites to form diasporite, and partly diffused farther into the bauxite. In the oolites, boehmite was unstable with respect to diasporite. Farther into the bauxite, the remobilized Al was partly consumed in the matrix to form new boehmite and partly remobilized from the matrix into coexisting oolites, forming there both diasporite and new boehmite. On the other hand, dissolved Fe from both the matrix and the oolites of both alteration zones diffused into the descending solution. Thus, complex kaolinite-diasporite and boehmite-diasporite alteration fronts formed and moved simultaneously into the bauxite.

This complex alteration pattern suggests that the kaolinization of the bauxite was associated with boehmitization and diasporization, but in a complex manner. Kaolinization took place in the matrix, boehmitization in both the matrix and the oolites, and diasporization in the oolites.

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