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Light Metals-

Bauxite Mineralogy

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Residual rocks, in which the alumina trihydrate and monohydrate minerals gibbsite, boehmite, and diaspore predominate, are classified as bauxites. Other residual minerals are developed in the unique type of rock weathering which produces bauxites, and these minerals kaolinite, halloysite, goethite, hematite, magnetite, anatase, quartz, and some phosphatic and manganiferous minerals may form the lesser constituents of bauxites. Since bauxites have formed from a variety of rock types, minor quantities of residual minerals, which occur only as traces in the original rock, may become concentrated in bauxites together with unaltered remnants of minerals resistant to weathering. Traces of the elements barium, boron, carbon, bismuth, beryllium, calcium, cesium, cerium, chromium, cobalt, copper, hafnium, gallium, gold, lanthanum, lead, nickel, columbium, magnesium, molybdenum, strontium, sulfur, tantalum, thorium, tin, uranium, vanadium, yttrium, zinc, and zirconium have been found in bauxites. Some of these elements are presumably present as secondary minerals, while others are present in unaltered mineral remnants. Quartz, ilmenite, magnetite, zircon, and rutile usually predominate as mineral remnants, and tourmaline, gahnite, xenotime, staurolite, sillimanite, andalusite, kyanite, sphene, corundum, topaz, and micas sometimes occur. In younger bauxites small amounts of alumina-silica-hydrogels may be present, and an aluminous goethite is present in some ferruginous bauxites.

Kaolinite is the chief clay mineral in older bauxites. Thick residual kaolinic clays sometimes envelope and usually lie immediately under older bauxites. These residual kaolinic clays become more quartzose and halloysitic at depth near the weathered rock contact.

Halloysite is rare in older bauxites, but it is a common constituent of younger bauxites and with quartz is usually the main constituent of the residual clays underlying younger bauxites. Gibbsite, kaolinite, goethite, and anatase are also present to a minor extent in these primary residua. On certain alkaline rocks, the primary residuum sometimes consists almost entirely of gibbsite with minor amounts of halloysite, kaolinite, goethite, and anatase. It appears therefore that, except in the case of alkaline rocks, gibbsitic bauxites are not produced directly from rock weathering, but from the desilication of quartzose halloysitic clays formed directly as the primary residuum of weathered rock.

The alumina hydrates and hydrous aluminum silicates of bauxites are derived chiefly from the weathering of felspathoids and felspars of igneous, volcanic, and metamorphic rocks, from aluminum silicates, felspars, micas, and clay minerals of sedimentary and metamorphic rocks, and from the less soluble minerals in particularly pure calcareous limestones. Some alumina hydrates and hydrous aluminum silicates are produced also from the breakdown of amphiboles and pyroxenes in igneous, volcanic, and metamorphic rocks. Although certain almost pure calcareous rocks form bauxite, no bauxite has been found which is known to be derived from coarse high silica or ultrabasic rocks.

In older bauxites it is often difficult to determine the type of rock from which the bauxites are derived, since the fresh rocks below the bauxites, which are often separated from the bauxite by considerable thickness of residual clay, are not the actual rocks from which the bauxites were formed. Correlating the remnant of the unaltered heavy minerals in the bauxites with the heavy minerals in the rock types found below or in the vicinity of older bauxites is often the only means of identifying the probable rock types from which the bauxites were derived. In rare cases in some modern bauxites, the underlying rocks may be found to grade directly upward into the bauxite. The analyses of some of these modern gibbsitic bauxites, with the analyses of the rocks from which they are derived, are given in Table I, and those of some older bauxites, derived from rock types based on the evidence of heavy mineral results only, are given in Table II. The chemical analyses of modern bauxites where the rock types are known indicate that bauxites derived from different types vary only to a slight degree in chemical composition. Bauxites derived from alkaline and intermediate volcanic. igneous, metamorphic, and sedimentary rocks are usually lower in Fe₂O₃ and TiO₂ than bauxites derived from basic volcanics, while bauxites derived from limestones are usually higher in Fe₂O₃ but lower in TiO₂ than those derived from basic volcanics. The color of bauxites. which varies from white, cream, yellow, green, gray, pink, brown, red to black, depends on the quantity, state of hydration, and particle size of the iron minerals in the bauxites and is unrelated to the alumina hydrate minerals.

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	TABLE 1							
	Analyses	of Various	Rock	Types and	of Derived	Gibbsitic	Bauxit	es .
AC	aa	2 ^b	3°	4^{d}	5 ^{e.}	6 f	7g	8 ^h
H ₂ O	28.7	3.57	31.76		27.25	0.95	28.20	0
SiO_2	5.8	52.79	1.21	56.60	2.05	46.80	0.43	0.01
Fe ₂ O ₄	· 9	4.78	8.18	4.70	21.00	1.75	18.20	0.13
FeO				8.20	Nil	8.05	-	
TiO_2	1.2	0.50	0.67	2	0.90	1	2.20	0.01
Al_2O_3	55.3	22.05	58.04	15.90	48.60	15.95	48.70	0.01
CaO		1.43	0.07	6	0.37	13.25	0.42	55.27
MgO		0.04	0.01	2.66	0.34	11.28	0.31	0.46
$\rm CO_2$								43.92
MnO			0.02	·			0.21	Trace
P_2O_5	,	0.17	0.06	Trace	1		1.20	0.03
Na ₂ O	-	7.36		2.30	0.14	1.65		
K_2O		5.79		1.64	0.34	0.25		
SO_3								0.20
Total	100 ⁱ	98.48	100.02	100	100.99	100.93	99.87	99.86

^a Concretionary bauxite derived from phonolite (No. 2), Pocos de Caldas, Brazil. Analyzed by Aluminio Minas Gerais, S. A., Saramenha, Brazil.

^b Phonolite, Pocos de Caldas, Brazil. Analyzed by Aluminium Co. of Canada, Ltd., Arvida, Canada.

^c Concretionary bauxite derived from metamorphosed andesite (No. 4), Johore, Malaya. Analyzed by Municipal Analyst, Singapore.

^d Metamorphosed andesite, Johore, Malaya. Analyzed by municipal analyst, Singapore.

^e Porous concretionary bauxite derived from metamorphosed norite (No. 6), Malacca, Malaya. Analyzed by municipal analyst, Singapore.

^f Metamorphosed norite, Malacca, Malaya. Analyzed by municipal analyst, Singapore.

^g Soft shaley bauxite derived from Miocene limestone (No. 8), Mandeville, Jamaica. Analyzed by Aluminium Laboratories, Ltd., Arvida, Canada.

^h Lower Miocene limestone, Mandeville, Jamaica. Analyzed by Aluminium Laboratories Ltd., Arvida, Canada.

ⁱ Alumina by difference.

Observations in the field in areas where laterization is in progress indicate that weathering of rocks to residual clays is universal in the high rainfall areas of the tropics and subtropics, but that bauxites form only under special climatic, hydrological, and biological conditions. Bauxitization occurs only above the water table where there is alternating downward movement of acid solutions and upward movement during drier periods of alkaline solutions in rocks which contain sufficient sodium and calcium aluminum silicates or calcareous rocks containing small amounts only of soda, ferric oxide, silica, and alumina, but with the latter oxides in the ratio 1:1. In bauxites which are still being formed, the predominant alumina hydrate mineral is gibbsite.

Recently formed bauxites derived from rocks other than limestones are usually composed of loosely consolidated hard gibbsitic stalactites, nodules, and plates in a soft gibbsitic, ferruginous and more siliceous matrix, or when the recently formed bauxites are derived from limestones, they consist of nonplastic very fine grained gibbsitic ferruginous

	TA	ABLE II		
Analyses of	Bauxites Deriv	red from Var	rious Types of R	ocks

111	1ª	2 ^b	3°	4^{d}	5°	6 f	7s	8^{h}
H ₂ O	28.5	27.6	24.9	27.1	21.9	18	12.1	12.7
SiO_2	5.7	5.1	8.6	6.5	8.3	6.3	2.8	1.7
Fe ₂ O ₃	9.2	14.2	20.3	5.8	15.4	18.8	24.2	20.4
TiO ₂	1.4	2.8	1.2	1.2	4.2	1.7	3.3	2.9
Al_2O_3	55.3	50.3	45	59.4	49.1	34	56.5	60.9
P_2O_5		4 <u>19</u>	Store -			13.2	0.8	
CaO	nota da ofi	21, ++1000	$\eta r \rightarrow 0$	linlikg er vi	bires .	6.7	0.1	 ;
Total	.100 ⁱ	100 ⁱ	100 ⁱ	100 ⁱ	99	98.7	99.7	98.6

• Gibbsitic bauxite derived from nepheline syenite, Kassa, Guinea. Analyzed by Aluminium Laboratories Ltd., Arvida, Canada.

^b Gibbsitic bauxite derived from basalt, Fiji. Analyzed by Aluminium Laboratories Ltd., Canada.

^e Gibbsitic bauxite derived from hornblende schist, Mackenzie, British Guiana. Analyzed by Demerara Bauxite Co. Ltd., Mackenzie, British Guiana.

^d Gibbsitic bauxite derived from phyllite, Johore, Malaya. Analyzed by municipal analyst, Singapore.

• Gibbsitic bauxite derived from mica schist, Darling Range, Western Australia. Analyzed by Aluminium Laboratories Ltd., Arvida, Canada.

^f Phosphatic gibbsitic bauxite derived from limestone, Fiji. Analyzed by Aluminium Laboratories Ltd., Arvida, Canada.

^s Boehmitic bauxite derived from limestone, Istria, Yugoslavia. Analyzed by Aluminium Laboratories Ltd., Arvida, Canada.

^h Diasporic bauxite derived from limestone, Distomon District, Greece. Analyzed by Aluminium Laboratories Ltd., Arvida, Canada.

ⁱ Alumina by difference.

material with scattered small and more ferruginous pisolites. Older gibbsitic, boehmitic, and diasporic bauxites, not lying on limestones, are often composed of hard massive layers of gibbsitic, boehmitic, and diasporic lenticular pisolitic and botryoidal nodules and plates cemented and ramified with a ferruginous and more siliceous matrix, or they consist of hard gibbsitic, boehmitic, and diasporic ferruginous pisolites in a softer and usually less ferruginous and more siliceous matrix. Older boehmitic and diasporic bauxites on limestones are often composed of gibbsitic, boehmitic, and diasporic ferruginous pisolites in a more siliceous but less ferruginous matrix or are hard massive blocky or soft shaley fine-grained rocks. The predominant siliceous mineral in the matrix of recently formed bauxites is either halloysite or kaolinite and in older bauxites it is usually kaolinite.

Initially bauxitization proceeds because potassium, sodium, and calcium aluminum silicates can be broken down by carbonic acid supplied by rain and later by organic acids supplied by plants, bacteria, and other organisms into alkaline carbonates and hydroxides, and hydrated aluminum silicates and silica. Although calcium carbonate is insoluble in water, it is soluble in weak acids including carbonic acid. Under suitable conditions sodium carbonate will react with calcium hydroxide solutions, and calcium carbonate is precipitated leaving sodium hydroxide in solution in which both silica and aluminum hydroxide are soluble. Weak solutions of sodium carbonate also attack other silicates and silica, producing sodium silicate and carbon dioxide, which combines with water to form carbonic acid. Aluminum hydroxide, ferric hydroxide, and silica acid also form hydrogels, and salt solutions can diffuse through these hydrogels. All cryptocrystalline bauxites exhibit characteristics of a colloidal state at one stage in their history, which is indicated by their oölitic and pisolitic structure or by stalactitic, banded, mammillary, and botryoidal nodules and plates.

Peneplains and other low-lying and gently sloping land forms, such as volcanic domes and plateaux and karsted plateaux, covered with a mantle of suitable tropical vegetation and subject to an abundant rainfall, with, however, alternating drier periods and with little erosion for prolonged periods of time, appear to provide the necessary topographical conditions for bauxitization. Since bauxitization takes place only where the drainage is good, the proper rock structures—both the large-scale features and the textures and microstructure—are also important. Very fine grained microcrystalline to glassy-textured rocks with easily weathered aluminous minerals; rocks with scoriaceous and vesicular structure and columnar, prismatic jointing; argillaceous sedimentary and metamorphic rocks with near vertical cleavage or platy fracture; or fine-grained well-jointed pure limestone provide the most suitable rock structure.

The tropics and subtropics appear to provide the proper climatic conditions, since it is only in these areas that gibbsitic bauxites are known to be forming today. In Malaya, where gibbsitic bauxites are forming from metamorphosed acid volcanics and sediments on a peneplained area, the annual range of temperature is from 68 to 94°F, the rainfall from 85 to 110 in., and the moisture content of the bauxites from 5 to 14%, and in the Hawaiian Islands, where gibbsitic bauxites are forming from alkaline basalts and andesites on the wet side only of volcanic domes, the annual range of temperature is from 62 to 77°F, the rainfall from 60 to 150 in., and the moisture content of the bauxites from 26 to 41%. While in Jamaica, where gibbsitic bauxites are forming on karsted Tertiary limestone plateaux, the annual range of temperature is from 60 to 80°F, the rainfall from 50 to 95 in., and the moisture content of the bauxites from 20 to 23%.

Both topography and climate influence the type of vegetable mantle and fauna and flora of the soil. The roots of plants in turn affect to a marked degree the movement and pH of the subsoil water. The debris of dead plants also provide a source of humic and other organic acids, and plants probably contribute also to bauxitization as desilicators, specific mineral extractors, and mineral collectors. It seems significant that bauxites do not appear to have been formed before terrestrial plants became abundant.

Climatic variations and diastrophe during or after bauxitization probably account for subsequent mineralogical changes of gibbsitic bauxites. Under a drier environment boehmite may be produced from gibbsite and hematite from goethite, while under reducing conditions siderite, marcasite, pyrite, and chamoisite may develop from goethite, hematite, and magnetite, and kaolinite from halloysite. Static and dynamic metamorphism of some older bauxites probably has assisted the dehydration of gibbsite to boehmite and caused the replacement of boehmite by diaspore, goethite by hematite in some diasporic bauxites, although weak thermal and static metamorphism has changed boehmite to diaspore and kaolinite to aluminous chlorites in some Greek bauxites. Strong thermal metamorphism appears to change bauxites to emery. a rock consisting of corundum, magnetite, and hematite. Some tourmaline-corundum rocks may be hydrothermally metamorphosed bauxites or terra rossa. Alunite has been recorded in bauxitic material although it is not usually a constituent of bauxites. The alkalies and alkaline earths, which are easily soluble in the solvents which initiate bauxitization, do not accumulate in bauxites and where found either indicate small relics of the unweathered rock in the bauxite or postbauxite precipitation of these elements from solutions carried down from the rocks above through cracks and joints in the bauxite.

TABLE IV

Descriptive Mineralogy of the Chief Residual Minerals in Bauxites

Lixht Metals

Summaries of the physical, crystallographic, and optical properties of the three alumina hydrate minerals, gibbsite, boehmite, and diaspore, of the chief hydrated aluminum silicate minerals, halloysite, kaolinite, and quartz, and of the chief iron and titanium minerals, goethite,

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Properties of Alumina Hydrate Minerals ^{a,b}					
Mineral	Gibbsite	Boehmite	Diaspore		
Chemical formula	$\mathrm{Al}_2\mathrm{O}_3\ \mathrm{3H}_2\mathrm{O}$	$Al_2O_3 H_2O$	$\mathrm{Al}_2\mathrm{O}_3~\mathrm{H}_2\mathrm{O}$.		
$Al_2O_3, \%$	65.4	85	85		
H_2O , %	34.6	15	15		
Crystal system	Monoclinic	Orthorhombic	Orthorhombic		
Space group	C_{2h}^5	D_{2h}^{17}	V_h^{16}		
Unit axis	a 8.62	2.85	4.40		
lengths, A	b 5.06	12.2	9.39		
	c 9.70	3.69	2.84		
	angle 85° 26'				
X-ray diffraction	4.82 (10)	6.11 (10)	3.99 (10)		
d values in A and	4.34(4)	3.16(6)	2.56(3)		
intensities of	4.30(2)	2.35(5)	2.32(6)		
strongest lines	2.44(1)	1.86(3)	2.13(5)		
	2.37(2)	1.85(3)	2.08(5)		
	2.03(1)	1.45(2)	1.63(4)		
	1.98(1)	1.31(1)	1.48(2)		
	1.79(1)				
Index of refraction $n_{\rm D}$	α 1.568	1,649	1.702		
	$\beta 1.568$	1.659	1.722		
	$\gamma 1.587$	1.665	1.750		
Cleavage	(001) perfect	(010)	(010) perfect		
Hardness (Moh)	2.5-3.5	3.5 - 4	6.5-7		
Density	2.42	3.01	3.44		
Temp. of decomposition ^a	140–260°C	400-450°C	400-450°C		

^a Varies according to size, atmosphere, and rate of heating (Brindley and Choe, 1961).

^b Based mainly on V. W. Newsome, H. W. Heiser, A. S. Russell, and H. C. Stumpf, ("Alumina Properties," Tech. Paper No. 10, 2nd revision, Aluminum Co. of America, 1960) and A. S. Russell ("Alumina Properties," Tech. Paper No. 10, Aluminum Co. of America, 1953).

Mineral	Halloysite	Kaolinite	Quartz
Chemical formula	Al ₂ O ₃ 2SiO ₂ 2H ₂	O Al ₂ O ₃ 2SiO ₂ 2H ₂ O) SiO_2
Al2Os, %	39.8	39.8	har search an search and
SiO2, %	46.3	46.3	100
H_2O , %	13.9	13.9	<u></u>
Crystal system	all at high and	Triclinica	$Hexagonal^{b}$
Unit axis lengths, A	6. S	a 5.16°	a 4.90
en di la successione de la successione		b 8.94	c 5.39
		c 7.38	
	81	ngle α 91.8°	
		β104.5°	
		γ 90°	1. A 1.
X-ray diffraction	7.5 (0)0	$7.15(10)^{d}$	4.26 (3) ^d
d values in A of	$7.2 \int^{(8)^c}$	3.57(10)	3.34(10)
strongest lines	4.42 (10)	2.49(8)	2.46(1)
	2121	2.33(9)	2.28(1)
	3.63(8)	2.28(8)	1.82(2)
	2.56(7)		1.54(2)
			1.37(1)
	1.68(5)		
en da anti-	1.48 (8)		
Index of refraction $n_{\rm D}$	1.551-1.567*	al. 561*	€1.553°
	1.001 1.001	<i>B</i> 1,565	$\omega 1.554$
		$\gamma 1.566$	1
Cleavage		(001) perfect	None
Hardness (Moh)	Soft	Soft	7e
Density	2.55-2.56°	2.60-2.68°	2.66^{e}
Temp. of decomposition	110-500°Cª	390–525°Cª	Above 570°C

^a Ross, C. S., and P. F. Kerr, "The Kaolin Minerals," U. S. Geological Survey Prof. Paper 165E, 1931.

^b Cullity, B. D., *Elements of X-Ray Diffraction*, Addison-Wesley, Reading, Mass., 1956.

^o Grim, R. E., Clay Mineralogy, McGraw-Hill, New York, 1953.

^d ASTM Special Tech. Publ. 48K, X-Ray Powder Data File.

• Larsen, E. S., and H. Berman, "The Microscopic Determination of the Nonopaque Minerals, U. S. Geol. Survey Bull. 848, 1934. Light Metals

Properties of Iron and Titanium Minerals					
Mineral	Goethite	Hematite	Anatase		
Chemical formula Fe ₂ O' ₃ , % H ₂ O, % TiO ₂ , %	Fe ₂ O ₃ H ₂ O 89.9 10.1	Fe ₂ O ₃ 100	TiO ₂ 100		
Crystal system	Orthorhombic ^a	Rhombohedral- hexagonal ^b	Tetragonala		
Unit axis lengths, A	$a 4.65^{b}$ b 10.2 c 3.03	a 5.431 ^b 55° 17' or a 5.039 c 13.76	a 3.783° c 9.51°		
X-ray diffraction d values in A of strongest lines	4.18 (10)° 2.69 (7) 2.44 (8) 1.72 (7)	$3.68 (7)^{e}$ 2.69 (10) 2.51 (8) 2.20 (7) 1.84 (7) 1.69 (8) 1.48 (7) 1.45 (8)	$3.51 (10)^{\circ}$ 2.379 (2) 1.891 (3) 1.699 (2) 1.665 (2)		
Index of refraction $n_{\rm D}$	$\alpha 2.26^{a}$ $\beta 2.39$ $\gamma 2.40$	$\begin{array}{l} \epsilon \ 2.78_{\rm Li}{}^{\rm d} \\ \omega \ 3.01_{\rm Li} \end{array}$	ϵ 2.493 ^d ω 2.554		
Cleavage	(010) perfect ^a (100) less	(0001) parting ^d	(001) perfect ^a (011) perfect		
Hardness (Moh)	5.0-5.5 ⁿ	5.0-6.0 ⁿ	5.5-6.0ª		
Density	4.2 ^b	5.20ª	3.90ª		
Temp. of decomposition	250°Сь				

TABLE V

* Palache, C., H. Berman, C. Frondel, Dana's System of Mineralogy, Vol. I, Wiley, New York, 1944, 7th ed.

^b Rooksby, H. P., "Oxides and Hydroxides of Aluminium and Iron, X-Ray Identification and Structure of Clay Minerals," Mineralogical Soc. of Great Britain, Monogr., 1951) in kx converted to A.

^e ASTM Special Tech. Publ. 48K X-Ray Powder Data File.

^d Larsen, E. S., and H. Berman, "The Microscopic Determination of the Nonopaque Minerals," U. S. Geol. Survey Bull. 848, 1934.



hematite, and anatase, found in bauxites, are shown in Tables III, IV, and V. X-ray diffraction patterns of typical bauxites and of the residual clays associated with them are shown in Figures 1 and 2, and electron micrographs of similar material in Figures 3, 4, 5, 6, 7, and 8. X-ray diffraction pattern (e), Figure 1, of coarsely crystalline gibbsite occurs as pods up to 4 ft in length in a low-grade supergene manganese deposit in Minas Gerais. The gibbsite crystals fluoresce yellow under short wave ultraviolet light. These coarse gibbsite crystals give a very strong d = 4.82 line and a weaker d = 4.34 than usual for gibbsite in gibbsitic bauxites. X-ray diffraction pattern (d), Figure 1, of fine-grained red bauxite derived from limestone in Jamaica is from the same area as No. 7, Table I, and shows the lines of goethite, anatase and phosphate. which are the normal lesser constituents of Jamaican bauxites. The electron micrograph Figure 3 of Jamaican bauxite shows the small size and form of the gibbsite crystals in the Jamaican bauxites derived from limestone compared with that of gibbsitic bauxites derived from phyllite shown in electron micrograph Figure 4 from Minas Gerais, Brazil.

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X-ray diffraction pattern (c), Figure 1, is of boehmitic bauxite derived from limestone from France, and the form of the boehmite crystals is shown in electron micrograph Figure 5. X-ray diffraction patterns (a)and (b), Figure 1, are of diasporic bauxites derived from limestones from Greece. Pattern (b) shows the lines of hematite and anatase, which are the normal lesser constituents in these bauxites, and (a) is of thermally metamorphosed low-grade diasporic bauxite in which the kaolinite has been converted to chlorite, which was identified optically as daphnite.

X-ray diffraction patterns shown in Figure 2 are of the residual clays underlying or forming the matrix of bauxite deposits. Pattern (d), Figure 2, is of a residual halloysitic clay underlying the bauxite in



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Fig. 1. X-ray diffraction patterns of bauxites. Equipment: Philips model 12021 diffractometer. Conditions: radiation $\operatorname{FeK}_{\alpha}$ (Mn filter), tube potential 35 kv, tube current 4 ma, scanning speed 2 rpm. (a) Low-grade thermally metamorphosed bauxite derived from limestone, Salonika area, Greece. Chemical analysis (in %): H₂O, 10.4; SiO₂, 18.9; Fe₂O₃, 16.7; TiO₂, 2.4; and Al₂O₃, 51.6 (alumina by difference). (b) Diasporic bauxite derived from limestone, Distomon area, Greece. Chemical analysis (in %): H₂O, 12.5; SiO₂, 1.8; Fe₂O₃, 26.2; TiO₂, 2.4; and Al₂O₃, 57.1 (alumina by difference. (c) Boehmitic bauxite derived from limestone, Var, France. Chemical analysis (in %): H₂O, 14.7; SiO₂, 3.7; Fe₂O₃, 1.8; TiO₂, 4.7; and Al₂O₃, 75.1 (alumina by difference). (d) Red bauxite derived from limestone, Kendal, Jamaica. Chemical analysis (in %): H₂O, 27.3; SiO₂, 2.3; Fe₂O₃, 19.2; TiO₂, 2.4; Al₂O₃, 46.6; MnO, 0.2; CaO, 0.4; P₂O₅, 1; CO₂, 0.3; and undetermined, 0.3. (e) Coarsely crystalline gibbsite, Minas Gerais, Brazil. X-ray fluorescence analysis (in %): H₂O (H₂O by difference), 32.2; SiO₂, 0.9; Fe;O₃ 1.8; TiO₂, 0.1; Al₂O₃, 63.8; and MnO, 1.2.

Jamaica. The electron micrograph of this clay, Figure 8, indicates that most of the halloysite has unrolled. X-ray pattern (c), Figure 2, is of kaolinic floor clay underlying bauxite (analysis No. 4, Table II) derived from phyllite. The bauxite has been below water level after it was formed. The residual kaolinite clays found below bauxites which after bauxitization have been below water level give x-ray diffraction patterns similar to (c), Figure 2, and consist of well-crystallized kaolinite, as shown in electron micrograph Figure 6 of the kaolinic floor clay immediately below bauxite in British Guiana. X-ray diffraction pattern (b), Figure 2, is of the clay matrix of low-grade bauxite averaging H₂O 19.5%, SiO₂ 4.6%, Fe₂O₃ 35.6%, TiO₂ 7%, and Al₂O₃ 33.3%, derived from melilite nepheline basalt from Kauai. Electron micrographs of this residual clay indicate that it consists of halloysite tubes similar to those in Figure 7 of a residual halloysitic clay derived from metamorphosed rhyolite in Malaya. The latter is, however, a quartzose halloysitic clay, as indicated by the x-ray diffraction pattern and chemical analysis, which gave a composition of H₂O 8.20%, SiO₂ 67.75%, Fe₂O₃ 1.30%, TiO₂ 0.35%, and Al₂O₃ 21.30%. X-ray diffraction pattern (a), Figure 2, is of bauxitic clay from the base of the bauxite at the bauxiteresidual clay contact in Malaya. The bauxites and residual clays are derived from metamorphosed andesite, and analyses of the bauxite and andesite are shown as Nos. 3 and 4, Table I. The x-ray diffraction pattern indicates that the main constituents are gibbsite, quartz, kaolinite or disordered kaolinite (Brindley²), and possibly halloysite and hematite.

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In addition to x-ray diffraction, differential thermal analysis can also be used to determine the major minerals in bauxites. X-ray fluorescence is used for quantitative analysis of major oxides and spectrographic analysis for quantitative minor element determination. All the above furnish a rapid method for quantitative determinations of vary-



Fig. 3. Electron micrograph of gibbsite in bauxite, Jamaica.



Fig. 4. Electron micrograph of gibbsite in bauxite, Minas Gerais, Brazil.

ing reliability of the major oxides and minerals in bauxites and can be used for preliminary rapid assessment of bauxite deposits. The bulk of the world's bauxite deposits are, however, mined for the production of aluminum, and accurate information on the quantity and type of alumina hydrate minerals present, particularly of the hydrated aluminum silicates, is required for bauxites used for the aluminum in-

Fig. 2. X-ray diffraction patterns of residual clays and bauxitic clays associated with bauxites. Equipment: Philips model 12021 diffractometer. Conditions: radiation FeK α (Mn filter), tube potential 35 kv, tube current 4 ma, scanning speed 2 rpm. (a) Bauxitic clay below bauxite derived from metamorphosed andesite, Johore, Malaya. X-ray fluorescence analysis (in %): H₂O (H₂O by difference), 20.9; SiO₂, 28.1; Fe₂O₃, 5.7, TiO₂, 1.1; and Al₂O₃, 44.2. (b) Halloysitic clay matrix of low-grade bauxite derived from melilite nepheline basalt, Kauai, Hawaii. Chemical analysis (in %): H₂O, 17.6; SiO₂, 15.8; Fe₂O₃, 30.9; TiO₂, 4.4; and Al₂O₃ (alumina by difference) 31.3. (c) Kaolinic residual clay below bauxite, Johore, Malaya. X-ray fluorescence analysis (in %): H₂O (H₂O by difference), 15.6; SiO₂, 42.3; Fe₂O₃, 2.2; TiO₂, 1.9; and Al₂O₃, 38. (d) Halloysitic residual clay below bauxite, Kendal, Jamaica. Chemical analysis (in %): H₂O, 11.6; SiO₂, 46.5; Fe₂O₃, 9.1; TiO₂, 1.7; Al₂O₃, 27.2; CaO, 1.7; MnO, 0.1; P₂O₅, 0.1; and undetermined, 2.



Fig. 5. Electron micrograph of boehmite in bauxite, Var, France.



Fig. 6. Electron micrograph of kaolinite in kaolinic clay below bauxite, Mackenzie, British Guiana.

dustry, so that the final assessment of bauxite deposits is based mainly on chemical determinations.

Gibbsite is quite soluble in 10 to 20% solutions of sodium hydroxide at 142°C. The pressure at this temperature is below 10 atm. Pure alumina trihydrate can be economically extracted from gibbsitic bauxites which are low in hydrated aluminum silicates. The silicates also react with weak solutions of sodium hydroxide. After autoprecipita-



Fig. 7. Electron micrograph of halloysite (tubular) and quartz in residual clay under bauxite, Malaya.



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Fig. 8. Electron micrograph of halloysite in clay below bauxite, Jamaica.

tion, the pure alumina trihydrate can then be calcined to alumina and reduced electrolytically to aluminum. Boehmite is only slightly soluble in weak sodium hydroxide solutions under the conditions at which gibbsite is normally extracted. Boehmite, however, is quite soluble in 20 to 30% sodium hydroxide solutions at 225°C (which conditions result in pressures below 35 atm), but under these conditions sodium

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hydroxide reacts strongly with hydrated aluminum silicates. Therefore boehmitic bauxites must contain low amounts of hydrated aluminum silicates if the production of alumina trihydrate from them is to be economically feasible. Diaspore is insoluble in sodium hydroxide solutions under the conditions at which gibbsite and boehmite are soluble. However, the diaspore of diasporic bauxites and both the boehmite and diaspore of boehmitic and diasporic bauxites, after preheating to 600-700°C, are soluble in sodium hydroxide under the conditions at which boehmite is also soluble. The production of alumina trihydrate from diasporic bauxites and diasporic bauxites high in boehmite is accomplished either by a sinter process with sodium carbonate followed by water leach or by a smelting process with limestone where the alumina is converted into a calcium aluminate slag. The alumina in the slag can be leached with a dilute solution of sodium carbonate. The smelting process requires a cheap source of power and a steady demand for the relatively large amount of pig iron by-product produced in the process.

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Discussion

A. Lippman, Jr. (*Reynolds Metals Co.*): In which phase (or phases) does the phos phatic impurity occur in Arkansas bauxites?

H. R. Hose: I have no information on phosphate in Arkansas bauxite. However, in the case of some Jamaican and Fijian bauxites, the phosphate mineral in the bauxites appears to be crandallite. In the x-ray diffraction pattern (d), Figure 1, for Jamaican bauxite containing $1\% P_2O_5$ there is a line at d = 2.95 attributed to crandallite. The x-ray diffraction pattern of Fijian phosphatic bauxite with $13\% P_2O_5$ (No. 6 in Table II) gave in addition to the strongest line at d = 2.95 strong lines at d = 5.75, 4.90, 3.50, 2.17, 1.905, and 1.75, which are close to those given for crandallite in the ASTM Special Technical Publication, X-Ray Powder Data file.