STRUCTURES OF ALUMINUM HYDROXIDE AND GEOCHEMICAL IMPLICATIONS[1]

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ABSTRACT

Synthesis experiments in the alumina-water system at room temperature indicate that the gibbsite polymorph precipitates slowly from solutions whose pH is below the point of minimum solubility (pH 5.8), and the bayerite polymorph precipitates rapidly from solutions whose pH is above 5.8. Nordstrandite, the third polymorph of aluminum hydroxide, forms from bayerite during aging at intermediate to high pH values. In solutions of intermediate pH, both gibbsite and bayerite form, but with aging, early-formed gibbsite disappears as more bayerite forms. During aging, the pH's of the mother liquors decrease if gibbsite precipitates and increase if bayerite precipitates.

The principal structural difference among the three aluminum hydroxide polymorphs is in the mode of stacking successive layers. This, in turn, is controlled by the shape of, and charge distribution on, hydroxyl ions located at the surfaces of the layers. The extent of polarization by the aluminum cations determines whether the hydroxyl ions will possess cylindrical symmetry as in bayerite or tetrahedral symmetry as in gibbsite. We suggest that the extent of polarization of the hydroxyl ions within the solid phases is inherited from the polarization attained by the hydroxyl ions in aqueous aluminum complexes in the mother liquors.

The usual abundance of the silicate ion in natural alkaline environments may explain the scarcity of nordstrandite, for the silicate ion may favor the precipitation of aluminosilicate minerals rather than aluminum hydroxide. Near absence of bayerite in nature may indicate that it is metastable and will invert to nordstrandite in alkaline solutions.

INTRODUCTION

The role played by aluminum during weathering of the earth's crust is an enigma. The claim by Rankama and Sahama (1950) that "The cycle of aluminum is simple, and its details are well known." is no longer adequate. As our understanding of the geochemistry of other common elements improves, gaps in our knowledge of the geochemistry of aluminum stand out.

For example, the presence of abundant authigenic aluminosilicate minerals in sedimentary rocks means that large quantities of the constituent elements were in solution. Aluminum is one of the few elements whose solubility is so low in most natural waters as to appear incapable of taking part in the formation of vast amounts of authigenic aluminosilicates. Similarly, the synthesis of aluminosilicates in the laboratory at room temperature and under conditions resembling natural environments is not easily attained. Bauxite deposits, the primary ore of aluminum, form by residual concentration of hydrous aluminum oxides during weathering of aluminosilicate minerals. We infer that silica and other cations, with the exception of aluminum, go into solution. But this

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mechanism fails to explain bauxite deposits formed on exceedingly low-aluminous rocks. Nor does the common presence of concretionary pisolites in bauxite deposits strengthen our conviction in the absolute immobility of aluminum during weathering. The dogma of aluminum's low solubility at intermediate pH values leads biologists to propose that aluminum is nonessential in life processes in spite of its wide distribution in organisms (Hutchinson, 1945).

Our principal gaps in understanding the geochemistry of aluminum arise from the lack of detailed knowledge of the controls on solubility as well as the kinds and amounts of substances in solution. In addition, the aluminous solids that precipitate from supersaturated solutions must be adequately characterized. A fuller knowledge of the geochemistry of aluminum will help clarify the origins of the most abundant minerals in crustal rocks, as well as form an acceptable theory of genesis for bauxite ore deposits, and perhaps even shed light on critical economic problems surrounding the formation of alumina catalysts.

Recent studies of the alumina-water system at room temperature by the U. S. Geological Survey aim to clarify and fill some of these gaps in knowledge. This paper, an outgrowth of the studies by Hem and Roberson (1967) and Hem (1968), and of their continuing research into the nature of aluminum in natural waters, describes the problems of identification of small amounts of fine-grained synthetic aluminum hydroxide precipitates formed in dilute solutions. The results of our X-ray diffraction study provide a basis for suggesting a mechanism controlling the formation of various polymorphs of aluminum hydroxide. An explanation of the distribution in nature of the minerals gibbsite, nordstrandite, and bayerite follows as a consequence of the application of this mechanism.

PRIOR SYNTHESIS STUDIES

There has been extensive research for many years on factors that control the formation of compounds in the alumina-water system in the laboratory. We give here only a summary of the most recent work as background for the part of this paper dealing with synthesis of aluminum hydroxide.

A chapter by Rooksby (1961) on the oxides and hydroxides of aluminum and iron summarizes earlier work on the alumina-water system. According to Rooksby, gibbsite $(Al(OH)_3)$ is the only naturally occurring polymorph of aluminum hydroxide as, at that time bayerite $(Al(OH)_3)$ and the unusual form nordstrandite $(Al(OH)_3)$ were known only as products of synthesis. A year later, Hathaway and Schlanger (1962) reported nordstrandite as a mineral from Guam, and Wall and others (1962) from Sarawak (Borneo). And in 1963, Bentor and others described the first natural occurrence of bayerite corroborated by X-ray diffraction. Regarding conditions of synthesis, Rooksby stated that the slow acidification with CO_2 of a sodium-aluminate solution results in precipitation of aluminum hydroxide with the gibbsite crystal structure if carried out at temperatures near 100°C and results in the bayerite crystal structure if the temperature is nearer room temperature. Aging of this bayerite, however, may convert it to gibbsite. He believed that nordstrandite

precipitated from solutions of extremely high pH after long-term aging.

In a brief review of the literature, Deer and others (1962) state that gibbsite forms in a sodium- or potassium-aluminate solution at 30–75°C by autoprecipitation or by introducing preheated CO_2 into the solution. Bayerite, they stated, forms by more rapid precipitation from cool or less alkaline or even acid solutions.

The first synthesis of nordstrandite by Van Nordstrand and others (1956) yielded mixtures of all three polymorphs in solutions whose pH ranged from 7.5 to 9. Subsequent work by Papée and others (1958) showed that the proportion of nordstrandite increased if the pH of the solution was high (pH 13 in one case).

Summing up the results of earlier work, Bye and Robinson (1964) proposed a scheme of aging whereby amorphous aluminum hydroxide gel crystallizes to pseudoboehmite which in turn converts to bayerite and finally to gibbsite. Bye and Robinson stated that these changes are spontaneous at temperatures below 70°C in the presence of the mother liquor, and the rate of each conversion increases with increasing pH and decreases in the presence of foreign anions. In their own synthesis work, Bye and Robinson used aluminum *s*-butoxide and various organic liquids as starting materials in order to avoid the obstructive effects of foreign ions. They obtained pseudoboehmite precipitates that converted in about 10–20 hours to bayerite, but did not detect gibbsite even after aging for 1 year.

Hauschild (1963) managed to produce pure nordstrandite by various techniques, all of which employed aqueous solutions of ethylenediamine for aging the aluminum hydroxide gels. Presumably, the large organic anions have less effect in hindering crystallization.

Hsu (1964) investigated the complications caused by foreign anions and found that the inhibition is directly proportional to concentration of the anion, and the efficiency is in the increasing order: chloride < sulfate < phosphate < fluoride. Recent work by Hem (1968) on the stability of aqueous complexes of aluminum with fluoride, sulfate, and hydroxyl ions indicates that complexing is partly responsible for the effects observed by Hsu. Complexing of aluminum by anions permanently reduces the amount of aluminum available for precipitation. In addition, there apparently is a slowing of crystallization due to entrapment or proxying of other anions for hydroxyl ions. This effect can be overcome by allowing sufficient time for crystallization (John D. Hem, oral commun., 1969).

Experiments by Herbillon and Gastuche (1962) using aluminum chloride, nitrate, and sulfate showed that only amorphous gel or pseudoboehmite would form regardless of pH. They ascribed this to ionic impurities which they then removed by dialysis. This permitted the relatively rapid precipitation of pure gibbsite at pH 4.6, mixed bayerite and pseudoboehmite at pH 6.5, and mixed gibbsite and bayerite at pH 8.

A study by Barnhisel and Rich (1965) indicates that, at room temperature, gibbsite forms in acid solutions, nordstrandite forms in slightly acid to neutral solutions, and bayerite forms in alkaline solutions. Hsu (1966) and Hem and Roberson (1967) reported similar results in regard to the acid and alkaline environments favoring precipitation of gibbsite and bayerite, respectively. Hsu (1966) proposed that the difference between the formation of the two polymorphs was in the source of the hydroxyl ion. When a strongly alkaline solution is used, the hydroxyl ions almost immediately couple with the aluminum ions to form bayerite. But in acid solutions the hydroxyl ions must come from the slow dissociation of water with the consequent formation of gibbsite.

Hsu and Bates (1964a) believe that in acid solutions the aluminum ion reacts with hydroxyl ions, as they become available, according to the following steps:

$$Al^{3+} + (OH)^{1-} = Al(OH)^{2+}$$
$$Al(OH)^{2+} + (OH)^{1-} = Al(OH)_2^{1+}$$
$$6Al(OH)_2^{1+} = Al_6(OH)_{12}^{6+}.$$
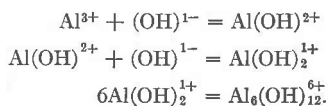
This last ionic species, $Al_6(OH)_{12}^{6+}$, constitutes a hexagonal closed ring. Further polymerization can yield higher polymers such as $Al_{10}(OH)_{22}^{8+}$ or $Al_{13}(OH)_{30}^{9+}$. But, as the positive charge on the polymer increases, further polymerization slows down because of electrical repulsion. Only when sufficient hydroxyl ions form to discharge the polymers, will they cluster and form crystalline $Al(OH)_3$.

Hem and Roberson (1967) proposed a somewhat different mechanism to provide an explanation of the observed behavior of aluminum hydroxide precipitates at all pH values. At pH values two or more units below the point of minimum aluminum solubility (about pH 5.8), the aluminum ion is coordinated by six polar water molecules. The strong positive charge of the aluminum ion repels the two protons of each water molecule and, as pH increases, eventually drives off a proton forming the monomeric complex ion $Al(OH)(OH_2)_5^{2+}$. At about pH 5, this complex ion and hydrated aluminum are in equal abundance with more of the hydrated aluminum at lower pH values and more of the complex ions at higher pH values. Two of these complex ions may join by losing two water molecules to form a dimer:

$$2Al(OH)(OH_2)_5^{2+} = Al_2(OH)_2(OH_2)_8^{4+} + 2H_2O.$$
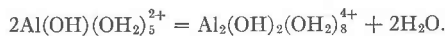
Further deprotonation, dehydration, and polymerization of monomers and dimers yields a ring structure of six octahedrally coordinated aluminum ions with the formula:

$$Al_6(OH)_{12}(OH_2)_{12}^{6+}.$$
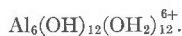
Coalescence of rings into layers by further growth and stacking of layers results in the formation of gibbsite ($Al(OH)_3$). Above the point of minimum solubility, precipitation of bayerite must involve the anion $Al(OH)_4^{1-}$, generally considered to be the dominant aluminum species in alklaine solutions. The reaction may be:

$$Al(OH)_4^{1-} + H^{1+} = Al(OH)_3 + H_2O.$$
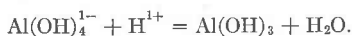
Reading this reaction to the right, crystalline $Al(OH)_3$ (bayerite) precipitates with an accompanying increase in pH of the solution.

This summary of some of the previous work on the synthesis of aluminum hydroxides shows the confusion that exists, especially in the earlier work, regarding the environment in which the various solids precipitate as well as the identity of these solids. As Hsu (1967) points out, conflict and confusion in the literature on the alumina-water system stems from the metastability of intermediate products and slow reversibility of reactions. In addition, we would mention the problem of incomplete identification of solid products. This paper is concerned primarily with clarifying the identification of synthetic aluminum hydroxide precipitates.

Method of Synthesis

We prepared most of the synthetic aluminum hydroxides described in this report by mixing three aqueous solutions. Solution I contained ions of hydrogen, perchlorate, sodium, and aluminum (4.53×10^{-4} molar). Solution II contained ions of sodium, perchlorate, and hydroxyl (6.53×10^{-3} molar). Solution III contained ions of sodium, perchlorate, and aluminum (9.06×10^{-4} molar). The desired amount of solution II (20.0 to 36.5 ml) was added to 25.0 ml of solution I in a polyethylene bottle with vigorous stirring. An amount of solution III equal in volume to solution II was added at the same time to maintain the concentration of aluminum at 4.53×10^{-4} molar. The rate of addition was about 1 ml per sec. We chose the perchlorate anion for this study because of its freedom from a tendency to complex with aluminum. The perchlorate concentration was 0.01 molar in all solutions in order

to maintain a relatively constant low ionic strength (and, therefore, a constant activity coefficient for reacting ions).

The mixed solutions were stored in a CO_2-free atmosphere at $25°C \pm 2°$ for periods ranging from 16 hours to 10 days. At the conclusion of aging, we measured the pH of the solutions with glass and calomel electrodes and then filtered the solutions through plastic membrane (Millipore) filters having pore diameters of 0.45 μm (in a few experiments 0.10 μm filters were used). Immediately after filtration, we affixed the plastic membrane filter to a glass slide with rubber cement and X-rayed it with a Norelco or Picker diffractometer and copper Kα radiation.

The amount of precipitate often was small ($\sim$5 mg) and the X-ray diffractograms were, therefore, incomplete. In order to make positive identification, we prepared larger amounts of solution which yielded as much as 50 mg of precipitate. This was then filtered, dried at room temperature, scraped off the filter, ground lightly, and X-rayed in a standard aluminum holder to provide a complete X-ray diffractogram with reduced preferred orientation. Samples for electron microscopy were prepared in a standard manner (Kay, 1965) by allowing a crop of mother liquor, containing some precipitate, to dry on Formvar plastic film and using carbon shadowing.

We made all our measurement of X-ray peak intensity on peak height above background rather than on total area. Where the half-widths of X-ray peaks differed considerably, we made no attempt to compare reported intensities quantitatively.

We did not chemically analyze any of the aluminum hydroxide precipitates described in this report. The matching of X-ray diffraction peak positions and intensities between standards and precipitates was considered adequate for identification. We are aware of reports proposing that small amounts (usually less than one percent) of sodium and potassium found in aluminum hydroxide are necessary to stabilize the lattice (Saalfeld and others, 1968). The crystallochemical difficulties of incorporating sodium or potassium ions into the aluminum hydroxide lattice, and the kinetic effects of other foreign ions, mentioned elsewhere in this paper, lead us to believe that purity of precipitate is of no consequence to this study.

RESULTS AND INTERPRETATION

Table 1 lists the results of the X-ray study of the synthetic aluminum hydroxides. They were prepared under a variety of conditions, and the sample identifier listed in the first column of Table 1 can be used to determine what these conditions were. The starting pH (related to the amount of hydroxyl-containing solution II added) varied from acid in samples with Arabic numeral 1 to alkaline in samples with Arabic numeral 5. The letters A, B, and C in the sample identifier refer to aging periods of 16 hours, 2 days, and 10 days, respectively. In order to assess the reproducibility of the results, we prepared a second group of samples with almost identical starting pH values. Roman numeral II identifies this second group of samples, and Roman numeral I the first group.

Column 2 of Table 1 lists the ratio of the hydroxyl ions bound to aluminum, to the total aluminum present. This represents an average for the number of hydroxyl ions bound to each aluminum ion in the system, including both aluminum in solution and in the precipitate. A ratio of 3.00 indicates that just enough hydroxyl ions were added to

form $Al(OH)_3$ with all the aluminum present. A ratio less than 3.00 indicates an acid solution in which some aluminum remains in solution as a hydrated ion or a cationic complex, and a ratio above 3.00 indicates an alkaline solution in which some aluminum remains in solution as the anionic complex $Al(OH)_4^{1-}$. Column three lists the length of aging and column four, the final pH of the solution before filtering. The last six columns of Table 1 list the equivalent interplanar spacing in angstroms and intensity in counts per second of three distinct groups of X-ray diffraction peaks. These groups are 4.7 to 4.9, 4.4, and 2.2 Å.

Table 1 shows that the number of X-ray peaks and their intensity generally increases with increasing final pH of the mother liquor and with increasing aging time. The 4.8 Å peak is developed best, however, in those intermediate pH samples (3C1) aged the longest (Fig. 1A). Prolonged aging of the high pH samples (for example 4AI, 4BI, and 4CI) causes the 4.8 Å peak to disappear (Fig. 1B, C, D) as the 4.4 and 2.2 Å peaks increase in intensity. This indicates that the phase that produces the 4.8 Å peak is different from the phase or phases responsible for the 4.4 and 2.2 Å peaks, and that these last two peaks probably are caused by the same phase.

We sought identification of the phases responsible for these three X-ray peaks from among the three aluminum hydroxide polymorphs: gibbsite, nordstrandite, and bayerite. Figure 1, E and F depict diffractograms of pure synthetic gibbsite and bayerite, respectively. Figure 1G is a diffractogram of natural nordstrandite from Guam (Hathaway and Schlanger, 1965).

Occurrence of the 2.2 Å peak with the 4.4 Å peak is characteristic of bayerite. The reason for the absence of the strong 4.71 Å bayerite peak and the low intensity of the 2.2 Å peak, as listed in Table 1, will be explained presently. The 4.8 Å peak is produced by gibbsite. Verification of this identification required the study of a larger amount of precipitate (about 50 mg) over an aging period of 76 days. With time, the less intense peaks of gibbsite appeared and the 4.8 Å peak became sharper. The sample aged for 76 days yielded the complete gibbsite diffractogram shown in Figure 1 E.

Table 1 shows that there is a change in final pH with aging. This pH drift is, in general, toward lower values for samples whose initial pH was below the point of minimum solubility (about pH 5.8) and toward higher values for samples whose initial pH was above that point. Barnhisel and Rich (1965, Table 3) observed the same change in pH.

Drift of pH toward lower values may be due to growth of the gibbsite crystals during aging. Hem and Roberson (1967, p. A50) suggested that the hydroxyl ions in the gibbsite structure that are on the surface of the
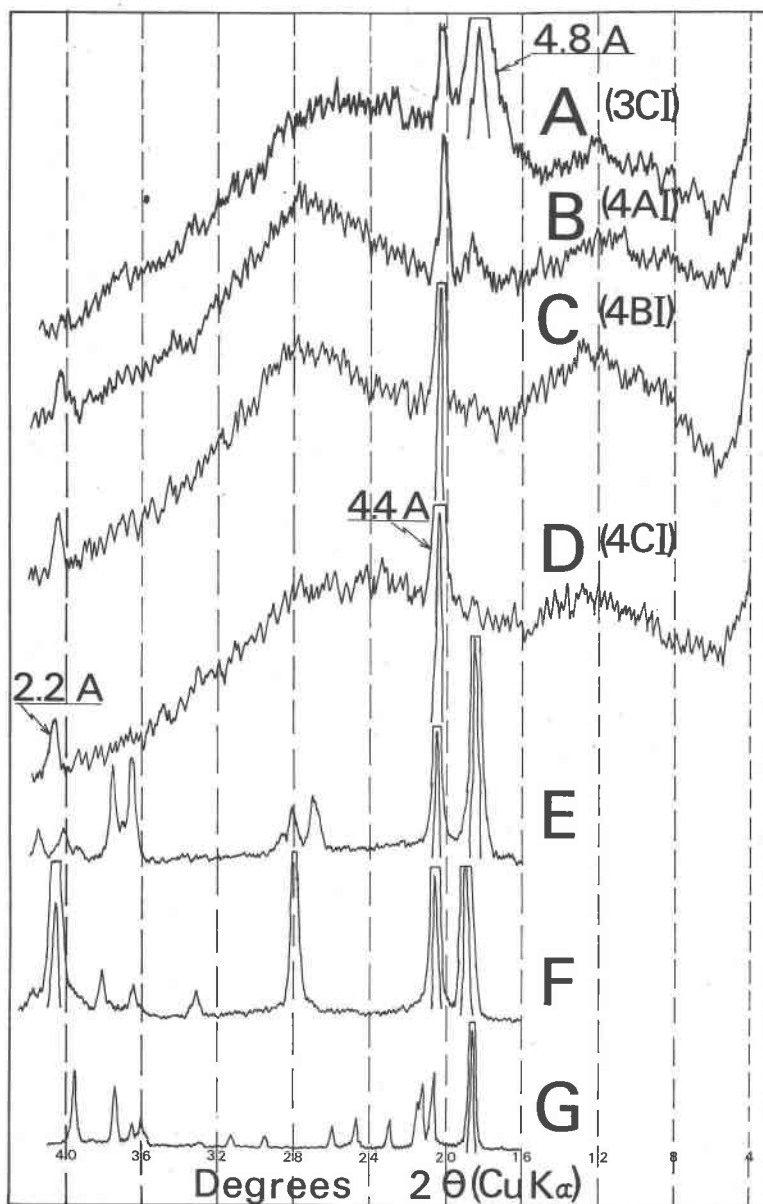
FIG. 1. X-ray diffractograms of typical synthetic products developed during short-term aging in the alumina-water system (A, B, C, D) and Al(OH)₃ standards (E, F, G).

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TABLE 1. X-RAY DIFFRACTION RESULTS ON SYNTHETIC Al(OH)$_3$

Sample Identifier	(OH)$_B$/Al	Age	Final pH	Spacing and Intensity					
				$d(Å)$	I	$d(Å)$	I	$d(Å)$	I
1 A I	1.79	16 hrs	4.73						
B I	1.79	2 days	4.66						
C I	1.79	10 days	4.56						
1 A II	2.32	16 hrs	4.94						
B II	2.32	2 days	4.83	4.70	20	4.37	24		
C II	2.32	10 days	4.70						
2 A I	2.79	16 hrs	5.28						
B I	2.79	2 days	5.17						
C I	2.79	10 days	4.83	4.90	28	4.40	24		
2 A II	2.79	16 hrs	5.24						
B II	2.79	2 days	5.10						
C II	2.79	10 days	5.02	4.82	20				
3 A I	2.90	16 hrs	6.15						
B I	2.90	2 days	5.93						
C I	2.90	10 days	6.95	4.88	130	4.37	60		
3 A II	2.90	16 hrs	5.85						
B II	2.90	2 days	5.69						
C II	2.90	10 days	6.45	4.87	36	4.40	20		
3C II-1	2.90	10 days	6.45	4.90	76	4.42	52		
4 A I	3.15	16 hrs	8.87	4.77	28	4.40	80	2.23	24
B I	3.15	2 days	9.01	4.77	14	4.36	188	2.22	36
C I	3.15	10 days	8.95			4.44	160	2.24	28
4 A II	3.00	16 hrs	6.37						
B II	3.00	2 days	6.49						
C II	3.00	10 days	8.48			4.42	140	2.23	44
5 A I	3.52	16 hrs	9.48	4.75	20	4.37	120	2.23	36
B I	3.52	2 days	9.69	4.77	16	4.37	240+	2.23	48
C I	3.52	10 days	9.54			4.37	280+	2.22	48
5 A II	3.52	16 hrs	9.23			4.37	48	2.23	16
B II	3.52	2 days	9.47			4.40	152	2.23	32
C II	3.52	10 days	9.64			4.37	232+	2.22	40

crystal may have an alkaline effect on the pH of the solution. Because surface area per unit volume decreases during crystal growth, hydroxyl ions in the crystals should exert a decreasing effect on the pH of the solution as the crystals grow larger. Other likely explanations for the observed downward pH drift are the deprotonation reaction during polymer growth as well as the dissociation of water proposed by Hsu (1966).

The preceding hypotheses, however, do not explain the upward pH drift of solutions containing bayerite. Hydroxyl ions on the surface of bayerite crystals should have little effect on the pH because the crystals grow rapidly in the alkaline environment and quickly achieve large size. X-ray diffraction and electron microscopy indicate that bayerite crystallites attain sizes in excess of 1,000 Å within 24 hours. Instead, the observed upward drift in pH probably is due to the reaction:

$$Al(OH)_3 + Al(OH)_4^{1-} = 2Al(OH)_3 + (OH)^{1-}$$

in which aluminate ions are added to bayerite crystals as slow growth continues during aging.

All samples produced some very broad X-ray peaks. There was a tendency for a broad peak at about 9 Å to migrate toward 7 Å with increasing crystallinity of the sample. This broad maximum may indicate the incipient formation of pseudoboehmite, a monohydrate of aluminum. Another broad peak near 4 Å tended to migrate toward 3 Å in more crystalline samples, and may also be a pseudoboehmite peak.

Filtration of sample 3CII through a 0.45 μm membrane produced an opalescent filtrate so we refiltered the filtrate through a 0.10 μm plastic membrane filter. Listed in Table 1 under identifier 3CII-1 are the results of the X-ray diffraction study of this 0.45 μm-0.10 μm size material. Comparison with the data listed for sample 3CII indicates that much crystalline material was less than 0.45 μm and therefore was missed in the study of other samples listed in Table 1. Subsequent studies using 0.10 μm plastic membrane filters, however, did not result in any changes in the identification of phases.

Figure 2 depicts the results of one of the later studies using 0.10 μm plastic membrane filters. Samples prepared at $(OH)_B$ to Al ratios of 2.7, 2.8, and 2.9, and aged for periods of 7 days, 7 days, and 8 days, respectively, gave final pH values of the mother liquors of 4.74, 4.80, and 4.86, respectively. Figure 2, A and B show no crystalline material by X-ray diffraction. Figure 2C, of material prepared with an $(OH)_B$ to Al ratio of 2.9, exhibits a broad peak at 4.8 Å identified as gibbsite by other long-term aging experiments. X-ray of the 2.9 ratio sample 1 hour after filtration (Figure 2D) shows a large increase in intensity of the broad
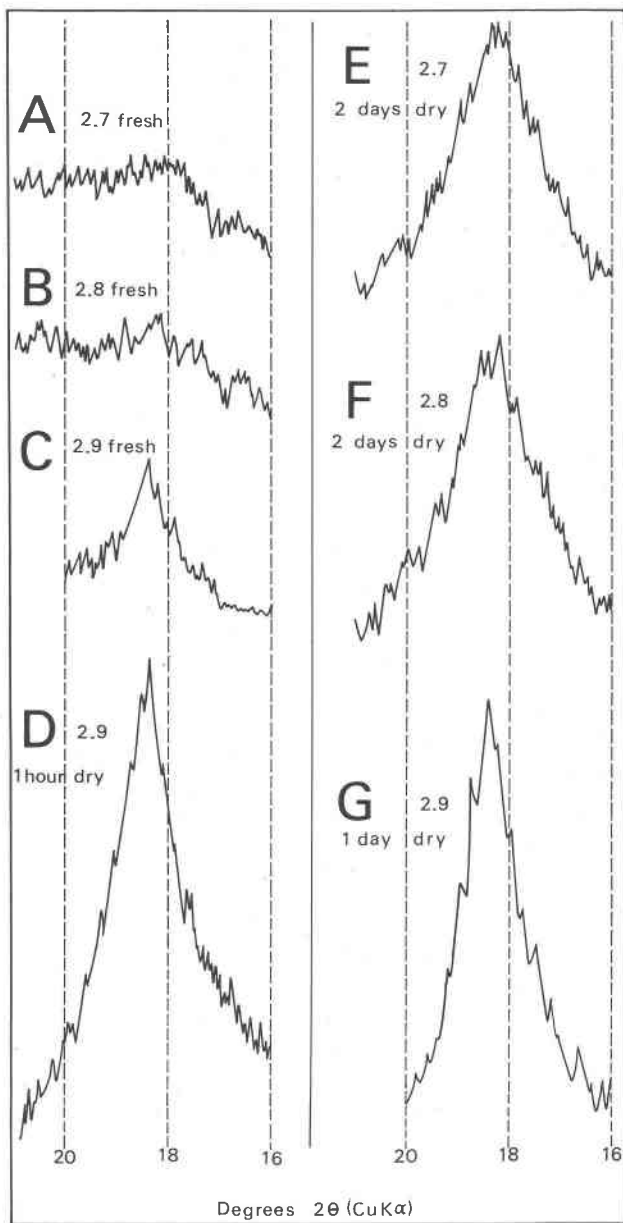
FIG. 2. X-ray diffractograms showing the development of synthetic gibbsite during aging and drying as a function of the ratio $(OH)_B/Al$.

gibbsite peak. X-ray of the 2.7, 2.8, and 2.9 ratio samples after 2 days, 2 days, and 1 day, respectively, of drying on the plastic membrane filters resulted in Figure 2, E, F, and G respectively. These diffractograms indicate that gibbsite formed in all solutions though drying was necessary to make the gibbsite in the 2.7 and 2.8 ratio samples detectable by X-ray diffraction. Apparently, many low pH solutions prepared earlier contained gibbsite that was too fine to be trapped on 0.45 μm filters. This may account for the erratic distribution of gibbsite peaks reported in the upper half of Table 1.

The diffractograms presented in Figure 2 reveal several other things about the gibbsite formed. Diffraction from the (002) or basal planes of the gibbsite crystals causes the single X-ray peak. The great breadth of this peak indicates that the crystallites are relatively small in the basal (crystallographic c-axis) direction. Calculation of this dimension using the Scherrer formula (Klug and Alexander, 1954, p. 512) results in 45 Å for samples 2.7 and 2.8, and 80 Å for sample 2.9. Measurements of crystallite shadows on electron micrographs corroborate these dimensions (Ross Smith, oral commun., 1968). But at least one dimension of these crystallites must exceed 1,000 Å because they were trapped on 0.1 μm filters. Figure 3 shows a hypothetical gibbsite crystal possessing these dimensions and the hexagonal form seen in electronmicrographs such as Figure 4. Apparently, the growth habit of gibbsite favors the formation of thin platelets, whose upper and lower surfaces are parallel to the basal planes responsible for the observed X-ray peak. According to Van Nordstrand and others (1956, p. 712), " . . . gibbsite usually grows as platelets parallel to the layers of its layer lattice." (basal planes).
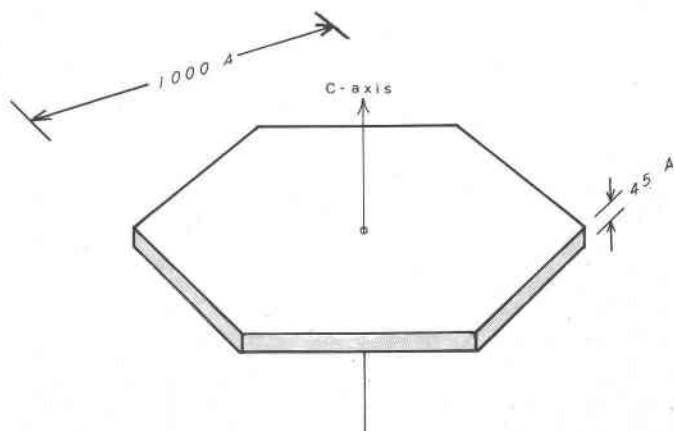

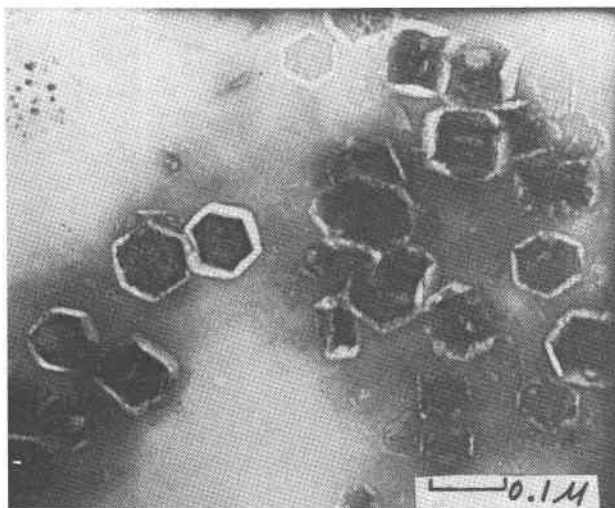FIG. 3. Sketch of hypothetical gibbsite crystal formed during synthesis.

FIG. 4. Electronmicrograph of synthetic gibbsite crystals.

Figure 2, C and D show that drying of the precipitate produced more crystallites capable of diffracting X-rays. But drying did not appreciably increase the size of these crystallites parallel to the c-axis as shown by the lack of change in peak breadth. Perhaps evaporation of interstitial moisture precipitated more gibbsite crystallites or caused the platelets to grow only in the a and b crystallographic directions. Removal of moisture films from the crystallites would also decrease absorption of X-ray energy, thus tending to increase the X-ray signal received from the crystalline material.

In general, aging of gibbsite or bayerite in the mother liquor results in an increase in the size of the crystallites (Figure 2 versus Figure 1E). In addition, a complete development of all crystal planes by aging results in all permissable X-ray diffractions being observed as in Figure 1, E and F. The only example of crystallites becoming smaller during aging is the gradual disappearance of gibbsite formed in mixtures with bayerite at intermediate pH values (Table 1). This implies that gibbsite is unstable with respect to bayerite in these solutions. The rise in pH of the solution, caused by precipitation and growth of large bayerite crystallites, may be responsible for making the smaller gibbsite crystallites unstable.

The diffractogram of well-crystallized bayerite (Figure 1 F) shows three peaks of extreme intensity at 4.71 Å, 4.35 Å, and 2.22 Å. The newly-formed bayerite samples of Table 1, however, show only a strong 4.4 Å peak and a weak 2.2 Å peak; the 4.71 Å peak is missing. Part of the reason for these anomalous intensities is the rate of development of

the crystal planes responsible for these three diffractions. The 4.35 Å peak originates from (100) prism planes in the crystal and the 2.22 Å peak orginates from (111) pyramid planes. The 4.71 Å peak originates from (001) basal planes comparable to those responsible for the strong 4.85 Å peak in gibbsite. Absence of the 4.71 Å (001) peak in newly-formed bayerite implies a poor development of basal planes in the crystallites. Crystallites with well-developed (100) prism faces and less well-developed (111) pyramid faces might look like Figure 5. This agrees with the reported habit of bayerite as ". . . rods or tapered rods the long direction of which appears roughly perpendicular to the layers of the layer lattice." (basal planes) (Van Nordstrand and others, 1956, p. 714). Results of electron diffraction by Lippens (1961, p. 69–70) support this perpendicularity between the basal layers and the longitudinal direction of the bayerite particles. An electronmicrograph of bayerite aged for 10 days (Fig. 6) proves the general correctness of this concept of the shape of newly-formed bayerite crystallites.
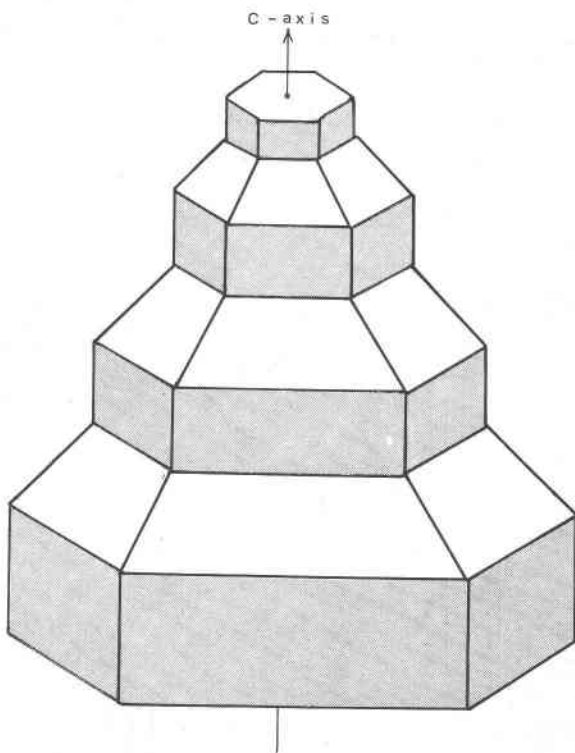

Fig. 5. Sketch of hypothetical bayerite crystal formed during synthesis.
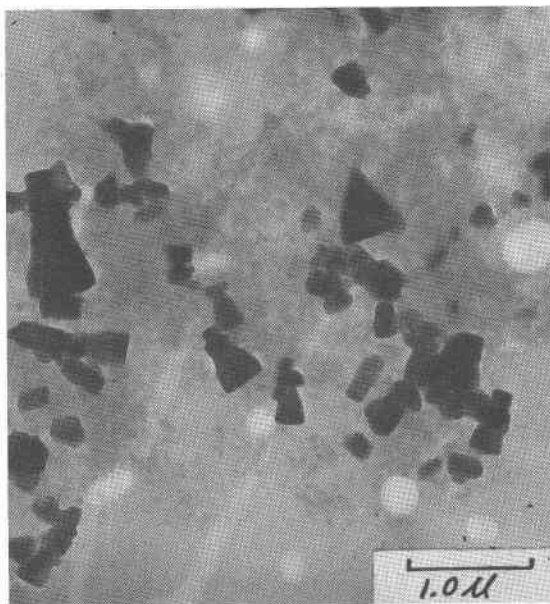
FIG. 6. Electronmicrograph of synthetic bayerite crystals,
probably including a few nordstrandite crystals.

There are at least three reasons why the intensities of X-ray peaks
from newly-formed bayerite should not match those of aged bayerite.
First, the particle shape, which is elongated parallel to the c-axis, tends
to produce only (hk0) diffractions because the basal planes at right an-
gles to the c-axis are small initially. But after ten days aging (Fig. 6), the
basal planes are large enough to produce sharp X-ray diffractions. Ab-
sence of these peaks in our 10-day old samples must be a consequence of
the elongated particle shape and the resultant preferred orientation oc-
curring during filtration. Basal planes of bayerite crystallites on the plas-
tic membrane filters, though large enough, are not in a favorable position
to diffract X-rays. Figure 1F, the diffractogram of bayerite scraped from
the filter and mounted to minimize preferred orientation, exhibits all
peaks with proper intensities. Finally, the small amount of aluminum
hydroxide precipitate deposited on the plastic membrane filter is not
sufficient to satisfy the X-ray requirements for a sample of infinite thick-
ness (Alexander and Klug, 1948). X-ray peaks at high two-theta angles,
therefore, are especially subject to diminution of intensity with respect
to lower angle peaks. This explains the relative weakness of the 2.2 Å
peak.

The growth of gibbsite in acid solution and bayerite in alkaline solution

occurs by the addition of units of aluminum hydroxide. These units attach themselves at a greater rate to the edges of gibbsite crystallites than to the top and bottom surfaces. The result is that the slowest growing faces (that is, the top and bottom surfaces) eventually form the prominent crystal faces of gibbsite. Conversely, the aluminum hydroxide units attach themselves preferentially to the basal planes of bayerite crystallites with the result that the slower growing side faces (prism and pyramid) eventually form the dominant crystal faces.

To complete our understanding of the crystal form of the three aluminum hydroxide polymorphs, we must examine the electron microscope and electron diffraction data of Lippens (1961, p. 73–74) on nordstrandite. He, as well as Hauschild (1963, Fig. 2) found that nordstrandite crystallites take the form of long rectangles or more rarely long parallelograms. The few small rectangles and parallelograms in Figure 6 correspond closely to those figured by Lippens and Hauschild and may be nordstrandite.

The cross section of nordstrandite crystallites is hexagonal, and, as in bayerite, the c-axis parallels the long direction of the crystallites. But the b-axis always appears to coincide with the width of the crystallites indicating a relatively poorer development of the a-axis direction. Lippens found the a-axis direction to range between one-half and one-sixth the length of the b-axis direction. Figure 7 is a sketch of a hypothetical nordstrandite crystallite embodying these characteristics.
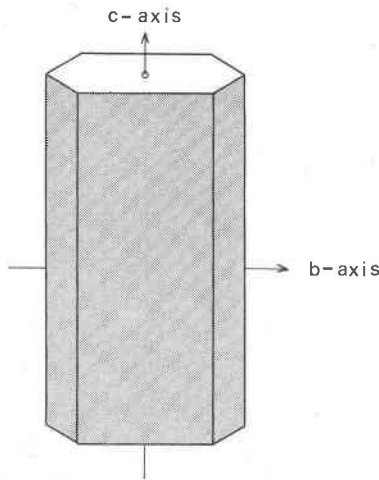

FIG. 7. Sketch of hypothetical nordstrandite crystal formed during synthesis.

None of the samples described thus far showed X-ray evidence of containing nordstrandite, the third polymorph of aluminum hydroxide. As already described, much confusion exists in the literature regarding conditions of synthesis of nordstrandite. Ideal pH conditions seem to range from "slightly acid to neutral" (Barnhisel and Rich, 1965) to "pH 13" (Papée and others, 1958).

To help resolve these inconsistencies, or at least to provide additional data, we prepared a series of four solutions for long-term aging whose initial pH ranged from 9.46 to 12.0. Concentrations of ions were greater in these solutions than in those previously described, and in one solution potassium and sulfate were present for use in another experiment.

We had hoped to find the aluminum hydroxide polymorphs bayerite and nordstrandite restricted to well-defined pH regions. Or, failing this, we hoped to discern a distinct increase in the amount of one phase and decrease in the amount of the other during aging. The X-ray results, to date, are equivocal. Pure bayerite without admixed nordstrandite formed initially in the pH 12.0 solution. But within 90 days aging, X-ray detectable nordstrandite formed as the pH increased to 12.82. The other three less alkaline solutions produced bayerite admixed with nordstrandite almost from the start. Nordstrandite X-ray peaks increased in intensity during two and one-half years of aging, but so did the bayerite peaks. To date, peak ratios show no distinct trend.

In contrast to these results, an electronmicrograph (Fig. 8) of material similar to that shown in Figure 6, but aged for two years, shows a definite increase in the size of nordstrandite crystallites relative to bayerite. Figure 8 also shows rounding of the edges of bayerite crystallites and the development of etch pits parallel to the basal cleavage. These features indicate resorption of the bayerite into the mother liquor.

These results imply that slightly alkaline environments promote the precipitation of nordstrandite and strongly alkaline environments the precipitation of bayerite. But bayerite is unstable with respect to nordstrandite in alkaline solutions.

Structure of Aluminum Hydroxide Polymorphs

The preceding experimental results corroborate the observations of Barnhisel and Rich (1965) that acid environments favor the crystallization of gibbsite, neutral environments nordstrandite, and alkaline environments bayerite. In order to understand why the pH of the aqueous environment controls the structure of the aluminum hydroxide polymorph, we must review what is known about the detailed structures of the three phases.
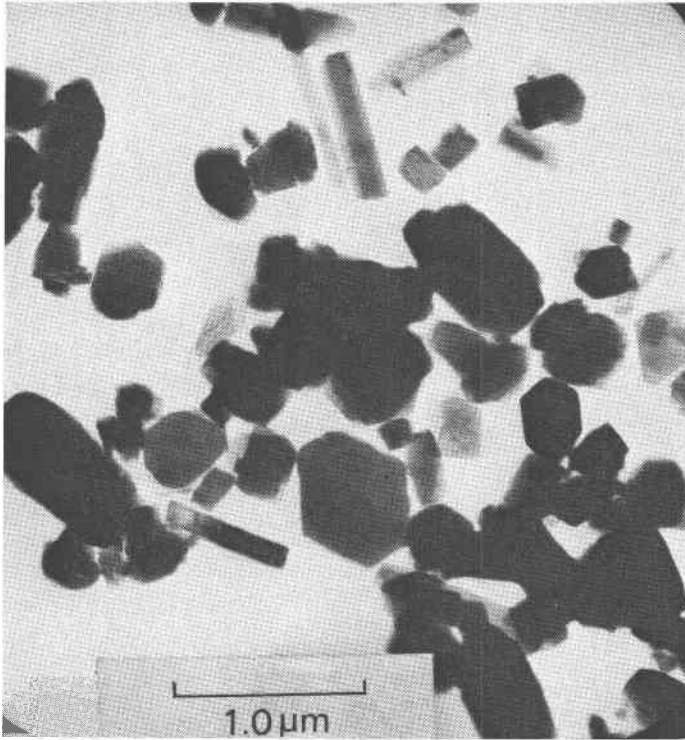
Fig. 8. Electronmicrograph of synthetic bayerite (barrel-shaped) and nordstrandite (long sharp-cornered rectangles) aged at about pH 9 for two years.

Gibbsite. According to Megaw (1934), gibbsite is monoclinic (pseudo-hexagonal) with $a = 8.624$ Å, $b = 5.060$ Å, $c = 9.700$ Å, and $\beta = 94°34^1$. These dimensions have remained essentially unchanged by more recent investigators, although Saalfeld (1960) described a natural triclinic variety.

The simplest structural unit of gibbsite, a layer, consists of two sheets of close-packed negatively charged hydroxyl ions bound together by positively charged aluminum ions that occupy two-thirds of the interstices between the hydroxyl sheets (Fig. 9). Growth of this layer of gibbsite occurs by superposition of other layers and by lateral extension of layers. During the lateral extension of gibbsite layers, the constraints on ionic bonding are that each aluminum ion be bound to six hydroxyl ions by bonds of one-half strength, and that each hydroxyl ion be coordinated to two aluminum ions by bonds of one-half strength and also coordinated to one "hole" or interstice where there is no cation. This satisfies the charges on the aluminum and hydroxyl ions and no ionic forces remain to attach superposed layers.
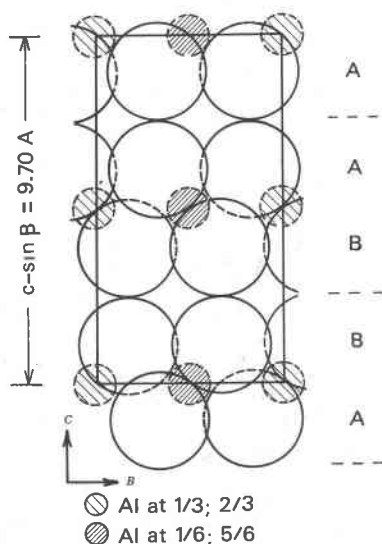
Fɪɢ. 9. Diagrammatic representation of idealized gibbsite layer structure projected on a plane perpendicular to the *a*-axis (from Megaw, 1934).

Incomplete filling of the interstices of the gibbsite layer results in the "holes" being less electrostatically positive than surrounding portions of the cation sheet. This asymmetry of charge distribution has an affect on the orientation of the oxygen-proton bond within each hydroxyl ion. The protons, instead of being oriented straight up away from the cation sheet, tend to be displaced toward the neutral holes.

In addition, the very high polarizing power of the aluminum ion produces a more significant distortion of the hydroxyl ions. Bernal and Megaw (1935) proposed that this polarization produces a hydroxyl ion with tetrahedral symmetry analogous to the water molecule. Two aluminum ions bind two of the negatively charged corners of the four-cornered ion. The remaining negatively charged corner and the positively charged corner containing the proton are available for the formation of ionic bonds with other hydroxyl ions, both within the gibbsite layer and between layers. A distribution of both positively and negatively charged corners of tetrahedral hydroxyl ions on the surfaces of the gibbsite layers favors the buildup of superposed gibbsite layers. A bond forms between the negatively charged corner of one hydroxyl ion and the positively charged corner of a hydroxyl ion in the superposed layer. There is one so-called hydroxyl bond for each hydroxyl ion.

The constraints imposed by this type of bonding result in the hydroxyl ions of each superposed layer of gibbsite lying directly on top of the hydroxyl ions of the layer below in a configuration resembling open-packing (Fig. 9). The effective radius of hydroxyl ions in one layer to hydroxyl ions in a superposed layer (that is, B—B or A—A in Fig. 9) is only 1.39 Å, close to the 1.34 Å effective radius between hydroxyl ions and the cations (Table 2). This indicates that distortion of the hydroxyl

TABLE 2. EFFECTIVE INTERIONIC DISTANCES IN GIBBSITE AND BRUCITE
(from Bernal and Megaw, 1935)

	Effective hydroxyl radius toward cation	Effective hydroxyl radius toward hydroxyl in the next layer
Gibbsite	1.34 Å	1.39 Å
Brucite	1.39 Å	1.61 Å

ion by polarization produces an "open-packing" in which the centers of ions are almost as close as in true close-packing. This stacking arrangement of double-sheet gibbsite layers can be described by the symbol:

$$AB \mid BA \mid AB \mid BA \qquad \text{and so forth}$$

where A and B denote hydroxyl sheets in different positions as shown in Figure 8, and the vertical dashes represent the boundaries between double-sheet layers.

Bayerite. The absence of large, single crystals of bayerite with which to make structural determinations, renders the detailed structure of this polymorph uncertain. Montoro (1942) concluded from X-ray powder analysis that bayerite possessed a hexagonal lattice with $a = 5.01$ Å, $c = 4.76$ Å, containing 2 molecules of $Al(OH)^3$. This is a layer structure similar to gibbsite but without the distortion of the sheet of anions around each vacant cation site that makes gibbsite pseudo-hexagonal. Instead of the hydroxyl ions in adjacent layers being in a state of open-packing as in gibbsite (Fig. 9), the hydroxyl ions interdigitate in a state of close-packing (Fig. 10). This proposed structure for bayerite is identical with the structure of brucite $(Mg(OH)_2)$, except that in brucite every cation position is filled and in bayerite one-third of the cation positions are vacant.

Milligan (1951) and Kroon and Stolpe (1959) took exception to the

brucite-like structure proposed by Montoro. Other workers (Yamaguchi and Sakamoto, 1958; Lippens, 1961) using material of greater purity than Montoro's, confirm the general correctness of the brucite model for bayerite. Lippens showed that bayerite is slightly distorted from hexagonal symmetry and is more likely orthorhombic with $a = 8.67$ Å, $b = 5.06$ Å, and $c = 4.71$ Å. For comparison, the hexagonal brucite model of Yamaguchi and Sakamoto yields an orthohexagonal a-axis of 8.74 Å.

The brucite structure consists of two sheets of close-packed, negatively charged hydroxyl ions held together by positively charged magnesium ions occupying all the interstices between the hydroxyl sheets. These two sheets of hydroxyl ions, together with the intervening sheet of magnesium ions, constitute a layer of the mineral brucite, and this layer is the smallest unit that can exhibit the properties of brucite. Larger brucite crystals form by the superposition of layers on top of one another, as well as by the lateral growth of all the sheets. Lateral growth occurs simply by the addition of magnesium and hydroxyl ions in a configuration where every magnesium ion binds six hydroxyl ions with bonds of one-third strength and every hydroxyl ion binds three magnesium ions. These bonds are ionic and three, one-third strength magnesium-hydroxyl bonds completely satisfy the charge of a hydroxyl ion. Therefore, there are no ionic forces available to bond together the hydroxyl ions of superposed brucite layers. In addition, the proton-oxygen bond within each hydroxyl ion points straight up at right angles to the sheets of ions and away from the sheet of magnesium cations (Elleman and Williams, 1956). This results in a sheet of protons on the upper and lower surfaces of each layer of brucite, and it produces a tendency toward cylindrical symmetry in the hydroxyl ions.

Growth of brucite by the superposition of layers, therefore, must take place without the help of any ionic bonding and must overcome the electrostatic repulsion of sheets of adjacent protons. The bonding between brucite layers is due to van der Waals forces supplemented by forces related to the interaction of the rotating hydroxyl dipole ions. As a result of all these constraints, the hydroxyl ions in successive brucite layers interdigitate in such a way as to keep adjacent protons as far apart as possible. This interdigitation, similar to that found within the brucite layer, has been called "close-packing" but it is much more open than that. Table 2 shows that the effective hydroxyl ion radius toward hydroxyl ions in the next layer in brucite is 1.61 Å (1.57 Å in bayerite according to Lippens, 1961), whereas the effective hydroxyl ion radius toward a cation is 1.39 Å. This indicates how much more open this so-called "close-packing" between layers of brucite really is.

This discussion of the structure of brucite ($Mg(OH)_2$) applies directly

to the structure of bayerite $(Al(OH)_3)$ if we keep in mind the substitution of two aluminum ions and one vacancy for every three magnesium ions. The presence of holes in the cation sheet introduces some distortion into the bayerite structure compared with the perfect hexagonal symmetry of brucite. Bayerite, however, does not suffer the additional distortion caused by hydroxyl bonding within the layers that affects gibbsite.

Comparison of Figures 9 and 10 shows that the simplest unit of structure of gibbsite and bayerite is identical (a double sheet of hydroxyl ions), and the difference between the two polymorphs is solely in the manner of stacking superposed layers. The symbol AB|AB|AB and so forth, describes the stacking scheme for bayerite as depicted in Figure 10.
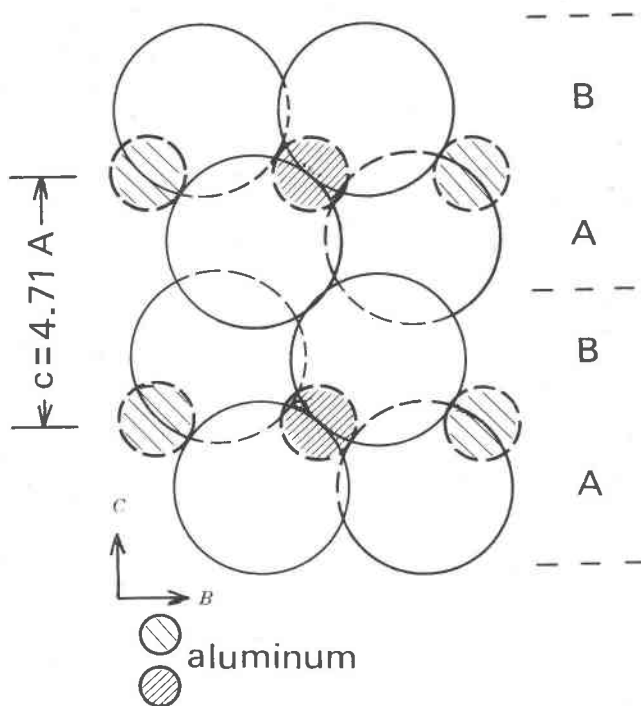

FIG. 10. Diagrammatic representation of brucite-bayerite layer structure.

Nordstrandite. Because of the lack of good single-crystals and the relative recency of the discovery of nordstrandite, both as a synthetic product (Van Nordstrand and others, 1956) and as a naturally occurring mineral (Hathaway and Schlanger, 1962; Wall and others, 1962), the detailed

structure of nordstrandite remains obscure. By analogy with the X-ray patterns of gibbsite and bayerite, Van Nordstrand and others (1956) proposed that nordstrandite (called "bayerite II" by them) possessed a layered structure with a spacing between layers equal to the average of the gibbsite and bayerite spacings. They proposed that the new phase might be a screw dislocation polymorph in which the gibbsite packing and bayerite packing alternated and in which the Burgers vector was two layers high.

Lippens (1961) examined the structure of nordstrandite as well as gibbsite and bayerite. His powder samples for X-ray study contained gibbsite, bayerite, pseudoboehmite, and nordstrandite in varying proportions, requiring him to ignore X-ray lines attributable to the other three phases. For this reason, as well as the lack of single-crystal data, Lippens' results are only a reasonable approximation to the structure of nordstrandite.

Lippens (1961) reported that his synthetic nordstrandite was monoclinic with $a = 8.63$ Å, $b = 5.01$ Å, $c = 19.12$ Å, and $\beta = 92.00°$. The c-dimension of 19.12Å indicates that the unit cell of nordstrandite contains two layers of gibbsite (4.85 Å each) and two layers of bayerite (4.71 Å each). These may be stacked in either of two ways: I-bayerite, gibbsite, gibbsite, bayerite; or II-bayerite, gibbsite, bayerite, gibbsite. By an analysis of the 00l-diffractions, Lippens concluded that arrangement II was most probable. This coincides with the arrangement proposed by Van Nordstrand and others (1956), and is depicted in Figure 11. The symbol for this stacking sequence is:

$$AB \mid AB \mid BA \mid BA \mid \text{ and so forth.}$$

An attempt at single-crystal studies on the natural material from Guam by Hathaway and Schlanger (1965), met with failure when all nordstrandite crystals selected proved to be multicrystalline or distorted. A similar attempt on the natural material from Sarawak apparently was successful (Saalfeld and Mehrotra, 1966).

As recently reported by Saalfeld and Jarchow (1968), nordstrandite is triclinic with $a = 8.752$ Å, $b = 5.069$ Å, $c = 10.244$ Å; $\alpha = 109.33°$, $\beta = 97.66°$, $\gamma = 88.34°$. These authors report that "From the structural point of view nordstrandite can be regarded as intermediate between gibbsite and bayerite." But unlike the stacking sequence of nordstrandite proposed by Lippens (1961), Saalfeld and Jarchow (1968), in their Figure 3, depict the unusual stacking sequence:
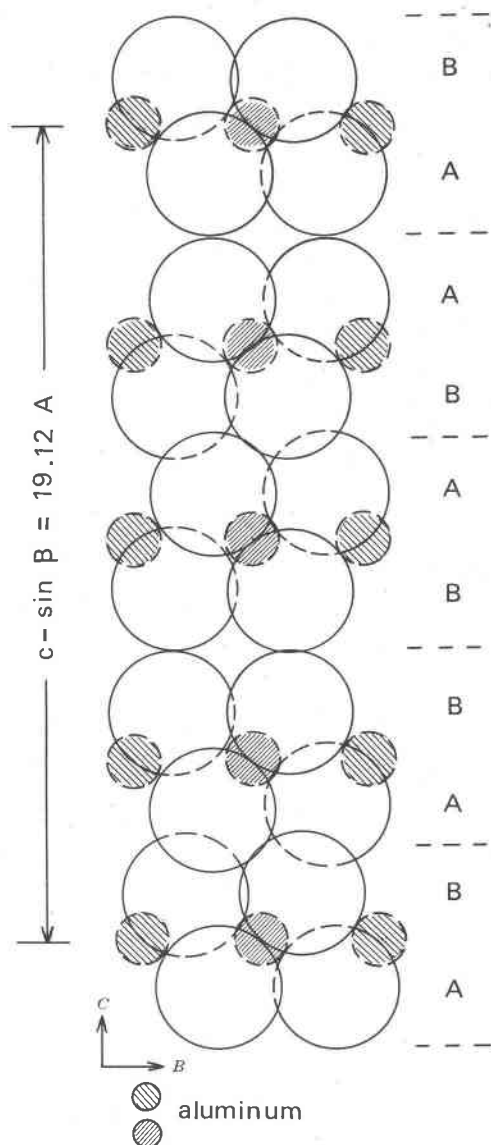
$$BA \mid AC \mid CB \mid \text{ and so forth}$$

Fɪɢ. 11. Diagramatic representation of nordstrandite layer structure showing alternation of gibbsite and bayerite modes of stacking.

The validity of this model requires further elaboration and confirmation.

Pending a complete and precise description of the nordstrandite structure, the regular interlayer model (Fig. 11) has much in its favor. By analogy with another large group of layer structures, the clay minerals, interlayering is a common phenomenon in response to environmental changes. And, as in the clay mineral group, there seems to be a definite tendency for a 1:1 regular interlayered structure to be more stable than either irregular interlayering or other proportions of the component layers. In addition, a single layer of aluminum hydroxide possesses a marked proclivity to interlayer, both in nature (the chlorite mineral group) and with other clay minerals in the laboratory (Hsu and Bates, 1964b).

STABILITY OF ALUMINUM HYDROXIDE POLYMORPHS

Several suggestions have been offered to explain why gibbsite or bayerite may be favored during precipitation of aluminum hydroxide. Van Nordstrand and others (1956) suggested that if nordstrandite is a screw dislocation polymorph with a Burgers vector of two layers, bayerite can be considered to be a screw dislocation ploymorph in which the Burgers vector is one layer. They suggested that unspecified constraints imposed by this type of growth might prevent the gibbsite-type open-packing from developing. Barnhisel and Rich (1965) believed that some of their data showed a "seeding" effect by foreign mineral surfaces that might control the structure of the aluminum hydroxide polymorph. Hsu (1966), realizing the great difference in the rate of precipitation of gibbsite and bayerite, suggested that rapid precipitation may favor the bayerite structure, and slow precipitation the gibbsite structure. None of these suggestions, however, specified the mechanism of stability control.

Our study leads us to conclude that a different control from those already proposed is responsible for the structures of the aluminum hydroxide polymorphs. Comparison of Figures 9 and 10 shows that the only difference between gibbsite and bayerite is in the mode of stacking the aluminum hydroxide layers. And the two different modes of layer stacking reflect the shapes of the hydroxyl ions on the opposing sheet surfaces. If mild polarizing forces affect the hydroxyl ions, they assume a cylindrical shape, and the proton-containing ends of the ions move as far as possible away from the aluminum ions between the sheets of hydroxyl ions. When layers of aluminum hydroxide with this hydroxyl ion configuration superpose, the repulsive forces of the opposing protons force the layers to interdigitate. The brucite-bayerite type structure results. When stronger polarizing forces affect the hydroxyl ions, the cylindrical symmetry breaks down and tetrahedral ions form. The distribution of

electrostatic charges on these tetrahedral ions permits an ionic bond to form with tetrahedral hydroxyl ions in the superposed aluminum hydroxide layer. The strong attraction of these ionic hydroxyl bonds requires that the hydroxyl ions arrange themselves vertically above one another perpendicular to the layers. The gibbsite structure is the result. It is probable then that formation of gibbsite or bayerite depends upon the distortion, and consequently the degree of polarization, of the hydroxyl ions.

But how does the pH of the mother liquor cause such a difference in polarization of the hydroxyl ions in the precipitate? And what can account for the maintainence of a large disparity in degree of hydroxyl ion polarization in two solid phases of the same composition? The answers to these questions constitute what is, at present, only a reasonable guess. Additional specific investigations must be undertaken to evaluate the following hypothesis.

First, we must remember that aluminum is amphoteric and can exist in solution as a complex cation or anion depending on the pH. Proof of this statement is afforded by the observation that electrolysis of a solution of potassium aluminate causes deposition of aluminum hydroxide on the anode, whereas electrolysis of a solution of aluminum nitrate deposits aluminum hydroxide on the cathode (Berges, 1947). As described previously, Hem and Roberson (1967) showed that the predominant cationic aluminum complex between pH 4 and pH 5.8 is $Al(OH)(OH_2)_5^{2+}$. In this complex ion, the full polarizing power of the aluminum ion affects a single hydroxyl ion. Polymerization of the monomeric $Al(OH)(OH_2)_5^{2+}$ brings the polarizing power of additional aluminum ions to bear, and deprotonation of the water molecules continues with the formation of strongly polarized hydroxyl ions. The preceding chain of events would be expected in acidic solutions. Above pH 5.8, however, the dominant aqueous aluminum species is the complex aluminate anion $Al(OH)_4^{1-}$. We would expect the excess negative charge to nullify the polarizing power of the aluminum ion and form cylindrical hydroxyl ions. Therefore, the phase that precipitates from acid solutions should contain highly polarized hydroxyl ions because of their abundance in the acidic mother liquor, and the phase that precipitates from alkaline solutions should contain weakly polarized hydroxyl ions because of their abundance in the alkaline mother liquor. And this is exactly what we observe.

Judging from the preponderance of gibbsite in nature, we can infer that strong polarization of the hydroxyl ion in aluminum hydroxide is the most stable state under conditions prevailing at the earth's surface. It terms of crystal energy (Pauling, 1960, p. 509), the longer hydroxyl—

hydroxyl bond in bayerite, caused by the weak polarization of the hydroxyl ions, creates a smaller crystal energy than strongly polarized hydroxyl ions do and, therefore, a less stable structure. Bayerite should tend to undergo a slow increase in the polarization of its hydroxyl ions and recrystalize to gibbsite.

Our experimental results, however, do not support this. What forms during long-term aging of bayerite is not gibbsite but nordstrandite, a mineral of intermediate structure containing both strongly and weakly polarized hydroxyl ions. Nordstrandite, which is probably a regular interlayering of the gibbsite and bayerite modes of stacking, may be the stable polymorph of aluminum hydroxide in an alkaline environment.

A probable qualitative explanation for this is that even though the crystal energy associated with weakly polarized hydroxyl ions is less than that associated with strongly polarized hydroxyl ions, the relative activity of strongly polarized versus weakly polarized hydroxyl ions in the solution also affects the stability of the solid phase. If the solution is alkaline, the activity of weakly polarized hydroxyl ions $(Al(OH)_4^{1-})$ is much greater than that of strongly polarized hydroxyl ions $(Al(OH)(OH)_2)_6^{2+})$ (Hem and Roberson, 1967). This ratio of ion activities may make a structure containing both strongly and weakly polarized hydroxyl ions (nordstrandite) more stable than one containing only strongly polarized hydroxyl ions (gibbsite).

In other words, strongly polarized hydroxyl ions make a crystal cage that is more efficient at containing the internal energy of the enclosed atoms. But this crystal cage must be in a state of dynamic equilibrium with the solution surrounding it. If the surrounding solution contains an abundance of weakly polarized hydroxyl ions, the crystal cage must compensate for this. It does this by assuming a structure made up of strongly polarized hydroxyl ions for high efficiency in containing the internal energy of its atoms, and embodying weakly polarized hydroxyl ions in response to the high relative activity of these ions in the surrounding environment.

GEOCHEMISTRY OF ALUMINUM HYDROXIDE MINERALS

We now can compare the laboratory observations and hypothesis for polymorph stability with the natural occurrence of aluminum hydroxide minerals to see if we can obtain additional geochemical insight.

Gibbsite in nature. The most abundant aluminum hydroxide mineral is gibbsite. It is the principal mineral in most bauxite ore deposits, the primary source of aluminum metal. Gibbsite is also abundant in laterite, the ferruginous analog of bauxite. Harder (1952) described the geology

of many bauxite deposits and ascribed their genesis to the interplay of many factors.

Bauxite (and its dominant mineral gibbsite) is principally a residual weathering product of any kind of aluminum-containing rock. There is a complete spectrum of parent rock types from alkali-rich, aluminous igneous rocks through clays, basalts, and metamorphic rocks to aluminum-poor limestones. In addition to an easily soluble aluminous rock, warm climate, high rainfall, moderate topographic relief, and freedom from erosion are all necessary for the optimal development of bauxite deposits. The advent of extensive erosion will, of course, remove bauxite faster than it forms. And a change in the delicate balance of other factors will alter the geochemical conditions and end the formation of bauxite.

Some believe that bauxite deposits form by solution, transport, and precipitation of aluminum. Theobold and others (1963) summarized the background of this hypothesis and presented a small-scale natural example. They postulated the transport of aluminum in acid solution and (or) as a sulfate complex, derived from the oxidation of disseminated pyrite in the parent rock.

Many bauxite deposits of unquestioned residual origin show evidence of local solution and precipitation. It is still uncertain, however, whether this mechanism can produce large bauxite deposits some distance away from the source of aluminum.

One type of bauxite deposit, whose genesis still is an enigma, develops on aluminum-poor limestones. It seems quantitatively impossible to concentrate the one tenth of one percent or less of Al_2O_3 in the insoluble residue of these limestones to form thick bauxite deposits. Perhaps these unusual bauxites represent accumulations of aluminous material derived from a wide area and washed into sinkholes and other local basins. During filling of a sinkhole, large amounts of water percolate through the deposited sediments. And, after filling, peat bogs frequently develop at the surface resulting in continued percolation through the sediments of waters rich in humic acid (Clark, 1966; Bushinsky, 1964).

In addition to gibbsite, boemite (AlO(OH), one of the monohydrate minerals of aluminum, frequently occurs in tropical bauxite deposits near the surface where the heat of the sun may cause dehydration of gibbsite (Harder, 1952, p. 56). Although the temperature for this transition ranges from 130°C to 200°C in the laboratory, the presence of salts in the soil profile may reduce the activity of water sufficiently to make this dehydration possible at lower temperatures. Hsu (1967) showed that high salt concentrations would delay almost indefinitely the conversion of pseudoboehmite to bayerite. Boehmite also is the principal aluminous mineral in bauxite deposits around the Mediterranean Sea where regional

metamorphism of the rocks may have caused dehydration. Similarly, Hill (1955) noted abundant boehmite associated with faults in Jamaican bauxite and concluded that the dehydration of gibbsite was in response to the mechanical breaking of the rocks.

Bauxite frequently contains kaolinite which reduces the grade of the aluminum ore. Kaolinite generally forms by the leaching of other aluminosilicate minerals and is a precursor in the formation of gibbsite. It also may be a product of the resilication of gibbsite. Iron oxides such as hematite and goethite vary in amount from a few percent in bauxites up to several tens of percent in laterites. Resistant minerals from the parent rock such as quartz and anatase often become concentrated in the residual bauxite.

All the geologic and mineralogic evidence presented points to the formation of gibbsite in an environment with a rapid through-flow of meteoric water, where kaolinite forms from primary aluminosilicates, and where quartz is preserved. An environment of moderate acidity satisfies these several requirements. And this is in complete accord with our laboratory results where the synthesis of gibbsite was restricted to acid solutions.

Nordstrandite in Nature. First recognized as a synthetic product by Van Nordstrand and others, (1956), Hathaway and Schlanger (1962; 1965) discovered natural nordstrandite on the island of Guam, and Wall and others (1962) on the island of Borneo. Careful reexamination of rocks from suitable environments will probably disclose more examples of natural nordstrandite.

Nordstrandite from Guam occurs as clusters of tiny crystals radiating out into microscopic solution cavities in upper Miocene limestone. Calcite and red clay occur with the nordstrandite as cavity fillings. Abundant nordstrandite occurs only in the basal part of the limestone near the contact with old residual soils developed on Eocene and lower Miocene basalt flows and tuffs. The nordstrandite is younger than the enclosing upper Miocene rocks and probably is much younger.

Hathaway and Schlanger (1965) consider it probable that the nordstrandite from Guam precipitated from aluminous solutions flowing along the contact between the limestone and underlying basaltic soil. They suggest that the pH of these solutions did not exceed 8.5 to 9.0 because of the limestone environment in which the nordstrandite precipitated. Limestone can be stable, however, at extremely high pH values, therefore an upper limit should not be set on the pH of these solutions. The enclosing limestone environment can be used, however, to infer a pH above 7 during nordstrandite crystal growth. It was in solu-

tions above pH 7 that nordstrandite formed in our laboratory experiments thus supporting the inferred conditions of genesis of natural nordstrandite.

Another interesting aspect of the distribution of nordstrandite on Guam is the minor amounts found in limestone some distance from the contact with volcanic rocks. Hathaway and Carroll (*in* Schlanger, 1964, p. D44) speculate that it may be detrital gibbsite that recrystallized to nordstrandite in the limestone environment. The results of our synthesis experiments support the reasonableness of this hypothesis.

Nordstrandite from west Sarawak, Borneo, occurs as rounded pellets in terra rossa soil on the edge of a sinkhole in limestone (Wall and others, 1962). The authors suggest an origin related to weathering of probable overlying dacitic sills. Although the data given are meager, we may surmise that the limestone host terrain probably limited nordstrandite-precipitating solutions to a pH above 7.

Bayerite in Nature. The only well-documented occurrence of natural bayerite known to us is in Hartruim, Israel (Bentor and others, 1963; Gross and Heller, 1963). The investigators used X-ray diffraction to identify the bayerite, which occurs with calcite and gypsum in veinlets cutting sedimentary rocks of late Cretaceous age. The rocks are composed of calcite and spurrite (a calcium-carbonate-silicate usually formed by contact metamorphism) in a ratio of about two to one. The veinlets also contain vaterite, portlandite, tobermorite group minerals, thaumasite, and ettringite. Several of these minerals connote genesis at a very high pH (Gross and Heller, 1963), and this agrees with the conditions under which pure bayerite formed in our experiments (pH 12+).

A recent report of bayerite in a weathering crust of amphibolites and serpentinites in Russia (Khorosheva, 1968) is corroborated by X-ray diffraction. The associated minerals, in this obviously non-equilibrium environment, are gibbsite, diaspore, and possibly nordstrandite.

Bayerite-nordstrandite Enigma. The relative ease and speed with which bayerite, and to a lesser extent nordstrandite, form in the laboratory contrast with the apparent paucity of these phases in nature. Gibbsite, the slowest forming phase in the laboratory, is by far the most abundant of the three aluminum hydroxide polymorphs in nature.

We have shown that bayerite and nordstrandite form only in alkaline solutions, and the field evidence implies that the few natural samples of these minerals also formed in alkaline environments. Perhaps the scarcity of aluminum-bearing alkaline ground waters is part of the reason for the scarcity of bayerite and nordstrandite in nature. In addition, because

of the abundance of silica in most natural alkaline waters, it is tempting to speculate on the importance of silica in favoring the formation of aluminosilicate minerals rather than aluminum hydroxide.

If silica inhibits the formation of aluminum hydroxide, why does gibbsite form in the pH range from 4 to 7 where silica greatly exceeds aluminum in most natural waters? The answer may depend upon the dominant form of silica in solution. At pH values below 9, most of the silica is in the monomeric uncharged form H_4SiO_4. Above a pH of 9, increasing amounts of silica go into solution as the silicate ion $(H_2O)Si(OH)_5^{1-}$ (Iler, 1955). Perhaps the charged silicate ion is required to form aluminosilicate minerals, and the virtual absence of this ion at pH values below about 7 (except when the silica concentration is high) allows aluminum in solution to precipitate as gibbsite.

If the silicate ion inhibits the formation of bayerite and nordstrandite, the few known natural occurrences of these minerals must represent alkaline environments with very little silica in solution. The environment of nordstrandite deposition on Guam, described by Hathaway and Schlanger (1965), probably possessed a high pH and a low silica concentration. Initially, acid ground water in the underlying basalt and tuff should react with the unstable primary silicates to form secondary silicates, increase the pH of the water, and take aluminum into solution as the aluminate ion $(Al(OH)_4^{1-})$. Little silica should go into solution because these rocks contain almost no uncombined silica (Stark, 1963), and the solubility of the secondary silicates is low in alkaline solutions (Pickering, 1962).

From what we can deduce about the nordstrandite depositional environment in west Sarawak, it resembles that on Guam. Wolfenden (1961) described most of the bauxite deposits in Sarawak as forming from intermediate to basic igneous rocks, generally with little quartz. The immediate environment of the nordstrandite pellets on the edge of a sinkhole in limestone is roughly equivalent to that on Guam.

Barnes and others (1967) reported that ground waters high in pH (11–12) and low in silica (<6 mg/l) form during low temperature serpentinization of ultrabasic rocks. Similar reactions in rocks containing aluminous minerals and little free silica may provide ideal conditions for the precipitation of nordstrandite or bayerite.

We must realize that these nordstrandite occurrences are rare and limited in extent for good reason. The environment in which nordstrandite forms tends to be a small, closed system in which high pH, high aluminum concentration, and low silica concentration can equilibrate. Throughout most of the natural environment, meteoric water in equilibrium with the atmosphere is slightly acid and becomes alkaline only

by reacting with and destroying rock minerals The long-term through-flow of meteoric waters must result in the destruction of the rock in an environment that is slightly acid most of the time. The vastly lower solubility, in these waters, of aluminum relative to other metals, leads to the residual enrichment of aluminum hydroxide. And the generally acid nature of the environment through time causes the gibbsite structure to form.

Our laboratory aging of bayerite-nordstrandite mixtures, although underway for only 2 years, seems to indicate that during aging nordstrandite forms at a greater rate than bayerite (Fig. 8 versus Fig. 6). This, together with the almost complete absence of bayerite in nature, leads us to propose that bayerite is a metastable phase that will eventually recrystallize in alkaline solutions to the stable phase nordstrandite. How long it takes for complete recrystallization of bayerite to nordstrandite we do not know, though we detected increased amounts of nordstrandite in just a few months.

If this proposal is correct, the natural bayerite from Hartruim, Israel (Bentor and others, 1963; Gross and Heller, 1963), must be metastable. This natural bayerite formed, presumably, many hundreds or thousands of years ago. We can speculate that its slow rate of recrystallization to nordstrandite may be due to the extreme dryness of the region in which it occurs. Hartruim is located on the southwestern edge of the Dead Sea in a region with a mean annual rainfall of less than 50 mm (Orni and Efrat, 1964). The presence of vaterite (a metastable polymorph of $CaCO_3$) in these bayerite-bearing rocks attests to their dryness, for vaterite is unstable in the presence of water at room temperature and pressure (McConnell, 1960; Johnston and others, 1916).

The uncertainties of extrapolating from conditions of laboratory synthesis to natural conditions must always be kept in mind and the possibility of reinterpretation left open. In the alumina-water system the effect of most natural foreign ions has been thoroughly studied and found to slow, but not change, the course of crystallization. Our experiments, and those of others, show that pH is the overriding control on crystal structure. And, as the preceding discussion shows, the best pH that can be inferred for the environment of precipitation of natural aluminum hydroxides approximates the pH found in the laboratory.

Summary

The most important conclusions deriving from this study are:

1. The pH of the mother liquor controls the structure of the aluminum hydroxide precipitate.

2. The gibbsite structure forms when the pH is less than about 5.8. The bayerite structure forms when the pH is greater than 5.8.

3. The nordstrandite structure forms slowly at pH's greater than 5.8. Because nordstrandite seems to form at the expense of previously-formed bayerite, it may be the stable polymorph of aluminum hydroxide in alkaline solutions.

4. Though the structures of bayerite and nordstrandite are imperfectly known, they seem to differ from gibbsite and each other solely in the manner of stacking successive layers of aluminum hydroxide.

5. This difference in stacking is directly attributable to constraints imposed by polarization-induced distortions of the hydroxyl ions.

6. The strong and weak distortion of the hydroxyl ions in acid and in alkaline solutions, respectively, is inherited by the gibbsite and bayerite solids that precipitate from these respective solutions.

7. The structure of nordstrandite seems best explained as a 1:1 regular interlayering of the gibbsite and bayerite modes of stacking.

8. The suggested stability of nordstrandite relative to bayerite may reflect a compromise between the higher crystal energy afforded by strongly polarized hydroxyl ions and the dominance of weakly polarized hydroxyl ions in the surrounding solution.

9. The scarcity of nordstrandite and abundance of gibbsite in nature reflects, in part, the dominantly acid nature of most weathering environments.

10. The scarcity of nordstrandite, even in alkaline environments, may indicate a preference by aluminate ions to form aluminosilicates with the usually abundant silicate ions.

The conflict in earlier work regarding the conditions of stability of the aluminum hydroxide polymorphs arose for two reasons: (1) small quantities of often poorly crystallized material subject to strong preferred orientation favored misidentification, and (2) depending upon the presence of foreign ions and other experimental variables, metastable solids frequently formed. The conversion of these metastable phases to stable phases is often slow, especially if the metastable phases are well crystallized. Metastable products therefore have frequently been considered to be stable.

We found that syntheses using perchlorate ions, though they bear little relation to natural systems, decrease the effect of metastable precursors. Though the effect is decreased it is not eliminated as shown by our difficulty in converting well-crystallized bayerite to nordstrandite during reasonable periods of aging.

Though a good number of our conclusions represent hypotheses and speculations based on imprecise data, we feel that these proposals should

be made here so that they may guide future work aimed at their abandonment, revision, or acceptance.

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