SCANNING ELECTRON MICROSCOPIC AND X-RAY POWDER DIFFRACTION STUDY OF MANGANIFEROUS BAUXITE, KINCSESBÁNYA, HUNGARY

GYÖRGY BÁRDOSSY

Hungarian Aluminium Corporation, Budapest, Hungary

ANNA CSORDÁS-TOTH AND ANNAMÁRIA KLUG

HUNGALU Engineering and Development Centre, Budapest, Hungary

Abstract—Manganiferous karst bauxites are rare on a worldwide scale. One such body, recently mined at Kincsesbánya, Hungary, has been studied by chemical, petrographic, X-ray powder diffraction, scanning electron microscopic, and energy dispersive X-ray analytical techniques. The bauxite deposits of Kincsesbánya are of Paleocene to Lower Eocene age; however, the enrichment of manganese in them was a much later, epigenetic process. Lithiophorite is the main Mn mineral in this bauxite and occurs chiefly in clusters of <1-μm size crystallites. Well-developed crystallites, however, 5–10 μm in size, line the walls of many microfissures and voids.

The oxidation of pyritic bauxite and lignitic clays in the overlying beds apparently mobilized finely disseminated Mn and Fe. Downward-migrating acidic solutions were gradually neutralized, and Mn and Fe minerals precipitated. The manganiferous bauxite was found only along the eastern rim of heavily eroded Middle Eocene sedimentary rocks. Here, epigenetic oxidation and mobilization were optimum. Farther to the east, pyrite-rich overburden and bauxite were apparently eroded away before Fe and Mn could be mobilized.

Key Words—Aluminum, Bauxite, Lithiophorite, Manganese, Scanning electron microscopy, X-ray powder diffraction.

INTRODUCTION

Manganiferous bauxite was discovered in 1981 at Kincsesbánya, Hungary, in a newly opened surface mine. In general, karst bauxites contain about 0.2% MnO_2, and only two bauxite deposits are known that contain substantial amounts of this element. One is the La Braunhe deposit at Bédarieux, France, where the upper part of the deposit contains 3–5% MnO_2 (Bárdossy, unpublished data); the other is a group of small deposits at La Boissière, France, where the bauxite bodies homogeneously contain 1.5–3.0% MnO_2 (Bárdossy, unpublished data).

The Kincsesbánya manganiferous bauxite, therefore, represents an unusual type of bauxite from both a geochemical and a genesis point of view. The present paper reports the results of chemical and mineralogical investigations of this bauxite and describes a possible mode of origin for it.

EXPERIMENTAL WORK

Systematic geological observations, documentation, and sampling were carried out during the mining of the deposit. Chemical analyses were made of 250 samples for major elements, including: Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO, MgO, S, P_2O_5, MnO_2, and H_2O+. Chemical analyses of trace elements, thin section microscopy, X-ray powder diffraction (XRD), differential thermal (DTA) and thermal gravimetric (TGA) analyses, and scanning electron microscopic (SEM) investigations were conducted on samples representing all types of low-Mn and manganiferous bauxites found in the deposit. Scanning electron microscopy was the principal technique employed, based on the earlier study by Bárdossy *et al.* (1978) that demonstrated the efficiency of this technique for solving genetic problems of bauxites.

JEOL JSM-U3 and Philips SEM 505 scanning electron microscopes were used, generally at 25 kV accelerating voltage and 10 picoampere current intensity. The SEM study was accompanied by energy dispersive X-ray microanalyses (EDX) using an EDAX 711-type instrument which enables point analyses to be made of volumes as small as about 1 μm^3.

A Philips 1050/25-type X-ray diffractometer equipped with a graphite monochromator was used for the mineralogical studies, complemented by Guinier-camera (type XDC-700) measurements. The computerized, automated XRD phase-analysis method developed for bauxites by Bárdossy *et al.* (1980) was used in the present investigation.

GEOLOGIC SETTING

The Kincsesbánya (also called Iszkaszentgyörgy) bauxite district is in the Transdanubian Hills bauxite
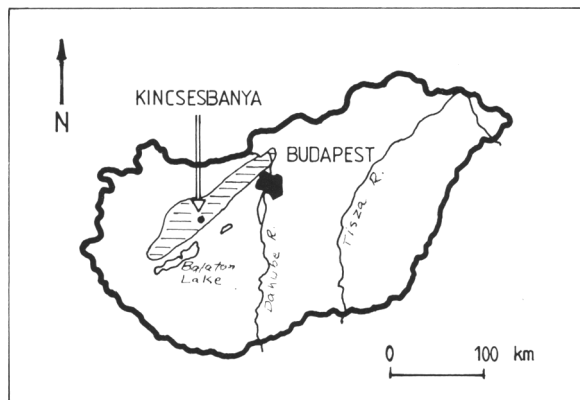
Figure 1. Location of Kincsesbánya district in principal bauxite region of Hungary.
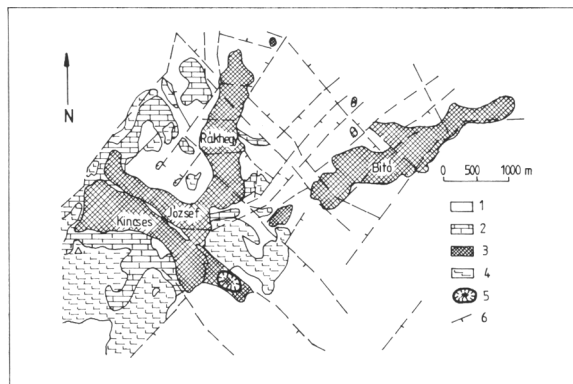

Figure 2. Geologic sketch map of Kincsesbánya district. (1) Miocene, Pliocene, and Pleistocene sediments; (2) Middle Eocene sediments; (3) bauxite deposits; (4) Upper Triassic dolostones; (5) open pit with manganiferous bauxite; (6) main fault lines.

region of Hungary (Figure 1). Two large stratiform deposits, dissected by block faulting, form the bulk of this group of deposits, accompanied by a number of smaller bauxite lenses (Figure 2). The bauxite covers an uneven, karstic surface of Upper Triassic dolostones and has a thickness of about 5–15 m. It is overlain by 10 to 200 m of Middle Eocene, Miocene, and Pliocene sediments. The bauxite is of Paleocene to early Eocene age; however, the enrichment of manganese was a much later epigenetic process (Bárdossy, 1982).

Mining started in the district in 1941 and has continued to the present day in open pits and underground mines. In 1981, a new pit was opened on the southeastern edge of the large stratiform Kincses-József-Rákhegy deposit, as indicated in Figure 2. Manganiferous bauxite was found in this pit in the form of a lenticular body about 70 × 100 m in area and 2–4 m thick within typical, low-Mn bauxite. The manganiferous bauxite graded gradually into the surrounding low-Mn bauxite. Systematic sampling was carried out during mining. The central part of the open pit, including the manganiferous bauxite, was mined until the end of 1982. The Middle Eocene overburden thins to the east due to erosion. The manganiferous bauxite body was found along the eastern rim of the remaining Eocene sediments. Farther east, Upper Pliocene mottled clays formed the immediate overburden to the bauxite deposit.

LITHOLOGIC FEATURES

Typical bauxites of this district are ochre to brownish-yellow color and possess high porosity and relatively low hardness. In the lower part of the deposits, they grade into clayey bauxites of the same color. On the top, the original bauxites have been reduced to gray, pyritic bauxites due to the influence of overlying, Middle Eocene lignitic clay that corresponds to a swamp facies. Where the Eocene overburden has been eroded, epigenetic oxidation of the pyritic bauxites has taken

place accompanied by a partial leaching of iron. Gray, pyritic bauxites were encountered in the underground mines, where the thick overburden has apparently protected them from secondary oxidation.

In the Kincses-József-Rákhegy open pit, pyritic bauxite has been entirely oxidized leaving white, pink, and light-violet bauxites, 1–2 m thick. Vacuoles, <1 mm in size, are common in these bauxites, and are probably the sites of original pyrite crystals that were oxidized and leached during the epigenetic processes. Part of the iron that precipitated in the lower part of this horizon formed hard brown crusts, impregnations, and concretions, several centimeters thick. Locally, vestiges of plant roots have been found, mainly in the upper part of the horizon. No manganese enrichment has been noted in this part of the deposit, the manganiferous bauxite being limited to the middle part of the deposit (Figure 3).

The manganiferous bauxite is gray to dark gray and contains oolitic-pisolitic to nodular structures. Most of the manganese occurs as irregular impregnations (<1 cm in diameter). Nodules, oolites, and pisolites commonly form the centers of the greatest manganese enrichment. Here, the manganiferous bauxite is dark gray or almost black. Despite the manganiferous impregnations, the bauxite has a high (20–30%) porosity. Ochre-colored, clayey bauxite, 1–2 m thick, occurs beneath the manganiferous bauxite and contains only a few scattered manganiferous impregnations.

A second enrichment of manganese in the form of a hard, black crust, <1 cm thick, is present along the contact of the bauxite and the underlying Triassic dolostone. Beneath this crust is a 10–30-cm thick zone of gray to dark gray, loose, pulverized dolostone. This zone is also enriched in manganese. The underlying, unaltered dolostone is light gray, hard, and massive.

White, reniform nests of alunite, 1–6 cm in diameter,

Table 1. Chemical composition of manganiferous bauxite, Kincsesbánya, Hungary.

Oxide	Composition (wt. %)	Mean (wt. %)	Enrichment factors
Al_2O_3	39–49	39.7	0.79
SiO_2	1–6	1.7	0.68
Fe_2O_3	18–39	31.2	2.15
TiO_2	1.3–2.0	1.7	0.74
CaO	0.3–1.0	0.6	1.33
MgO	0.2–0.6	0.3	2.14
P_2O_5	0.4–1.2	0.7	1.45
S	0.02–0.4	0.1	0.20
MnO_2	1.1–6.2	3.0	18.75
H_2O+	20–22	20.7	0.96

were found in the lower part of the manganiferous bauxite and at the bauxite-footwall contact.

CHEMICAL COMPOSITION

The average MnO_2 content of the Kincses-József-Rákhegy open pit bauxite (including the manganiferous bauxite), as well as all the deposits in the Kincsesbánya district, is typical of Hungarian bauxites (0.15%). On the basis of analyses of 56 drill hole samples, the open pit ore averaged 0.16% MnO_2. The average MnO_2 content of all bauxites in the district is 0.13%. The average chemical composition, calculated from 250 analyses of ochre-colored bauxite in the open pit is: Al_2O_3 = 50.5%, SiO_2 = 2.5%, Fe_2O_3 = 14.5%, TiO_2 = 2.3%, CaO = 0.45%, MgO = 0.14%, S = 0.5%, P_2O_5 = 0.48%, MnO_2 = 0.16%, H_2O+ = 21.5% (total sulfur is expressed as elemental S).

The composition of the low-Mn bauxite is almost uniform throughout the Kincsesbánja district, but the manganiferous bauxite varies considerably from this composition (Table 1). This bauxite is greatly enriched in Mn, as well as in Mg, P, and Ca, and depleted in Si, Al, and Ti. The compositions of other types of bauxites from the upper part of the deposit are shown in Table 2. The yellow bauxite contains more Fe than Al due to secondary iron precipitation. The pyrite of the original gray bauxite was oxidized, leached, and finally reprecipitated in this part of the profile. The relatively high S content of the residual pink and violet bauxites corroborate this interpretation.

The ochre-colored clayey bauxite in the lower part of the deposit is characterized by a higher silica content (10–25%) and a lower alumina content (35–45%) than the typical ochre-colored bauxite. The black manganiferous crust at the footwall contact has the following composition: Al_2O_3 = 3.8%, SiO_2 = 2.1%, Fe_2O_3 = 6.0%, TiO_2 = trace, CaO = 43.5%, MgO = 3.2%, S = 0.02%, P_2O_5 = 0.12%, MnO_2 = 3.2%, loss on ignition = 38.1%. Much of the initial Mg was leached leading to the recrystallization of dolomite to calcite. Mn, Fe, and Al oxides cement this crust. Less mobile Ti did not take part in this process. Downward, the pul-
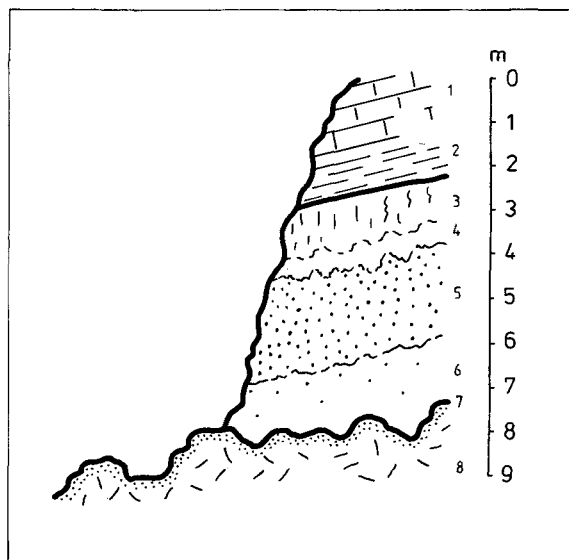

Figure 3. Geologic cross section of Kincses-József-Rákhegy open pit mine. (1) Middle Eocene lagoonal limestone; (2) Middle Eocene swamp-clay with lignite layers; (3) white, pink, and light violet bauxites; (4) yellow bauxite with iron crusts and concretions; (5) dark gray to black manganiferous bauxite; (6) ochre-colored clayey bauxite; (7) black, Mn-rich crust; (8) Upper Triassic dolostone, pulverized on top.

verized dolostone rapidly becomes depleted in Mn, Fe, and Al. Calcitization also diminishes, and the rock grades into a dolostone of normal composition, containing only 0.01–0.05 MnO_2.

MINERALOGICAL COMPOSITION

Typical ochre-colored bauxite from the open pit has the following mineralogical composition: gibbsite = 38%, boehmite = 19%, kaolinite = 5%, Al-goethite = 31%, Al-hematite = 2.5%, anatase = 1.4%, rutile = 0.4%, crandallite = 1.5%, lithiophorite = 0.8%, calcite = trace, dolomite = trace. This mixed gibbsite-boehmite composition is similar to that of the other deposits

Table 2. Chemical composition of bauxite types in the upper part of the deposit.

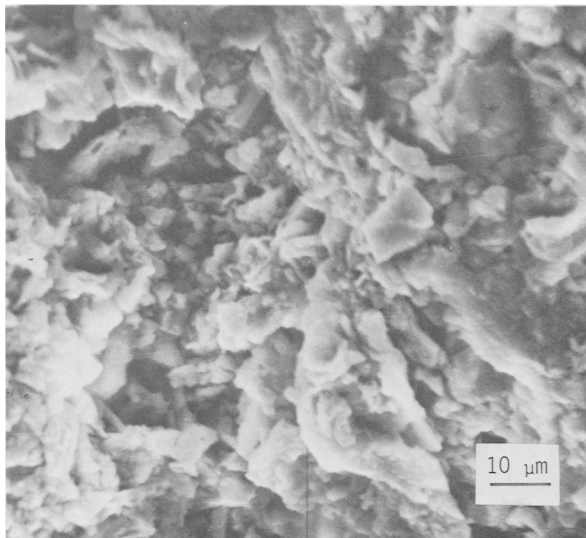| Oxide	Pink bauxite (wt. %)	Violet bauxite (wt. %)	Yellow bauxite with iron impregnations (wt. %)
Al_2O_3	56.9	50.0	31.9
SiO_2	5.0	8.6	1.2
Fe_2O_3	10.1	13.6	44.5
TiO_2	2.2	1.8	1.3
CaO	0.39	0.28	0.27
MgO	0.04	0.04	0.08
S	0.70	0.66	0.06
P_2O_5	0.36	0.20	0.70
MnO_2	0.02	0.02	0.24
H_2O+	24.3	23.9	19.8
Total	100.01	99.10	100.05

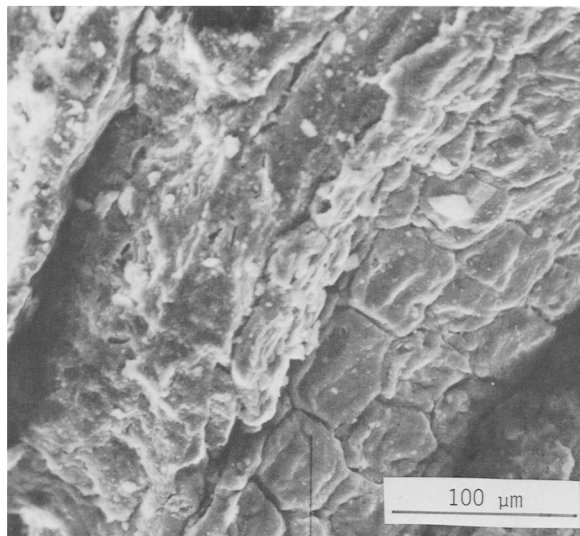Figure 4.   Scanning electron micrograph of typical, ochre-colored, Mn-poor bauxite.

Figure 6.   Scanning electron micrograph of plant tissue in upper bauxite horizon.

in the Kincsesbanya district, but the boehmite content increases and the gibbsite content decreases to the north-northeast. Goethite is the predominant Fe mineral in this deposit, giving the bauxite its ochre to yellow color. The hematite content gradually increases to the north-northeast and ultimately hematite becomes the principal Fe mineral. The increase in hematite is accompanied by a gradual change in the color of the bauxite from ochre to brick-red color. The gibbsite-goethite association is probably the result of a higher paleorelief

during the time of bauxite accumulation, whereas the boehmite-hematite association in the north-northeastern part of the Kincsesbánya district suggests a lower altitude, coastal-plain environment having a groundwater level close to the surface (Bárdossy, 1982).

According to the XRD, DTA, and TGA data, the goethite contains 20–25 mole % $AlOOH$; thus, this mineral is properly designated Al-goethite. The hematite contains 2–3 mole % Al_2O_3 in solid solution. The degree of Fe substitution could not be determined directly for the bauxite minerals from the open pit because of the small amount of hematite in the sam-
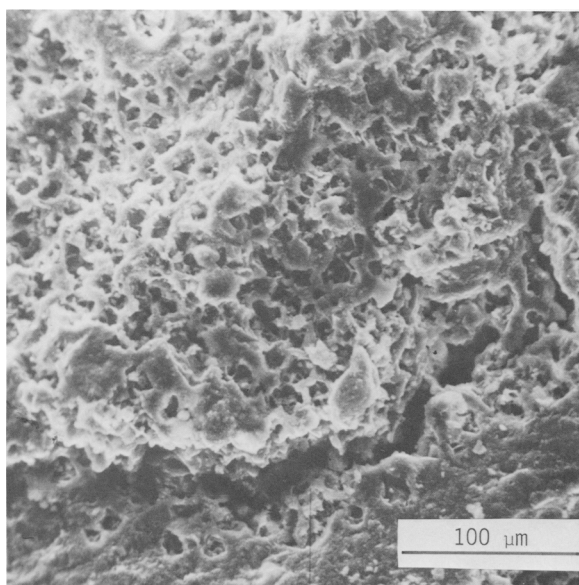

Figure 5.   Scanning electron micrograph of pink bauxite with cavities formed by leaching of pyrite crystals.
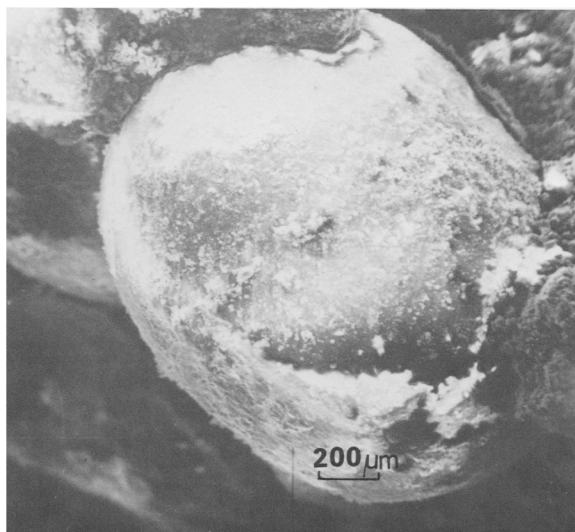

Figure 7.   Scanning electron micrograph of Mn and Fe enrichments in shells of ooids in manganiferous bauxite.
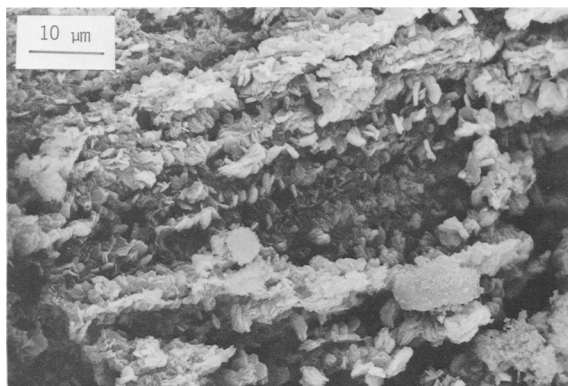
Figure 8. Scanning electron micrograph of lithiophorite crystals on walls of microfissures. Bar = 10 µm.

Figure 10. Scanning electron micrograph of pyramidal Mn crystals on surface of microvoid.

ples, but it is probably similar to other hematitic bauxites from this district (Bárdossy, unpublished data).

Kaolinite was the only silicate mineral detected in the bauxite samples examined. Anatase is more abundant than rutile. The only phosphate mineral noted was crandallite. Sulfur is present in the form of alunite; no traces of the original pyrite were noted. The white alunite concretions mentioned above consist of well-crystallized alunite accompanied by 5–10% crandallite and 5–10% disseminated Al-goethite. The alunite contains 2.5–5.0% Na_2O and 4.0–7.5% K_2O.

Lithiophorite was the principal Mn mineral found in the manganiferous bauxite samples examined. Only 0.002–0.03% Li_2O was detected in separated lithiophorite samples, indicating that Al substitutes for Li in the crystal structure, a common feature of lithiophorites in bauxites (Bárdossy, 1982). In addition, a few
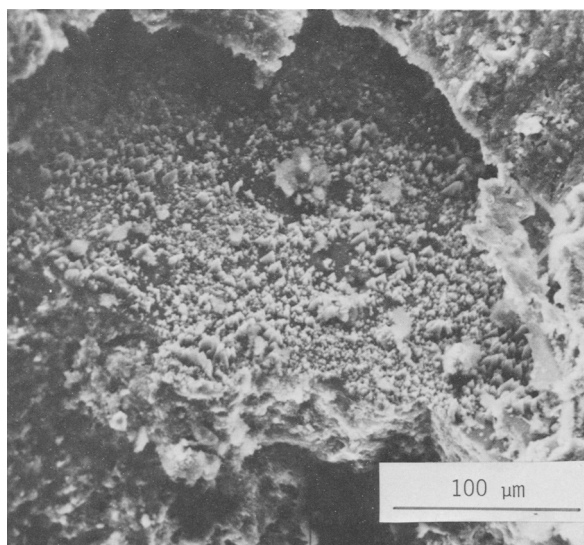
samples were found to contain 1–3% todorokite, another Mn-bearing mineral. Detailed XRD investigations by Guinier camera of separated Mn-rich samples showed weak reflections of γ- and η-MnO_2. The occurrence of these phases is limited locally to fissures and pores.

SCANNING ELECTRON MICROSCOPIC STUDIES

Individual crystallites in a typical Kincsesbánya bauxite are <0.1–0.3 µm in size and generally form densely packed clusters, 2–8 µm in diameter. The clusters in turn form complicated, aggregate structures that give rise to high porosities. Abundant micropopres and fissures can be seen in SEM micrographs (Figure 4). The clusters and voids produce a type of void geometry that corresponds to the so-called "stacky void-geometry" described by Bárdossy *et al.* (1978) for most karst

Figure 9. Scanning electron micrograph of pyramidal Mn crystals on surface of microfissure.

Figure 11. Scanning electron micrograph of radiate manganite crystals. Bar = 10 µm.
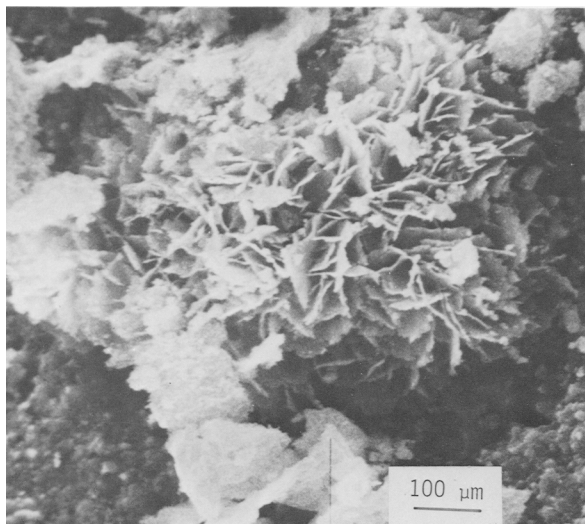
Figure 12.　Scanning electron micrograph of aggregates of platy Mn minerals.

Figure 14.　Scanning electron micrograph of large, secondary calcite with small, surface flakes of lithiophorite, goethite, and kaolinite.

and lateritic bauxites. The manganiferous bauxite was found to be even more porous than the low-Mn bauxite. The pink and violet bauxites from the upper ore horizon have a similar void geometry, and many voids, 5–15 μm in diameter, were noted in these two types of bauxite (Figure 5). Based on their shape and distribution, the voids are probably molds of former pyrite crystals. Several remains of plant tissue were also found in samples of the upper bauxite horizon (Figure 6). The ochre-colored clayey bauxite below the manganiferous bauxite has practically the same microtexture and void geometry as the ochre-colored bauxite described above.
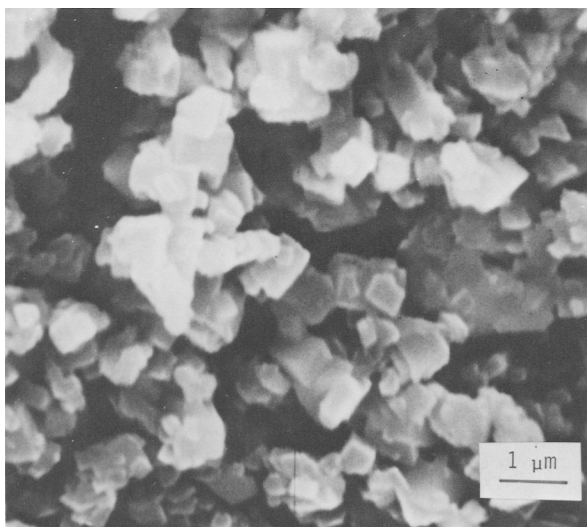
In the manganiferous bauxite (Figure 7), EDX shows

Figure 13.　Scanning electron micrograph of alunite crystals in alunite concretion.

that Fe and Mn are both enriched in the outer shells of ooids and pisolites, with Fe > Mn. The best developed and largest lithiophorite crystals were found on the walls of microfissures and generally have a lamellar shape similar to the lithiophorite crystals described by Ostwald et al. (1983) (Figure 8). The corresponding EDX spectrum corroborates their high Mn content. Less common are Mn minerals of pyramidal shape which appear to have formed on the surface of microfissures and microvoids (Figure 9). The largest crystals are 5–10 μm in size; a high Mn content is apparent from their EDX spectrum, along with lesser amounts of Fe and Al. A spectacular assemblage of these pyramidal Mn minerals on the surface of a void is shown in Figure 10. Note the perfect shape of most of the crystallites. Radiate clusters were noted in some microvoids (Figure 11). By analogy with the crystals shown in SEMs by Ostwald et al. (1983), these crystals are probably manganite.

Rare, spherical clusters of irregularly grown, thin (<0.05 μm), platy Mn minerals (Figure 12) were also noted containing, in addition to Mn, relatively large amounts of Sr. Minute (0.02 μm) Mn minerals were found coating fossil plant tissues and other small plant remains. Locally, 2–10-μm size grains of monazite and xenotime of detrital origin were noted. The alunite concretions consist of 0.05–0.1-μm size crystals (Figure 13) of a mixed potassic-sodic composition, with K ≫ Na. The concretions are highly porous, and some contain phosphorus.

In the manganiferous black crust immediately above the Triassic dolostones, the secondary recrystallization of dolomite to calcite is clearly visible in SEM micrographs. Individual calcite crystals are as large as 50–

300 μm (Figure 14). Small, flaky crystals on the surface of the calcite are mainly lithiophorite and goethite, along with lesser amounts of kaolinite and gibbsite.

GENETIC INTERPRETATION

The bauxites of Hungary, including those of the Kincsesbánya district, were derived by the lateritic weathering of several different rock types, including Paleozoic schists and granites and Mesozoic shales, volcanic tuffs and tuffites, marls, and carbonates. The weathering products of these rocks were washed by surface waters into karstic depressions in carbonate rocks in the area. The bauxites in the Kincsesbánya district were deposited into their present position presumably during the Paleocene and early Eocene (Bárdossy, 1982). From the data presented in the present paper, the enrichment of Mn appears to have been a much later epigenetic process.

As mentioned above, the bauxite deposits and their Middle Eocene overburden contained a small amount of finely disseminated manganese. During the Pliocene, an overall emergence of the Transdanubian Hills occurred, and the Eocene sediments were partly or completely eroded by surface waters. After this erosion, surface weathering led to the oxidation of pyrite in the organic-rich Middle Eocene beds and in the gray, pyritic bauxite. The sulfuric acid produced by this reaction dissolved Fe, Mn, and P from these rocks. The acidic solutions migrated downward and were slowly neutralized, giving rise first to Fe precipitation crusts, and then to a more disseminated precipitation of Mn. Crandallite and alunite precipitated locally in the form of concretions. Some of the acidic solution was neutralized at the top of the footwall dolostone accompanied by the transformation of dolomite to calcite. The remaining Mn formed a black crust immediately above the dolomite-to-calcite transformation zone.

This genetic interpretation appears to conform to all local conditions; however, similar geologic environments have been noted for other bauxite deposits in Hungary and in the Mediterranean bauxite belt without substantial Mn enrichment. The reason why Mn enrichment took place in the Kincsesbánya deposit and not elsewhere where similar conditions prevailed is not known.

REFERENCES

Bárdossy, Gy. (1982) *Karst Bauxites:* Elsevier, Amsterdam, 441 pp.
Bárdossy, Gy., Bottyán, L., Gadó, P., Griger, Á., and Sasvári, J. (1980) Automated quantitative phase analysis of bauxites: *Amer. Mineral.* **65**, 135–141.
Bárdossy, Gy., Csanády, A., and Csordás-Tóth, A. (1978) Scanning electron microscope study of bauxites of different ages and origins: *Clays & Clay Minerals* **26**, 245–262.
Ostwald, J., Turner, K. E., and England, B. M. (1983) Morphological studies of iron and manganese ores using a Philips SEM 505 scanning electron microscope: *Electron Optics Bull.* **119**, 1–7.