

THE ORIGIN OF HIGH-ALUMINA CLAY MINERALS —A REVIEW

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ABSTRACT

High-alumina minerals refer, in this paper, to Al-rich, normal sedimentary phases, including gibbsite, boehmite, diaspore, possibly "proto-diaspore" and "proto-alunite", "Al-chlorite", and corundum, in association with kaolin minerals. They may be derived from any common Al-containing rock. Processes of origin include direct bauxitization of non-clay silicate minerals and rocks, and the desilication of any of the common clay minerals, particularly of the kaolin group. Apparently aluminous gels were formed within certain marshy basins, and/or were transported into basins, giving rise to concretionary masses of high-alumina minerals. Concretionary deposits were formed by dissolution of Al and reprecipitation.

Alumina is probably more soluble, inherently, than is interpreted from geologic occurrences. Even after Al is dissolved under appropriate pH, or complexing reactions, its solubility is obscured by Al-immobilization through fixation within 3-layer clay minerals, or absorbed by other phases. A 14Å phase, probably aluminous, is not uncommon in certain soils, and in flint and boehmite-diaspore-containing clays. Subtraction of silica by plants, is accompanied by concentration of alumina.

INTRODUCTION

THE term "high-alumina clays" has been applied to various clays (rocks) that contain Al_2O_3 in excess of certain minimum amounts—the minimum commonly has been set by the use to which the high-alumina clay was put, as for refractories, abrasives, aluminum metal extraction, or other purposes. Probably the lowest alumina content applicable to high alumina has been about 35 per cent Al_2O_3 (Wilson and Treasher, 1938; Allen, 1946; Williams, 1960) or down to 20 per cent Al_2O_3 for high-alumina kaolinitic clay (Mark, 1962), for the purposes of this paper the low limit of high-alumina clays will be placed arbitrarily at 40 per cent, Al_2O_3 on the raw clay basis, i.e., just above the theoretical alumina content of kaolinite (39.5 per cent Al_2O_3). This requires that some aluminum oxide mineral (usually hydrated) be associated with the clay minerals comprising the clay rocks. The clay minerals in such high-alumina clays commonly are in the kaolin group, and the clay rocks (mixtures) ensuing may be those classified as nodular clays, burley clays, bauxitic kaolins, terra rosa, and

perhaps lithomarge, bole, and others. Clays having the highest alumina contents include the bauxites, diaspore and boehmite clays, and laterites of certain writers.

Interestingly, the clays highest in alumina content are composed of hydrated aluminum oxides, and paradoxically not of clay minerals, in the way they have been defined tentatively by CIPEA as "hydrated silicates with layer or chain lattices . . ." (Mackenzie, 1959).

Hydrated aluminum oxide minerals present in high-alumina clays include alpha-bayerite, $\text{Al}(\text{OH})_3$; boehmite, $\text{AlO}(\text{OH})$; diaspore, HAIO_2 ; and gibbsite, $\text{Al}(\text{OH})_3$; and possibly "cliachite, a mineraloid, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ " (although high-resolution diffraction may show this to be comprised of other crystalline minerals). Relatively unexplored as high-alumina minerals, or their associates, are double hydroxides of Al and Mg (Turner and Brydon, 1962), and poorly ordered—possibly "proto" varieties of—diaspore and alunite.

Corundum, although less commonly observed in normal sedimentary bauxite, was so reported by Beneslavsky in 1958 (published in 1962) when he quoted Terentieva's find of corundum in bauxite in 1949. Alpha alumina (corundum) was observed by Dr. R. C. Cross* (Aluminum Company of America) in the hard, dark, vitreous cores of bauxite pisolites ("Birds-eye ore") in the Arkansas residual deposits. We have observed, weak but recognizable, four major X-ray diffraction peaks for corundum from such pisolite cores collected from Arkansas bauxite. Although Gordon, Tracey, and Ellis (1958) do not mention corundum in the Arkansas bauxite mineralogy, they report (1959, p.86) an analysis of "brown to black pisolites" yielding "71 per cent Al_2O_3 " and "16.6 per cent ignition loss", which probably indicates the presence of corundum. Since the ideal formula for gibbsite calls for 65.4 per cent Al_2O_3 and 34.6 per cent H_2O , and for boehmite 85 per cent Al_2O_3 and 15 per cent water, neither of which ordinarily occurs ideally pure, it is probable that some corundum contributed to the 71 per cent Al_2O_3 and relatively low ignition loss in the brown to black pisolites.

The processes of origin of high-alumina minerals, based on first-hand observations and studies in particular districts, have been well documented in a number of papers (Mead, 1915; Harrison, 1933; Harder, 1952; Bolger and Weitz, 1952; Gordon and Tracey, 1952; and with Ellis, 1958; Bardossy, 1959; and Bates, 1962; and others). The purpose of this discussion is, not to try to improve on those excellent papers, but to find from them, plus some personal observations, common denominators of processes of origin for high-alumina minerals. Proceeding from the principle that a mineral is a response of appropriate geologic materials to energy impressed upon them—from which it follows that the mineral formed tends to represent the lowest-energy state available to the constituent elements—we shall

* Personal communication, 1963.

inquire what materials, and what energies (by way of processes) are productive of high-alumina minerals.

PARENT MATERIALS OF HIGH-ALUMINA MINERALS

Fox (1963) and Harder (1952) described bauxite deposits that had been formed on essentially every type of common rock and rock-forming mineral that contained Al. Thus, the parent material for the origin of high-alumina clay is not critical, except that it must contain Al. Parent minerals most favorable to high-alumina argillation were observed to be the feldspathoids and alkali varieties of dark minerals, i.e., subsilicic minerals, but under sufficiently intense conditions of leaching, intermediate and sialic (even quartz-containing) igneous rocks, clay residues from dissolving limestones, and metamorphic rocks of most kinds also produced large bodies of high-alumina clays. The formation of a high-alumina deposit, especially where metastable high-alumina minerals occur, is a step in a slow reaction process; subsilicic minerals react more quickly, but others eventually are desilicated under intense leaching. Likewise, solutions carrying dissolved Al ions yield fillings of high-alumina minerals in veins, and aluminous gels or colloids also give rise to high-alumina minerals.

High-alumina minerals may arise by concentration of Al compounds during the removal of non-aluminous associated elements, by exceeding the solubility of Al in aqueous systems, by sorption of Al, or ion-exchange for Al, and by flocculation or gelation of an Al-containing colloid. In ordinary geologic environments, the dissolution and precipitation of alumina may be modified by the pH, the presence of alkali metal and alkaline

TABLE 1.—PROCESS OF HIGH-ALUMINA ARGILLATION

Derivation from non-clay silicate minerals by weathering,
 Derivation from clay minerals by weathering,
 Dissolution and precipitation of Al in relation to pH,
 Flocculation and gelation of Al compounds,
 Precipitation with dissolved silica,
 Sorption by clays (e.g., Al-chlorite), Al-bonding, and
 "anti-gibbsitization",
 Authigenesis,
 Replacements,
 Structure of parent material,
 Organisms and organic residues.

earth cations, dissolved silica, the presence of sorbtive clay and other minerals, macro- and micro-floras and their residues, temperature, and pressure. Individual processes effective in high-alumina argillation are listed in Table 1.

PHASE RELATIONS IN THE SYSTEM $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$

The system $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ was studied in 1943 by Laubengayer and Weisz. They found reactions to proceed sluggishly, but that the transition, diaspore to corundum plus water, and reversal, could be made from both directions. They suggested that boehmite is never a stable phase in the $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ system.

In 1951, Ervin and Osborn confirmed the results of Laubengayer and Weisz and studied the system at higher temperatures and pressures. They found the sequence of stability field with rising temperature to be gibbsite to boehmite to corundum, and the "pressure and temperature minima for the stable existence of diaspore" to be 2000 lb/in², and 275°C. They noted that geologic field relations do not support their conclusions regarding minimum T and P for diaspore, and stated, in connection with experimental difficulties, that, "evidence for equilibrium is only indirect, and it is least satisfactory along the boehmite-diaspore transition curve".

Kennedy (1959) investigated further the $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ system and confirmed much of the work of Ervin and Osborn but modified the previous interpretation of the boehmite-diaspore relationship. Kennedy pointed out that, "the gibbsite-boehmite transition and the boehmite-diaspore transition are both exceedingly sluggish. Further, in many low temperature runs nucleation of diaspore is necessary . . ." "A good deal of evidence, internal to the phase diagrams, suggests that the results . . . do not represent equilibrium determinations." With regard to the boehmite-diaspore fields, "observed slopes of the boundaries separating the phases suggests rather strongly that a rate process rather than an equilibrium boundary is involved, as Laubengayer and Weisz suggested".

Kennedy further, "concluded that all boehmite forms metastably. The approximate slope of the boehmite-diaspore boundary, computed from thermodynamic data, indicates that diaspore in bauxite and clay deposits may have formed at atmospheric pressures and temperatures, a familiar conclusion from field observations." To this point, he wrote, "It thus appears that within the limitations of the thermodynamic and experimental data, boehmite is metastable at all temperatures and pressures and probably always forms metastably in natural despoits. Diaspore is then the stable phase in equilibrium with gibbsite."

From Kennedy's low H_2O -pressure diagram we would expect gibbsite to be formed at the earth's surface and this to be dehydrated to diaspore either directly, or via the metastable boehmite. Gibbsite, diaspore, and boehmite go to corundum when heated sufficiently, ordinarily above 1300°C in industrial application. Bratton and Brindley (1962) showed (as has also been observed by manufacturers of high-alumina refractories) that the path of conversion is modified by structure of the clay. Diaspore goes to corundum in a single step, whereas boehmite goes through gamma-

alumina and gibbsite may go through either of two avenues of transition before arriving at corundum. That heating far above room temperature to convert gibbsite to corundum is not necessary from thermodynamic considerations was calculated by Carpenter,* who found that the thermodynamic conditions for transition of gibbsite to corundum-plus-3H₂O to be 1.2 per cent relative humidity at 25°C. It is probable that such dehydration of gibbsite, or possibly syneresis of an alumina gel under low relative humidity, gave rise to the corundum in the Arkansas bauxite.

Because high-alumina clays in large deposits are regularly associated with kaolins or other clay minerals, the geological systems in which high-alumina clays are formed usually contain also SiO₂ along with Al₂O₃ and H₂O. Information on this system (SiO₂-Al₂O₃-H₂O) is scanty. Kennedy (1961) reported preliminary studies on it at high temperatures and pressures—too high to have yielded much information pertinent to the problem before us. At ordinary earth-surface temperature and pressure, reaction-yields of minerals in the system SiO₂-Al₂O₃-H₂O are exceedingly low (de Kimpe, Gastuche, and Brindley, 1961). Because chemical stability relationships are incompletely known we shall turn to geological observations, which are next described.

DERIVATION FROM NON-CLAY SILICATE MINERALS BY WEATHERING

Among early reports on high-alumina argillation, Mead's work on the Arkansas bauxite in 1915 is outstanding. At a time when favored interpretations of origin of bauxite included action of hot springs, replacement by rising thermal waters, bacterial action, and others (see Fox, 1932, pp.72-77) Mead's conclusion that subaerial weathering was the process by which bauxite was formed represented a distinct advance in thinking. Mead described the formation of bauxite as a process in gradual desilication of the nepheline syenite (Arkansas) in which kaolinite occurred as an intermediate stage between syenite and bauxite.

Harrison (1933), however, in careful, detailed, chemical and mineralogical work on Guiana bauxite and "pot clays" (largely kaolinite), concluded that much gibbsite ("primary laterite") was formed directly (not preceded by kaolinite) from basic and intermediate igneous and metamorphic rocks. He stated that, "*the mineral of first and direct formation from the plagioclase is gibbsite*" (p.37 of Harrison, his italics), and that resilication of the primary laterite resulted in lateritic earths or argillaceous laterite. Obviously this is a reverse mechanism of that proposed by Mead for the Arkansas deposits.

* Personal communication, Alden B. Carpenter, May, 1963, from a study in preparation for the 13th conf.

Gordon, Tracey, and Ellis (1958), who studied the Arkansas deposits in detail, concluded that "Bauxitization of the nepheline syenite resulted in the formation of granitic-textured bauxite that contains microcrystalline gibbsite as the main product. The place where this process occurred has been termed the zone of leaching" (Type I deposits, p.146). "Kaolin was produced chiefly by weathering of the nepheline syenite beneath the bauxite, following a rise in the water table that accompanied the deposition of the Eocene sediments." "Some of the silica released by this weathering process went into resilication of the bauxite." Thus Gordon *et al.* concluded that the nepheline syenite could alter to either gibbsite or kaolinite, depending upon the nature of the environment, and that either gibbsite or kaolinite could precede the other in genetic sequence.

Allen (1952), after extensive petrographic studies of bauxites and diaspore clays in the U.S., cited evidence for, and favored the process that, "The desilication of feldspars and parent rocks is usually a two-stage process in which clay minerals such as kaolinite, halloysite, and montronite are formed first and then silica is removed from them to form gibbsite, boehmite, and diaspore." Some occurrences in Georgia showed relationships, however, that to Allen (1952, p.678), "suggest that some 'chimney rock' specimens were formed by resilication of gibbsite".

Andesite in Hawaii is altered under present-day weathering mainly to halloysite or Al-gel, and thence to gibbsite, according to Bates (1962). He stated: "Halloysite forms from plagioclase usually by alteration of first the core and subsequently the rim of the feldspar laths. No kaolinite was observed, its absence being attributed to the absence of fine-grained mica as an intermediate weathering product. Gibbsite is produced by (1) removal of silica from halloysite, (2) dehydration of Al-gel, and (3) precipitation from solution. Although it is possible that the mineral (gibbsite) may form directly from feldspar, halloysite is the common crystalline intermediate on both the megascopic and microscopic scales."

The mechanism that Bates describes for the gibbsitization of andesite (feldspar in andesite) does not conform to that of Gordon *et al.* for nepheline syenite, and of Harrison for basic to intermediate rocks. One wonders if the different parent rocks, or different environments of weathering, account for the different mechanisms; or even further, was there a submicroscopic film of intermediary halloysite present in the rocks of Harrison, and Gordon *et al.*, but undetected by them? I have examined in thin section, under high magnification, the direct gibbsitization of a diabase from the "Hope Quarry" of Harrison (collected by E. C. Harder, sent to C. S. Ross, and given to me), and do not observe halloysite between the feldspar and the gibbsite, but one can always ask, "Would a transition layer have been seen if the resolution of the microscope had been better?" Since both Bates, and Gordon *et al.*, used both field and microscopic evidence for each of their conclusions, it is reasonable to believe that the results of each investigation, although antithetical, were reported correctly for the particular systems

with which each was concerned. We shall now inquire into possible ways by which high-alumina argillation operates.

MECHANISMS OF DIRECT (PRIMARY GIBBSITE) BAUXITIZATION

Gordon, Tracey, and Ellis (1958) considered in detail the effects of the following mechanisms in the weathering of nepheline syenite to bauxite: leaching, concretion, formation of boehmite and magnetic iron oxide, migration of Al^{3+} in solution, and formation of kaolin bodies. Bárdossy (1959, Tomus VI, pp.21-53) emphasized the effect of pH on the desilication of clay minerals to high-alumina minerals. Keller (1958) considered the possible effect of pH and metal cations on the surface of hydrolyzing silicates towards separating silica and alumina (direct bauxitization) during dissolution, or alternatively towards effecting their combination as clay mineral aluminum silicates.

Harrison, Gordon *et al.*, and Keller concur that direct bauxitization can

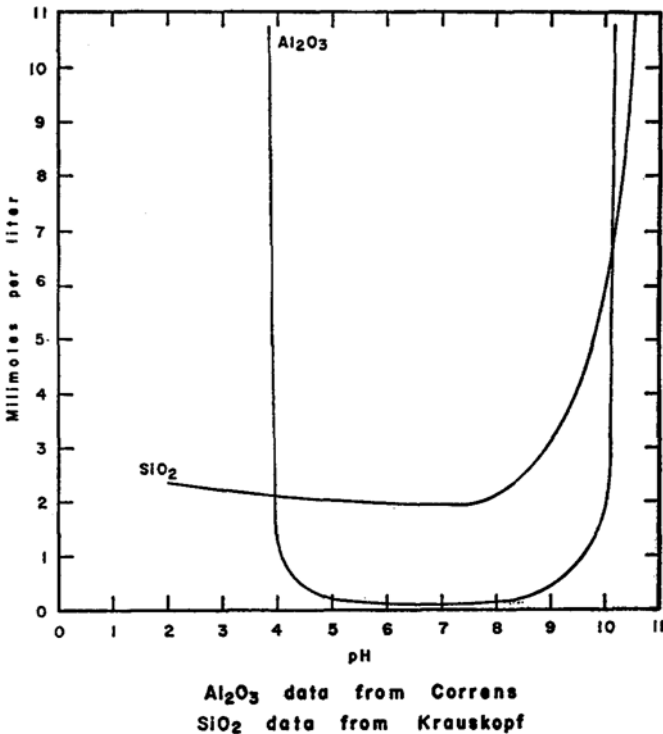


FIGURE 1.—Solubility of Al_2O_3 and amorphous SiO_2 in water.

result from the leaching of primary silicates. Harrison's conclusion has been quoted (p.133), and Gordon *et al.* state, "The first part of the bauxitization process resulted in the formation of bauxite that preserved to some degree the original texture of the nepheline syenite. . . . The principal end product was the microcrystalline form of gibbsite, derived chiefly from alteration of feldspar." Keller (1958) and Bárdossy (1959) independently related the separation of silica and alumina by differential solubilities influenced by pH. These relationships are explained as follows.

In Fig. 1 is shown the relation between pH and the solubilities of amorphous silica (Krauskopf, 1959) and Al_2O_3 (Correns, 1949) in distilled water. These data may be used as guides to relative solubilities of SiO_2 and Al_2O_3 in ground water, although the absolute solubility of SiO_2 is decreased significantly by associated alumina in solution (Okamoto, Okura and Goto, 1957), and may be greatly enhanced by the presence of certain organic matter (Lovering, 1959). Above pH 10, both SiO_2 and Al_2O_3 are relatively highly soluble, whereas between pH 5 and 9, Al_2O_3 is relatively insoluble although SiO_2 still remains dissolved in low concentration.

The pH of the solution of gibbsite in H_2O (at equilibrium) controls the distribution of Al^{3+} and AlO_2^- . At pH 5.1, the activities of Al^{3+} and AlO_2^- are approximately equal (at thermodynamic equilibrium), whereas at pH 4, the activities ratio of Al^{3+} to AlO_2^- is approximately $10^4 : 1$, and at pH 10.5, it is approximately $1 : 10^{22}$, respectively (personal communication, A. B. Carpenter).

Referring again to Fig. 1, when hydrolysis of an aluminum silicate occurs at pH 11, both SiO_2 and Al_2O_3 are relatively soluble and mobile, and can be removed, even to long distances if the pH remains at 11. Aluminum is present predominantly as AlO_2^- , as has been noted. As the solution becomes more acid, at pH 8 for example, aluminum preconditioned as AlO_2^- will be precipitated, probably as gibbsite, or possibly as metastable boehmite (?), $\text{AlO}(\text{OH})$, or diaspore, HAlO_2 , and the silica may remain in solution if sufficiently dilute. In this way, primary bauxite might be formed directly on the surface of the hydrolyzing silicate without intervening kaolinization, or precipitated elsewhere so that the pH was lowered.

Question may be raised if minerals yield pH 10 or above upon hydrolysis. Nepheline, diopside, and actinolite yield abrasion pH's of 11 (Stevens and Carron, 1948; Keller, 1958) showing that the surfaces of certain hydrolyzing minerals are highly alkaline. In a solubility experiment (Keller, Balgord and Reesman, 1963), nepheline and diopside were pulverized under distilled water exposed to the atmosphere by grinding 10 g of mineral in 100 ml water for one hour, at which time the pH's of the slurries were 8.8 and 9.0, respectively. Water taken from an intermittent seep in jointed bare nepheline syenite at Bauxite, Arkansas, about 3 hours after a summer shower yielded pH 7.9, measured in the field (Keller, 1960). Therefore, the pH range and solubilities shown in Fig. 1 are geologically realistic. In

the experiments by Keller, Balgord, and Reesman (1963), previously cited, nepheline yielded 39 ppm silica in solution (diopside 50 ppm), and 8.3 ppm alumina. In contrast, labradorite and microcline both at pH 8.0 yielded only 8.2 and 15.6 ppm SiO_2 and 1.25 and 3.25 ppm Al_2O_3 , respectively.

These data lend support to a possibility of alteration consistent with the conclusion by Harrison that "under tropical conditions basic and intermediate rocks . . . leave an earthy residuum of aluminum trihydrate! . . ." Under the tropical conditions of Harrison, it can be assumed that rain fell almost every day, keeping the rocks continuously wet and flushing away the hydrolysate so that concentrations of dissolved silica never reached the saturation point. On the contrary, if saturation of the solution had occurred for a considerable time, either because of (1) lack of rain, (2) evaporation, or (3) ionic build-up during water logging, probably a combination of silica and alumina would have formed kaolin minerals. High rainfall provides the important factor of always dilute solution of ground water.

The mechanism based on control by high pH and low concentrations of dissolved alumina and silica, is proposed as one way hypothetically, by which *direct bauxitization* of non-clay silicates may occur. Its operation may not have been unequivocally proved, but it describes logically a way by which the "cryptocrystalline or so-called amorphous form of gibbsite" in Arkansas (Gordon *et al.*, 1958, p.83) may be formed.

Kaolinization in association with bauxite. Kaolin minerals (meant to include endellite, hallysite, b-axis disordered kaolinite or "fire clay mineral", and well-ordered kaolinite) may form by partial desilication of the primary silicate rock or mineral (Bates, 1962) or resilication of gibbsite (Gordon *et al.*, 1958). Gordon *et al.* (1958, p.149) state, "It seems likely that both . . . migration of kaolin in solution and resilication of bauxite . . . may have taken place simultaneously, as Mohr has suggested that silica and kaolin behave alike under the same ground-water conditions". Harrison (1933, p.10) concluded that "under tropical conditions, *acidic rocks*, such as aplites, pegmatites, or granites and granitic gneisses, do *not* undergo primary laterization, but gradually change into pipe or pot-clays, and more or less quartziferous and impure kaolins". Harrison, like Mead, concluded that kaolins could be desilicated to bauxite: "Under tropical conditions, lateritic earths, and even pot clays, may undergo desilication, with the formation of concretionary and superficial masses of bauxite."

To account for kaolinization (not direct bauxitization) of aluminum silicates, Keller (1958) has interpreted the control by pH of solubilities of Al_2O_3 and SiO_2 as resulting in the combination of Al_2O_3 and SiO_2 below probably pH 6 to form kaolin minerals. In the laboratory, De Kimpe, Gastuche, and Brindley (1961) synthesized kaolinite at room temperature at pH 4.5 and lower. Patterson and Hosterman (1962) found the pH index of all 11 flint clay (kaolinite) samples (Table 5, p.F56) cited from Kentucky to range from 6.0 to 4.3. I have found the pH of water standing in pools

in deposits of flint fire clay (kaolinitic) in Kentucky, Ohio, Pennsylvania, Maryland, and Missouri, and in kaolins of Alabama and Georgia, to be consistently below 5. In occurrences where pyrite is or was present, acidity would be conditioned by sulphuric acid formed from pyrite, but pH 4.0 to 4.5 was found regularly also where no pyrite was observed, as in some Missouri flint clay pits. Pools of water in dolomite, on the other hand, occurring a hundred feet from flint clay (in Missouri) yield pH 6.8 to 7, obviously a function of reaction with the dolomite. A pH of 4.5, or less, in association with kaolinite is so common that it must be truly significant.

From free-energy calculations* in the system gibbsite-silica-water, gibbsite exists (25°C and 1 atmosphere) in thermodynamic equilibrium with kaolinite at pH 5.1, the activity of Si (from amorphous silica) at $10^{-4.2}$, and activity of Al at $10^{-9.46}$ (where Al^{3+} and AlO_2^- are equal in activity). This is a point of minimum activity for total Al^{3+} and AlO_2^- .

When the activity of Si is increased to $10^{-3.0}$ at the same pH (5.1), and activity of aluminum is only slightly less, $(\text{Al}^{3+})^{-10.7}$, $(\text{AlO}_2^-)^{-10.7}$, kaolinite is in equilibrium with amorphous silica. Therefore, a variation of only about ten-fold in the activity of silica at pH 5.1, ideally should reverse the gibbsite-kaolinite reaction.

The kaolinite stability field in contact with gibbsite widens as pH becomes either lower or higher than 5.1 and simultaneously the activity of silica remains almost constant but that of aluminum increases. The kaolinite-gibbsite stability fields widen most prominently from pH 5.1 up to pH 9.8, above which the gibbsite field widens at the expense of silica even though the activity of Si may increase 10-fold.

Factors other than pH that condition the reaction of gibbsite-kaolinite include adequate concentrations (activities) of Al_2O_3 and SiO_2 in solution related to rainfall and efficiency of ground water leaching, various complexing inorganic substances, complexing and protective organic compounds, effects of alkali metal ions to promote solubility of silica, and alkaline earth ions as flocculants of silica, and others.

Secondary, and other primary (?), effects by dissolution, reconstitution, and precipitation in a low-pH range. The preceding discussion has emphasized direct bauxitization in an environment of high pH wherein Al_2O_3 is relatively soluble. This viewpoint does not in the least preclude effective dissolution of alumina at low pH, 4.5 and less, and the development of endelite, and possibly allophane and alumina gel, in this range of acidity. Indeed, such acid environments have almost certainly been very important in the dissolution, reconstitution, and precipitation of high-alumina minerals.

Essentially every investigator of high-alumina deposits has reported second-stage overgrowths, cavity fillings, and veins of gibbsite, boehmite, diaspore and clay minerals in the deposits. I believe that most of this transfer of alumina has been done at low pH for the following reasons. In

* Personal communication, A. B. Carpenter, October, 1963.

the Arkansas bauxite region, a pyritic-marcasitic lignite overlies or is interbedded with, the bauxite. Sulphuric acid solutions yielding pH 1 (Hydrion paper test) are generated as oxidizing water percolates through the coal and into the bauxite. This acidity, and pH up to 4, renders alumina quite soluble. Water in the rills draining the bauxite under lignite is commonly at pH 3.5 (Hydrion paper test). Mining engineers in the area state that drainage water is exceedingly acid during a heavy rain following a dry spell. The formation of endellite under present-day alteration as clear massive porcelainous and white granular varieties by the action of sulphuric acid (from oxidizing iron sulphate) on a red, granular argillaceous progenitor has been observed in Kentucky (paper presented by title at this Conference; Keller, McGrain, and Saum). The moist endellite at this occurrence yields pH 3.0 to 3.5, and altering parent clay, pH 1.5. Our observations support and extend further those of Ross and Kerr (1934) who wrote that "halloysite . . . forms through weathering and by the action of cool sulphate-bearing solutions on aluminous materials". I suspect that the sulphate radical, in addition to the acidity, is significant in argillation within the kaolin group. Sulphur and silicon apparently interact in clay minerals to a certain extent (Lesar, Krinbell, Keller, and Bradley, 1946).

Veins of white and porcelainous endellite are common in parts of the bauxite in Arkansas. The development of endellite observed in Kentucky suggests strongly that the vein-type endellite within Arkansas gibbsite was formed by sulphide-coal-derived acid solutions reacting with pre-existing clay and/or bauxite.

One is tempted to query if, in addition to endellite, gibbsite may be formed directly (without intermediate solution stage) from primary silicate rocks exposed to pH 4.5 and less. Conceivably it might be, but probably it is not, because highly acid weathering solutions produce silica-rich and alumina-poor (also iron-poor) podsoles rather than lateritic soils from silicate rocks. I have seen good field confirmation of the loss of Fe_2O_3 and alumina, and enrichment of silica in the present-day formation of siliceous refractory clay deposits (report in preparation with J. F. Westcott). Therefore, I doubt that *direct* bauxitization occurred in a highly acid environment, but certainly high-alumina minerals have been observed to originate in abundance *secondarily* in an acid environment.

DERIVATION OF HIGH-ALUMINA MINERALS FROM CLAY MINERALS BY WEATHERING

The development of bauxitic-lateritic clays and compounds in the A-horizon of the soil by the desilication of common clay minerals (all types) is so well known that it need not be dwelt upon. Mohr and van Baren (1954) clearly show that leaching (as opposed to water-logging) in which silica and cations other than Al and Fe are removed results in bauxitic-lateritic soil minerals.

In Hawaii, beneath the subsoil in the zone of fresh rock, the andesite weathers to halloysite which, in turn, is desilicated to gibbsite. Bates (1962) has shown this mechanism to proceed on both macroscopic and microscopic scales. Bates (p.315) further stated: "An amorphous transition state, probably ranging in composition from allophane to Al-gel exists as part of the change from halloysite to gibbsite. . . . The nature and relative abundance of intermediate and end products of weathering depend primarily upon the rainfall, angle of slope, and texture of the rock."

Another type of high-alumina argillation is exemplified by the Cretaceous (?) Hungarian bauxites, the Pennsylvanian-age nodular diaspore clay in Pennsylvania, and the Missouri burley and diaspore (rarely boehmite) clays of Pennsylvanian age. The Hungarian and Missouri deposits were formed in low-lying, marshy to karst-type topographies into which a clayey sediment had been transported. Bárdossy (1959, Part IV, p.21) wrote of the Hungarian bauxites, "The original substance of Hungarian bauxites was deposited under a subtropical to tropical climate in periodically inundated depression of the ancient landscape. This original substance, of a clayey nature, has altered in the karstic depressions of the carbonatic bedrock into bauxite *in situ*. It is not yet fully clear as to where the original material of bauxite was derived from. So much seems to be certain, however, that it was transported to its present site by slow, quiet streams (fluvatile), in the form of muddy and colloidal suspensions. . . . The pH of the colloid solutions should have been presumably rather acid (pH, 4-6) as this is the only way of accounting for the joint transportation of Al, Fe, and Ti on a greater scale. . . . The suspensions gradually coagulated and settled . . . probably facilitated by the carbonatic character of the bedrock. . . . In all probability the predominant mineral was allophane or kaolinite of the fire clay type.

"Thus the kaolinitic (and fire clay-like) nature of the original primary substance indicates a subaerial or freshwater sedimentation, under intense leaching in an acid or neutral medium and an intensely oxidizing environment. These features also indicate a hot, moist climate. (Italics are Bárdossy's).

"In our opinion the gradual leaching of silica was begun by solutions turning alkaline (pH, 7-10) filtrating through the loose unconsolidated sediment . . . in the course of the dissolution of finely dispersed calcium carbonate in water, free of CO₂, Ca(OH)₂ is formed resulting in an intense alkalinity pH, 9-10, of ground water. . . . The resulting highly basic solutions decomposed the fire-clay mineral and the still amorphous aluminum silicates (allophane). The alkalinity of the solvent simultaneously made possible the leaching of the silica-gel and its washing out across the bedrock. At the same time aluminum was instantly precipitated on decomposition. . . ."

The mineralogy of Hungarian bauxites varies with deposits. Gibbsite occurs in maximum abundance at 75 per cent in the Kincses Jozef fields, boehmite up to 85 per cent in 4 other areas, and diaspore as much as 70 per cent of the deposit at Nezsza. Bárdossy proposed that upon destruction

of the kaolinite lattice and addition of water, gibbsite or boehmite result. If gibbsite forms, it may dehydrate to boehmite. If the pH decreases to the "neutral state", bayerite, boehmite, or amorphous trihydrate may form.

In regard to diaspore formation, however, Bárdossy (Part IV, p.32) believes that, "The formation of diaspore by the bauxitization of kaolinite is indeed hard to imagine, in the first place due to reasons of lattice geometry . . . the anionic lattice of kaolinite is cubic close packing, that of diaspore hexagonal close packing. It is well-known that the stablest part of the lattice is the anionic grid, whose rearrangement consumes an exceedingly great amount of energy." In the Transdanubian Mountains, and the Nagyxxzal and Nezsza deposits, "the primary occurrence of diaspore is unlikely". But, "the situation at the Nagyharsany locality is somewhat different. The very small iron content and the greater percentage of chlorite" (in some Missouri diaspore deposits chlorite also occurs) "of this bauxite is similar to the ones described by Schüller. . . ." "It is, in our opinion, possible that the none too great diaspore (10 per cent average) content of the Nagyharsany bauxite should be a primary formation." The preceding quotations were carefully selected from Bárdossy's discussion of the paragenesis of the Hungarian bauxites to present the most salient features of his ideas of their origin; the entire, comprehensive report of approximately 135 pages is recommended.

Description of the Hungarian bauxite deposits indicate many similarities with parts of the Missouri diaspore deposits. The outstanding mineralogic difference between them is that no gibbsite has been found in any Missouri high-alumina deposit, and boehmite is infrequent in occurrence. A comparison of theories of origin for the two regions will be made after the Missouri deposits are described. Considerable agreement in theory may be anticipated, but I find difficulty in accepting Bárdossy's proposal that water dissolving CaCO_3 will be CO_2 -free, enabling it to yield pH 9-10 (from $\text{Ca}(\text{OH})_2$).

The origin of high-alumina minerals, dominantly diaspore and minor boehmite, in Missouri diaspore clay deposits has been discussed by Allen, 1935, 1955; Burst, 1952; Keller, 1952; Keller, Westcott, and Bledsoe, 1954; McQueen, 1943; and others. All of these writers concur in the first phase of the origin of the clays, namely, that clay colloids were carried by probably slow-moving streams into low-lying marshes, karstic depressions, and sink holes dissolved into limestones and dolostones of Mississippian and Ordovician ages. Allen (1955) and McQueen (1943) interpreted that ground water, moving predominantly downward, leached and desilicated the clay minerals to yield diaspore and boehmite. Keller earlier subscribed to the same hypothesis, but modified it in part when the Bueker clay deposit (Keller, 1952; Keller, Westcott, and Bledsoe, 1955) was opened and exhibited unequivocal evidence that the high-alumina clay not only had been formed, but was subsequently subjected to weathering and oxidation, all of this occurring during Pennsylvanian time prior to the deposition of

the Excello Shale (Cabaniss Group) and Blackjack Creek Limestone of the Fort Scott Limestone of Pennsylvanian age (Searight, 1955). Keller, Westcott, and Bledsoe (1955) interpreted the removal of relatively large amounts of silica and metal cations, by dialysis from the clay colloids by means of the Donnan effect and flushing off the top of the low-lying marshy basins during slow sedimentational filling of the basins. Reasons for significant removal at the top that augmented downward leaching include, (1) no evidence of silica migration or deposition into the underlying shale, sandstone, or limestone (including dolostone) which enclose the clay deposits, (2) the high impermeability of clay colloids and the flint clay, (3) non-systematic distribution of high-alumina minerals in the flint clay, (4) no evidence of downward solution channels and associated high-alumina enrichment in the large diaspore deposits, (5) relatively horizontal layers of high-alumina minerals at the top of deposits and accompanying concentration of silica and fluxing metals in lower parts of deposit as would have occurred if fresh-water leaching started at the top and proceeded downward, and (6) completion of high-alumina argillation in pre-Fort Scott time. Desilication was aided extensively, it is thought, by the action of plants growing in and around the marshes.

The source of the clay colloids in the Missouri deposits was the clay fractions of weathered limestones of Mississippian and Ordovician ages surrounding the clay deposits (Robbins and Keller, 1952). These colloids may have ranged in alumina composition from illite to aluminous gels, modifying accordingly the extent of desilication necessary to yield diaspore and boehmite.

The formation of Missouri diaspore probably represents a rate change towards diaspore rather than achievement of equilibrium. X-ray diffractograms of certain diaspore-bearing clays exhibit variations in intensities believed to be dependent upon degree of ordering of the crystals of diaspore (not sample-orientation effects), and some of these may be interpreted as being produced by "proto-diaspore". Likewise, in at least one K-rich (low fusion, "alkali" clay) deposit, diffractograms suggestive of alunite have been obtained from the high-alumina clay. Interplanar spacings suggest alunite, although spacings and intensities deviate from those yielded by first-quality reference alunite. Possibly a "proto-alunite" was being evolved.

The origin of the Mercer fire clay (Pennsylvanian in age) occurring in Pennsylvania was interpreted in 1952 by Bolger and Weitz to be as follows: "the source material of the Mercer was a colloidal mixture of hydrous aluminum silicates and aluminum hydroxides. These colloidal gels were then concentrated and crystallized to form kaolinite, diaspore, and boehmite. After lithification, shrinkage cracks appeared, into which a silica-rich kaolinitic material was introduced, resulting in the replacement of diaspore by kaolinite. The silication of diaspore released free alumina, which recrystallized in voids as a later stage of diaspore." Bolger and Weitz do not elaborate on the source or composition of the silica-rich kaolinitic

material. They do not explain the chemical drive by which incoming silica is caused simultaneously to combine with diaspore to form kaolinite and release alumina into solution.

Chlorite has been referred to in previous quotations from Bárdossy (1959) on the Hungarian bauxites, and from Patterson and Hosterman (1962, pp.9, 54, 57) who noted probably chlorite in the flint clay in Kentucky. Eleven years ago, Keller (1952, p.125) reported a "chloritic clay mineral", and Hahn (1954) confirmed and studied this 14Å clay phase, presumably chlorite, in varying abundance in a Missouri diaspore clay deposit (Ocheskey) that was notably rich in boehmite. More recently, we have tried to concentrate and isolate the 14Å phase for detailed study, but repeated efforts to separate it from admixed kaolinite and boehmite by grinding, sedimentation in water, passing through an isodynamic magnetic separator, and suspension in heavy liquids have enriched the fraction only to a content of about 20 per cent (estimated conservatively) of the 14Å phase (Fig. 2). A chemical analysis of the best-fractionated sample yielded the results listed in Table 2.

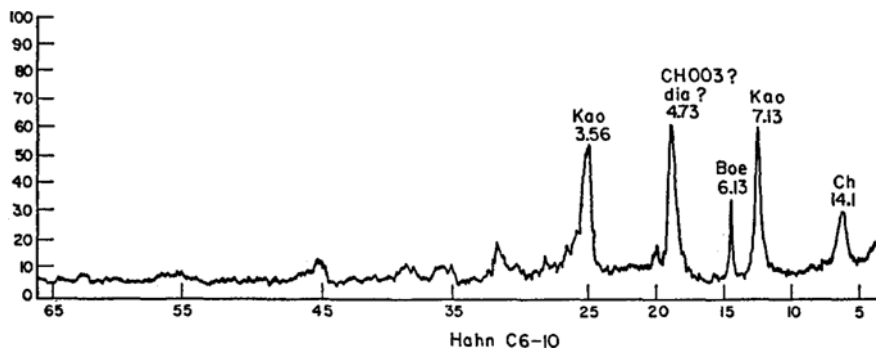


FIGURE 2.—X-ray diffractogram of the clay concentrate from the Ocheskey pit showing characteristic peaks of chlorite (?), 14.1Å, not destroyed by heating to 525°C; kaolinite, 7.13Å, which is destroyed by heating to 525°C; boehmite, 6.13Å; diaspore and 003 of chlorite (?), 4.73Å. The 060 spacing record of the trace is not definitive with respect to a di- or tri-octahedral character of chlorite.

Because the fractionated C-10 sample is not a pure single phase, and the mixture with kaolinite, boehmite, TiO_2 , and iron oxides is complex, it is not possible to estimate quantitatively the composition of pure 14Å-phase and calculate its structural formula. Nevertheless, the paucity of MgO, 0.11 per cent, demands that the chlorite (?), if it is a chlorite, must be aluminous. From Foster's (1962) study of chlorites, those highest in alumina run approximately the ratio 0.11 MgO:0.11 Al_2O_3 :0.12 SiO_2 :0.06 H_2O . In gram-per cent, utilizing all of the MgO for chlorite, 0.11 per cent MgO would yield about 0.4 per cent chlorite in the C-10 sample,

TABLE 2.—CHEMICAL ANALYSIS OF FRACTIONATED
C-10 SAMPLE, OCHESKEY DEPOSIT

SiO ₂	25.09
Al ₂ O ₃	56.71
Fe ₂ O ₃	0.70
FeO	0.20
CaO	0.07
MgO	0.11
Na ₂ O	0.52
K ₂ O	1.04
TiO ₂	1.48
Loss Ignition	13.99
	99.91

Analysis by Bruce Williams Laboratory, Joplin, Mo.
Cost of analysis defrayed by NSF GP-1057

which is obviously far, far below that estimated from the diffractogram—indeed, the X-ray would not “see and record” less than one per cent chlorite. A clay containing 20 per cent of “normal” Mg-containing chlorite highest in Al of those found by Foster should contain 4 to 6 per cent, not 0.11 per cent, MgO, which is actually present. Therefore, the 14Å phase in the Missouri clay must be high in alumina, presumably an Al-chlorite.

The origin for it is postulated to be precipitation-fixation by a 3-layer clay, most probably a weathered, expanding illite (“montmorillonite”), of migrant, dissolved alumina in the manner by which chlorite-like phases were synthesized by Slaughter and Milne (1960).

Although properties of the Al-chlorite (?) cannot be determined from the mixture, it was observed that it did not expand with ethylene glycol, the 14Å reflection was not diminished appreciably by digesting the sample in 6N HCl at about 90°C for 12 hours, and heating the clay to 525°C overnight did not modify the 14Å reflection. In these respects it is similar to a mineral Patterson and Hosterman (1962, p.F64) found in the Olive Hill, Kentucky, clay bed, which they called “probably chlorite . . . this mineral has a fundamental basal spacing of 14Å, and it does not swell with ethylene glycol or collapse when heated to 300°C . . . it was neither destroyed nor enhanced by heat treatment at 659°C, and was not destroyed by 3N hydrochloric acid treatment. . . . Possibly the clay mineral here reported to be chlorite is a highly aluminous variety.”

Aluminous gels have been referred to repeatedly in the origin of high-alumina deposits in contiguous U.S., Hawaii, Hungary and the U.S.S.R. Beneslavsky (1962) emphasized strongly the role of Al-gel, or “complex Al, Si, Ti, Fe-gel”, believing that gels go to corundum by complete dehydration, or to boehmite by ageing. Boehmite, in turn, may be aged further to diaspore or hydrated to hydrargillite. It appears more logical, however, that hydrargillite (gibbsite) should precede boehmite and diaspore in the

sequences of ageing and alteration. Documentation is scanty, but it would appear that Al-gels are compatible with an acid environment.

DISSOLUTION, PRECIPITATION, SORPTION, AND FIXATION OF Al^{3+} AND ALUMINA

That Al is dissolved readily at pH 11 or higher, and below pH 4 is certain. Less clear, however, is how alumina can be carried into geologic situations at presumably intermediate pH values, such as vein and other fillings for which there is indisputable evidence, as shown by Allen (1954, 1952), Bárdossy (1959), and Beneslavsky (1962). Gordon *et al.* writes of the migration of Al^{3+} . Keller described a diaspore clay cast of fossil wood in a Missouri diaspore pit (1938)—necessitating movement of diaspore. Perhaps an assumption that the pH at which alumina is dissolved and carried in intermediate range is in error.

Repeatedly observed evidence, coupled with the known migrations of alumina in soils and the dissolved alumina found in pulverized silicate mineral slurries (Keller *et al.*, 1963), indicates that alumina is notably more soluble and mobile than its behavior classically interpreted would indicate. Perhaps its "absence" (or extremely low dilution) in most geologic waters is more apparent than real, and due not to inherent low solubility, but to its property of acting as a bonding agent in Al silicates (Jackson, 1963), i.e., being picked up, immobilized, and/or fixed by almost omnipresent clay minerals, so that it is removed from mobile solution. Because it is trivalent and small in size, the Al^{3+} ion has a high energy of ion exchange. Therefore, it may be sorbed during cation exchange and held tightly by any of the clay minerals, and may be fixed by the 3-layer types to develop vermiculitic minerals, corrensite, or chlorite. This sort of behavior in soil clays has been called "anti-gibbsitization" by Jackson (1962-63).

CONCENTRATION OF ALUMINA BY ORGANIC PROCESSES

Plants and their residues may operate to concentrate alumina in several ways. Lovering (1959) in a thought-stimulating paper points out that "Some species of *Equisetum* (horsetail), sedge, reeds, and bamboo contain about 10 per cent SiO_2 (dry weight) and grasses are notorious high silica forage plants . . . the leaves of corn contain at 2.5 per cent SiO_2 Many tropical lumber trees and also some of the temperate-zone hardwoods are silica accumulators." By extracting silica from the soil and/or rocks, alumina may simultaneously be concentrated therein, assuming, of course, that the silica is blown or washed away when the plant residue falls or decomposes. That plant opal, opalized residues of squat, pear-shaped,

rod-like, and irregular forms up to 0.3 mm in length obtained from grasses and other plants is transported to marine sediments was observed by Kanno and Arimura (1958). Beavers and Stephen (1958) found up to 5.5 per cent plant opal in certain Illinois soil, and regard it as a potential index mineral for paleosols.

Lovering (1959, p.781) pointedly stated, "A forest of silica-accumulator plants averaging 2.5 per cent silica and 16 tons dry weight new growth each year would extract about 2000 tons of silica per acre in 5000 years, equivalent to the silica in 1 acre-foot of basalt. Comparison of lateritic soil with parent rock indicates that silic-accumulator jungle could convert basalt into lateritic soil rapidly—geologically speaking."

Alumina-accumulator plants which concentrate alumina removed from the soil may require acid soil; Lovering cites two species of aluminum accumulators in which the cell sap acidity is pH 3.6 to 5.2. One species of plant, the silky oak *Orites excelsa* of Australia (not a true oak), actually secretes aluminum succinate in cavities in the wood.

By increasing the solubility of silica in water, plant residues may enhance its removal and thereby concentrate the remaining alumina within an aluminum silicate being desilicated. Lovering (1959, p.789) cited an example, "extract from the *Equisetum* contained about 320 ppm silica—more than twice the amount in a saturated solution of amorphous silica in water". Indications are that geological chemists have hardly begun to recognize the reactions that can be carried on by plants and their residues. Complexing effects, and surface energies generated at interfaces by microflora, may yield products considerably beyond those of simple, obvious, inorganic reactions.

Summarizing, plants and plant residues exert diverse effects on alumina in geologic systems as follows:

1. Alumina which has been put into solution at pH 10 or above by other means may be acidified by plant acids and thereby precipitated.
2. Acids at pH 4 or less, derived from plants or their residues, may bring alumina into solution.
3. Organic complexes with silica increase the solubility and removal of silica, thereby concentrating less-soluble associated alumina.
4. Alumina-accumulating plants concentrate alumina in their tissues.
5. Humic acid solutions may mobilize alumina and iron (colloids?).

COMMON DENOMINATOR(S) IN THE ORIGIN OF HIGH-ALUMINA MINERALS

The stated objective of this paper was to search for a common denominator(s) of, or factor(s) common to, the processes of origin of high-alumina minerals in clay deposits. Those devoid of any qualification are few indeed;

it is better to add the qualifications. Some of the denominators found most common follow.

1. Aluminum must occur in the parent material.

2. Relatively fresh water in (a) great abundance, and (b) continuous supply must be available if the high-alumina argillation occurs by direct desilication of an aluminum silicate parent. An abundant and continuous supply of fresh water is necessary that the ambient ground water solutions remain so dilute as to hold Al and Si ions and compounds in solution. A rain-forest climate meets these conditions. The continuous supply of fresh water accommodates the required efficient removal of the solute (commonly a hydrolysate). The removal may be either downward through permeable rock, or by flushing off the top of a basin lined with impervious clay on its bottom.

3. Higher temperature accelerates chemical reaction, i.e., desilication and/or resilication, and tropical warmth acts accordingly. Climatic temperature of 77°F or above promotes destruction by the microflora of residues from the macroflora. Under certain conditions, the presence of plant humic residues causes precipitation of silica and mobilization of alumina, whereas destruction of plant residues would permit silica mobility and consequently, *in situ* concentration of alumina.

4. Desilication may be enhanced by:

- (a) pH above 4 and below 10 during dissolution
- (b) Na and K ions in solution,
- (c) growth of silica-accumulator plants in the parent material,
- (d) action of certain organic complexing with silica to increase silica solubility. Simultaneously it must be recognized that certain other humic compounds cause silica to be precipitated, and aluminum and iron became mobilized.

5. Alumina may be precipitated-concentrated by

- (a) slight acidification (CO₂ dissolved, plant or mineral acids) of Al-containing solutions originally at pH 10 or above,
- (b) evaporation from Al-solutions,
- (c) sorption, combination, cation-exchange, or fixation by clay minerals (or other minerals), silica gels, or silica in solution,
- (d) syneresis of Al-gel,
- (e) recrystallization of microcrystalline Al minerals,
- (f) alumina-accumulator plants.

UNSOLVED PROBLEMS IN THE ORIGIN OF HIGH-ALUMINA MINERALS

Unsolved problems of the origin of high-alumina minerals include the following:

What geochemical and geologic conditions control and differentiate the formation of gibbsite vs. boehmite vs. diaspoire in bauxite deposits? The question of what is the environment of diaspoire formation brings into sharper focus the problem of all three.

In the Missouri deposits absolutely no gibbsite has been found, and boehmite is a minor occurrence; why? Bridge's (1952) suggestion that long geologic ageing (back to the Paleozoic) is vital for abundant diaspoire formation is invalidated by the occurrence of diaspoire in younger deposits. Keller *et al.* (1954) suggested independently that gibbsite forms in the zone of leaching (above ground water table) but diaspoire subaqueously, and found later that de Lapparent (1936, p.378), long before, had concluded that gibbsite formation took place above the water table, boehmite within the water table. If these concepts are true, the occurrence of all three hydrates in deposits such as those in Hungary pose serious problems of water-table movement. Eyles *et al.* (1952, p.79) noted that, "since diaspoire is a denser mineral (3.33) than boehmite (3.06) *pressure* is the essential factor controlling its development *on a large scale*, and that rise in temperature alone would not be effective" and (p.80), "that the formation of monohydrates in *large amounts* results from a change of geological environment superimposed on gibbstitic laterites after the formation of the latter . . ." (italics by Eyles *et al.*).

The very intimate association of highly varied ratios of the three minerals, however, throws doubt on high pressure as a necessary factor to form bauxite. Is it possible that each of the conclusions is correct in part, as follows?:

Diaspoire requires a higher energy level for its formation than does gibbsite or boehmite, which can be supplied by either:

1. inheritance of structural energy as an octahedrally coordinated sheet from kaolinite,
2. deep burial or tectonic movement,
3. high temperature from deep burial, intrusion, or frictional movement.

Under what specific geologic conditions is alumina sufficiently soluble that it moves through joints and then is deposited as vein fillings?

What conditions promote specifically and critically the sequence from feldspar to alloysite to gibbsite, as Bates observed, and conversely, feldspar to gibbsite, to kaolinite, as Gordon *et al.* observed? Not only is the sequence reversed, but halloysite is in one sequence and kaolinite in the other.

Is a tropical or subtropical temperature necessary for bauxitization to operate? Is the minimum temperature (whatever it is) determined by reaction rate of dissolution; or by the balance between accumulation of organic matter from a macroflora off-set destruction of it by a microflora?

How extensive is alumina-gel present in weathering environments, in stream transportation, and in high-alumina mineral diagenesis, and is it necessary for the development of pisolitic structure in bauxite?

What are the specific organic complexes that increase the solubility of silica in water and alternatively, what mobilizing compounds of Al and Fe?

At a time when space, isotope, and nuclear geology appear very glamorous, the geochemistry of the third most abundant element on the earth's crust quietly still invites research.

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