

phase changes

Hall

[AMERICAN JOURNAL OF SCIENCE, VOL. 257, OCTOBER 1959, PP. 563-573]

**PHASE RELATIONS IN THE SYSTEM $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$
AT HIGH TEMPERATURES AND PRESSURES**

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ABSTRACT. The system $\text{Al}_2\text{O}_3\text{—H}_2\text{O}$ has been studied in the temperature range 100–600°C and at H_2O pressures ranging from 5,000 to 40,000 atmospheres. At 40,000 atmospheres pressure the maximum temperature at which the trihydrate, gibbsite, is stable is 295°. The monohydrate, diaspore, is stable at 40,000 atmospheres of H_2O to a temperature of approximately 590°. The relations of the polymorphs, diaspore and boehmite, are discussed and it is 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.

INTRODUCTION

At least four minerals in the system $\text{Al}_2\text{O}_3\text{—H}_2\text{O}$ are known. Knowledge of the phase relations in this system may provide evidence of temperatures and water pressures in a variety of geological environments. For example, the interpretation of the origin of the minerals of lateritic deposits, the chief sources of aluminum ore, depends upon an understanding of the phase relations in this system.

PREVIOUS WORK

The system $\text{Al}_2\text{O}_3\text{—H}_2\text{O}$ has been widely discussed. Early investigations have been summarized by Fricke and Hüttig (1944). Most of the early work consisted of differential thermal analysis studies and served only to give the maximum temperatures at which mineral phases may exist metastably at 1 atmosphere.

Laubengayer and Weisz (1943) attempted to determine equilibrium positions of phases in this system under hydrothermal conditions. In a series of hydrothermal experiments they determined the sequence of phases in the system $\text{Al}_2\text{O}_3\text{—H}_2\text{O}$ in contact with water under its own vapor pressure, up to the critical temperature of water. They also made a few experiments slightly above the critical temperature. In their runs, lasting 50 to 150 hours, gibbsite was converted to the monohydrate, boehmite, at approximately 150°C; bayerite was converted to boehmite at essentially the same temperature; diaspore appeared from boehmite at approximately 275°, and corundum appeared from diaspore at pressures of 400 bars and at temperatures slightly over 400°C. Laubengayer and Weisz suggest as a possibility that boehmite is never a stable phase in the $\text{Al}_2\text{O}_3\text{—H}_2\text{O}$ system but that the rate of change of boehmite to diaspore is exceedingly slow. These authors point out they were only certain of equilibrium in the transition of diaspore to corundum plus water. This particular equilibrium was established from either side of the transition point.

The later study of Ervin and Osborn (1951) closely confirms the results of Laubengayer and Weisz and extends these studies to higher pressures. Ervin and Osborn, under somewhat similar hydrothermal conditions, determined that gibbsite is converted to diaspore at approximately 300°C at vapor pres-

*Publication No. 98, Institute of Geophysics, University of California, Los Angeles.

tures equal to or greater than that of liquid water at this temperature, and that diasporite is dehydrated to corundum at approximately 400°C at pressures of 65-650 bars of water. In an extended series of comparable experiments the writer has produced essentially identical results and confirmed both of these earlier studies.

A good deal of evidence, internal to the phase diagrams, suggests that the results of Laubengayer and Weisz, the results of Ervin and Osborn and the writer's results, from hydrothermal studies in this temperature and pressure region, do not represent equilibrium determinations of the phase boundary positions. Only the boundary between diasporite and corundum has been reversed; that is, equilibrium has been approached from both directions in all three investigations. The gibbsite-boehmite transition and the boehmite-diasporite transition are both exceedingly sluggish. Further, in many low temperature runs nucleation of diasporite is necessary.

The slope and shape of the boehmite-diasporite boundary as reported by Ervin and Osborn is a most unusual shape for a solid-solid transition. The slope of a transition on a pressure-temperature plot, dp/dt , is equal to $\Delta s/\Delta v$. However, as compressibility and coefficient of thermal expansions of both phases is essentially identical, changes in volume with pressure and temperature changes on a phase, makes very little difference to the value of Δv ; Δv is normally independent of pressure and temperature. Similarly, as both minerals are close to their Debye temperatures the value of Δs is relatively independent of the temperature of the reaction. Therefore, we might well expect the boundary separating the field of boehmite from diasporite to be essentially a straight line. Most experimentally studied solid-solid transitions have a straight line boundary over an appreciable range of temperature and pressure. Thompson (1955) has discussed these transitions and states, "It can be shown that the ratio $\Delta s/\Delta v$ for solid reactions may be regarded as constant." Yoder and Weir (1951) have demonstrated theoretically that for the specific reaction, nepheline plus albite equals 2 jade, providing solid solution does not intervene, the slope of this boundary will be constant. Furthermore, a fairly good estimate can be made as to the sign of the slope, dp/dt , for the boehmite-diasporite transition. Most solid-solid transitions have positive slopes, that is, the higher the temperature of the transition, the higher the pressure required. This is particularly true for all the transitions where there is a fairly large percentage change in the gram-atomic volume. The gram-atomic volume of diasporite, based on computations from x-ray determinations of the size of the unit cell, is 4.46 cc, that of boehmite is 4.83 cc. This is roughly an 8.5 percent change in the gram-atomic volume and should be accompanied by a rather large positive entropy change. Therefore we might expect that the boundary on a p-t plane separating diasporite from boehmite should be reasonably close to a straight line and have a positive slope.

The phase diagram of Ervin and Osborn, however, shows in general a boundary with negative slope separating the stability fields of boehmite and diasporite. Further, in the temperature region between 300 and 400°, the slope of the boundary is essentially zero, whereas at temperatures of around 270° the slope of the boundary is essentially infinite. This implies that the value

$\Delta s/\Delta v$ changes from essentially infinite to essentially zero in a temperature interval of less than 50° .

The inconsistencies between the predicted and the observed slopes of the boundaries separating the phases suggests strongly that a rate process rather than an equilibrium boundary is involved, as Laubengayer and Weisz suggested. Further, the geologic field evidence strongly suggests the diaspore deposits which have been thoroughly studied in this country, particularly the ones in Missouri and North Central Pennsylvania, were certainly formed at modest temperatures and pressures. Most of the students of these deposits are emphatic on this point. Thus both the field and laboratory evidence and the thermodynamic inconsistencies in the past work suggest that the stability fields of these minerals have not been adequately delineated.

EXPERIMENTAL DATA

Two types of apparatus were used in the present attempt to delineate the stability fields of boehmite, diaspore and corundum: conventional hydrothermal apparatus and piston-anvil type apparatus.

All runs at high pressures, above 5000, bars were made in a piston-anvil type of apparatus as described by Bridgman (1935) and as modified by Griggs and Kennedy (1956). In this apparatus the sample is a wafer of material inside a stainless steel washer between two carboloy pistons.

Vapor pressures of hydrated phases can readily be determined in such

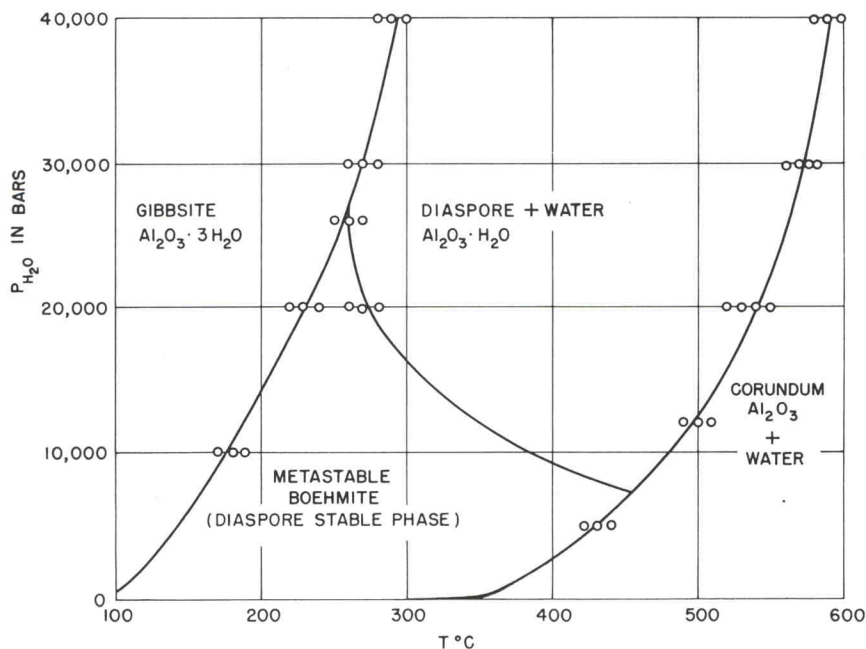


FIGURE 1. PHASE RELATIONS AT HIGH H_2O PRESSURES IN THE SYSTEM $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$

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an apparatus, for it the vapor pressure of the hydrated phase is less than piston pressure at a given temperature, the hydrated phase will persist during the run and can later be identified by x-ray or optical methods. If the vapor pressure of the hydrated phase at a given temperature is greater than applied piston load, the vapor will lift the pistons and escape, and anhydrous assemblages result. With this trial-and-error method the vapor pressure curves of various hydrates can be determined to very high temperatures and pressures. In this investigation, for instance, the vapor pressure of gibbsite was determined to 295°C where the H₂O pressure is approximately 40,000 bars (approximately 600,000 psi). The vapor pressure of diaspore reaches 40,000 bars at approximately 590°C.

Several hundred runs in the piston-anvil apparatus have been made in the system Al₂O₃—H₂O. Those used in delineating the phase boundaries are listed in table 1 and are plotted in figure 1.

The starting substance in all these runs was a mixture of roughly equal

TABLE 1
Runs with piston-anvil device in system Al₂O₃—H₂O

Temperature C°	Pressure in Kilobars	Products
420	5	Boe
430	5	Boe + Cor
440	5	Cor
170	10	Ba + Gi
180	10	Boe
190	10	Boe
220	20	Ba + Gi
230	20	Ba + Gi + Boe
240	20	Boe
260	20	Boe
270	20	Boe
280	20	Boe + Di
520	20	Di
530	20	Di
540	20	Di
550	20	Cor
250	26	Ba + Gi
260	26	Ba + Gi + Di + Boe
270	26	Boe + Di
260	30	Ba + Gi
270	30	Ba + Gi + Di + Boe
280	30	Boe + Di
560	30	Di
570	30	Di
575	30	Cor
580	30	Cor
280	40	Ba + Gi
290	40	Ba + Gi
300	40	Di
580	40	Di
590	40	Di
600	40	Cor

Gi = Gibbsite
Ba = Bayerite
Di = Diaspore
Boe = Boehmite
Cor = Corundum

parts of gibbsite and bayerite. The gibbsite was Baker's analyzed "aluminum hydroxide". The bayerite was prepared by neutralizing $AlNO_3$ with NH_4OH . The resulting gel was thoroughly washed and dried at $80^\circ C$. X-ray examination of the dried material showed it to be largely if not entirely crystalline bayerite.

All runs in the apparatus were for approximately one hour. Surprisingly, reaction in a sample compressed between pistons and brought to a selected temperature usually proceeds as far as it will go within the first few minutes at the chosen temperature and pressure. Runs of several days length have been tried, but normally in this apparatus reactions proceed within the first few minutes or not at all. Presumably the drastic change of reaction rate with time arises from the fact that a large amount of strain energy is stored in the sample on initial compression and is quickly relieved as the mineral recrystallizes. This initial strain energy appears to greatly accelerate reaction rate in the system, but the rate of conversion of one phase to another quickly declines as recrystallization takes place.

It is clear, from examination of the experiments listed in table 1, that in the vast majority of runs equilibrium was not achieved. Bayerite, precipitated metastably at one atmosphere from aluminum gel, persisted in all runs in the gibbsite field. This was most remarkable and unexpected as bayerite can be readily converted to gibbsite at one atmosphere pressure by heating at temperatures of approximately $200^\circ C$. Apparently at high pressures the viscosity of the bayerite is greatly increased and conversion to the more stable gibbsite inhibited. Bayerite has no known field of stability at one atmosphere pressure and is always synthesized metastably. However, it is somewhat denser than the stable trihydrate, gibbsite. The gram-atomic volumes of the two phases are respectively 4.47 cc and 4.57 cc, and at sufficiently high pressures we might expect bayerite to become a stable phase. However, conversion of gibbsite to bayerite was not observed. At temperatures above 260° and H_2O pressures of the order of 26 kb gibbsite dehydrates directly to mixtures of diasporite and boehmite. Below 260° boehmite is the phase formed on dehydration of the mixture of gibbsite and bayerite. It is clear that diasporite is the stable phase and the boehmite only forms metastably in most of the large area labeled "Metastable Boehmite" in figure 1. The transition of boehmite to diasporite is very sluggish. Long continued hydrothermal runs at low temperatures will convert boehmite into the diasporite in much of this temperature-pressure region of "Metastable Boehmite". The boundary separating the fields of metastable boehmite and diasporite in figure 1 is essentially the line of constant rate of conversion in the particular apparatus used. The rate of transition of boehmite to diasporite is speeded up both by higher pressures and higher temperatures. The effect of pressure on the rate of conversion of metastable bayerite to gibbsite and of metastable boehmite to diasporite is of opposite sign. High pressure inhibits the bayerite-gibbsite reaction but speeds up the boehmite-diasporite reaction.

The diasporite to corundum plus water boundary, shown in figure 1, is a sharp transition, readily delineated, and presents no problems.

In addition to the high pressure runs made in the piston-anvil device, a

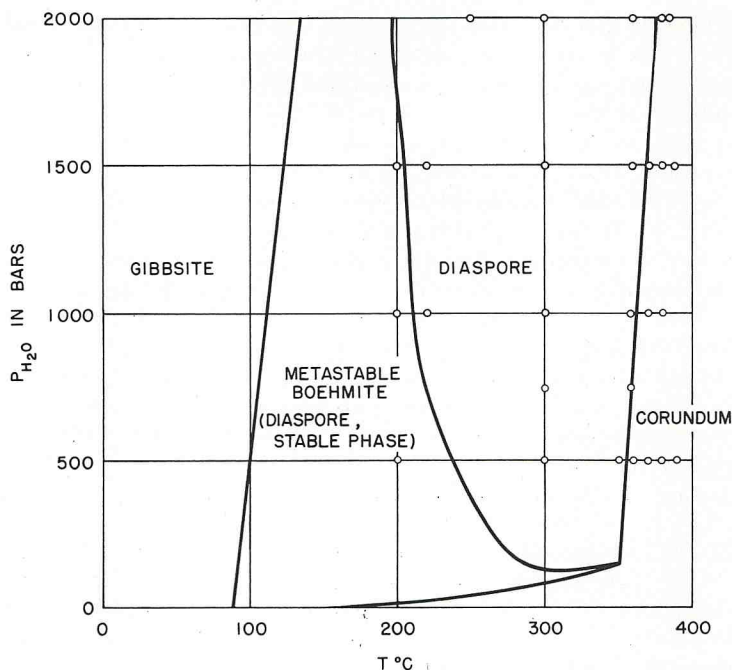


Fig. 2. Phase relations at low H_2O pressures in the system $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$.

number of hydrothermal runs have been made in conventional apparatus. These runs serve to delineate the low pressure part of the phase diagram. Some of the data from low pressure hydrothermal runs are shown in figure 2. The phase boundaries shown in this figure are based partly on the writer's data and partly on the data of Ervin and Osborn. The upper stability limit of gibbsite is sketched in figure 2. This boundary is based on the determined temperature of breakdown of gibbsite to boehmite at 10 kb and on the breakdown temperature at one atmosphere pressure. At one atmosphere pressure, gibbsite breaks down to boehmite at an exceedingly slow rate under appropriate conditions at approximately 90° (R. K. Iler, personal communication). This, of course, does not mean that natural boehmite forms at temperatures above 90° by the breakdown of gibbsite, for at sufficiently low H_2O pressures the breakdown can take place at almost any temperature, although, of course, as temperatures approach ambient temperatures, this transition is very slow. The gibbsite-boehmite boundary as shown in figures 1 and 2 is, of course, not an equilibrium boundary, as boehmite is not a stable phase. Presumably the equilibrium gibbsite-diaspore boundary should be almost coincident with this boundary but should lie at a few degrees lower temperature.

The area labeled "Metastable Boehmite", in figure 2, represents the range of temperatures and pressures in hydrothermal experiments in which metastable boehmite forms. Diaspore is the stable phase in this area. The field of "Metastable Boehmite" as deduced from hydrothermal apparatus is much smaller than the same field shown in figure 1, as determined from the piston-anvil type

apparatus—further evidence that this is a rate boundary and not an equilibrium boundary.

Experimental runs made by the author are shown as circles and were used to delineate the diasporic-corundum boundary and the boundary of the "Metastable Boehmite" field. Many of these runs, particularly the ones in the diasporic field, were maintained at temperature and pressure for as long as three months. Alumina gel was placed in a bomb which was seeded with a small trace of diasporic crystals. The lowest temperature at which the diasporic had appreciably increased in quantity and the crystals increased in size, in three months time, were the two runs shown at 220° at 1000 and 1500 bars H₂O pressure. The lower part of the diasporic field in figure 2 has been sketched in from data by Ervin and Osborn.

The breakdown of diasporic to corundum-plus-water has been delineated by a series of runs, each of approximately one month duration. This curve intersects the vapor pressure curve of liquid water at approximately 150 bars and 350° at which point it must, of necessity, turn and essentially follow along and slightly below the vapor pressure curve of water down to lower temperatures. The curves showing the vapor pressures of the reaction of gibbsite to metastable boehmite-plus-water and of diasporic to corundum-plus-water are both essentially straight and, within the precision of the particular experiments, show no appreciable curvature, unlike vapor pressure curves determined for reactions that take place at higher temperatures. The reason for this is that liquid water, not vapor, is the product of dehydration. The volumes of the liquid water are not particularly sensitive to pressure changes of the order of magnitude of those shown on figure 2. There is, of course, a sharp inflection in the slope of the diasporic to corundum-plus-water curve where this curve intersects the vapor pressure curve of pure water; here, a very large change in Δv takes place.

The high pressure data shown in figure 1, with some analogous curves obtained from studies in the system, SiO₂-Al₂O₃-H₂O, to be published at a later date, are shown in figure 3. Surprisingly, essentially straight lines are obtained at pressures of 4 kilobars and above, when the log of pressure is plotted against temperature. This relation does not hold at low pressures, of course, where water behaves more as an ideal gas. Here the log of the pressure must vary as the reciprocal of the absolute temperature.

The vapor pressure curves for the related hydrates shown in figure 3 are remarkably subparallel to each other, seeming to indicate a rather uniform change in compressibility in these systems as pressure is increased. It will be of interest to learn whether or not other mineral hydrates exhibit vapor pressure curves that are part of this set.

DATA FROM THERMODYNAMIC MEASUREMENTS

Recent thermodynamic data have thrown much light on the possibility of existence of a stable field for boehmite. K. K. Kelley and his colleagues at the Minerals Thermodynamics Experiment Station, particularly E. G. King, have recently made low temperature heat capacity measurements on both boehmite and diasporic. The sample of boehmite used was prepared hydrothermally by the writer for these measurements. The diasporic was from the famous locality

at Chester, Massachusetts and was kindly supplied the writer by C. Frondel. The diaspoire was rather impure and, though it was crushed and cleaned as well as possible, the final cleaned product contained 0.4 percent MgO.

The low temperature heat capacity measurements of Kelley and King indicate $S_{298}^{\circ} = 16.86 \pm .06$ cal/deg/mole for diaspoire and $S_{298}^{\circ} = 23.15 \pm .10$ cal/deg/mole for boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). The correction for the MgO in the diaspoire sample ranged from 1.0 to 11.6 percent, depending on the temperature (K. K. Kelley, personal communication, September 15, 1958). Thus the value of Δs for the reaction boehmite to diaspoire is $6.29 \pm .16$. The molar volume of diaspoire, from x-ray measurements is 35.66 cc, of boehmite 38.65 cc. Thus $\Delta v = 2.99$ cc.

The slope of the equilibrium boundary separating the stable phases diaspoire and boehmite should be as follows,

$$\frac{dp}{dt} = \frac{\Delta s}{\Delta v} = \frac{6.29 \pm .16 \text{ cal/deg/mole}}{2.99 \text{ cc}} = \frac{2.63 \text{ deci-joules/deg/mole}}{2.99 \text{ cc}}$$

$$\frac{dp}{dt} = +88 \text{ bar/degree}$$

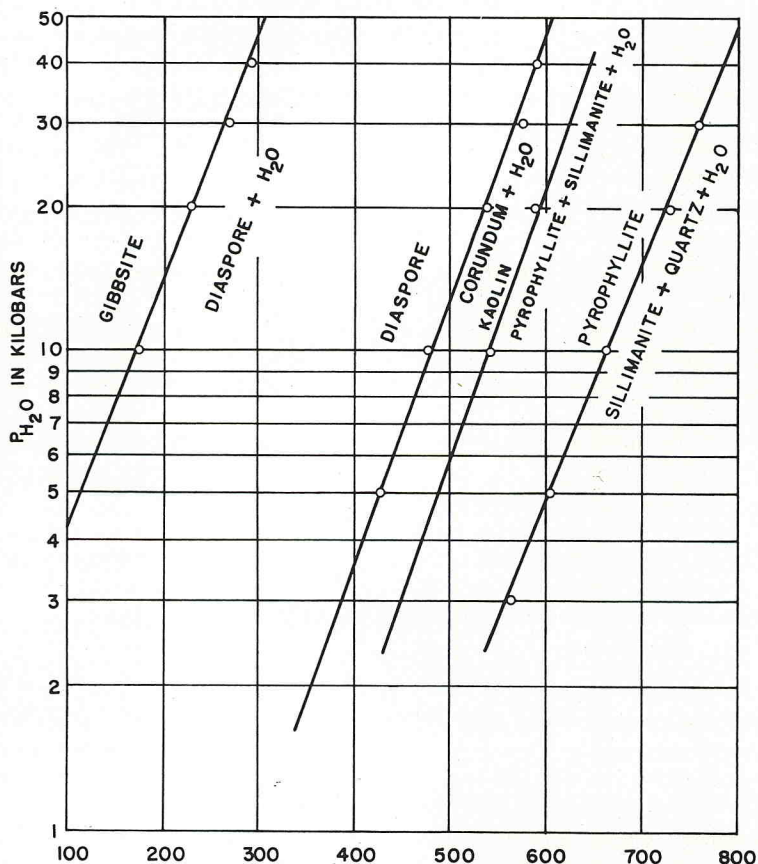


Fig. 3. Vapor pressures of some reactions in the system Al_2O_3 - SiO_2 - H_2O .

This value, +88 bar/degree, is the largest slope known to the writer for a solid-solid transition among natural minerals and results from the unexpectedly low value for the entropy of diaspora.

It is clear then, within the limitations of the assumption that Δs and Δv are essentially independent of temperature and pressure, that there can be no stability field for boehmite, for the field of boehmite must lie at higher temperatures and lower pressures than the field of diaspora. A line with the slope of +88 bar/degree passed through the highest-temperature lowest-pressure synthesis of diaspora from boehmite, as shown in figure 2 of this paper, or as taken from the data of Ervin and Osborn, shows that corundum lies at higher temperatures and lower pressures and there is no room for a boehmite field.

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 deposits. Diaspora is then the stable phase in equilibrium with gibbsite.

An assumption has, of course, been made that the diaspora and boehmite of natural deposits are reasonably pure phases and accept other elements to a very limited extent in their crystal structure. Such analyses of boehmite and diaspora as are available support this view. Though iron is an ubiquitous impurity in "boehmite" samples, it is assumed to be present as the separate phase and not in solid solution relations with boehmite.

DATA FROM THE FIELD

Much field information indicates that diaspora can form on the surface of the earth under essentially no confining pressure, given sufficient time and the right climatic or chemical environment. Indeed all three of the aluminum hydrates—gibbsite, boehmite and diaspora—are present in some bauxite deposits and other bauxite deposits are made up wholly of one or the other of these three phases. The lateritic clays and laterites, which contain all three phases, show geological evidence of having been formed under remarkably similar conditions of pressure and temperature. This strongly suggests that either one or the other of these phases is present metastably. Keller (1952) summarizes this; "Because of the intimate coexistence of diaspora and boehmite it is obvious that the physio-chemical conditions required for their formation in nature cannot be radically different."

There is a strong suggestion that diaspora tends to form most readily from the metastable boehmite in limestone environments. This suggests that CaCO₃ saturated solutions are better able to dissolve the metastable phase and precipitate the stable phase than are other types of laterite-producing solutions.

Allen (1952) has discussed in detail the mineralogical relationships between the phases gibbsite, boehmite and diaspora. His descriptions emphasize the extremely slow rates of conversion of one phase to another under geological conditions. Boehmite may be associated either with gibbsite, diaspora, or both, and metastable phases may persist over long periods of geologic time. Allen (1935) has described in detail the diaspora clays of Missouri. These clays are found filling sandstone lined depressions and sink holes in rocks of Pennsylvanian age. It seems unlikely that these deposits have formed at pressures of

more than a few atmospheres. Allen presents evidence that oolites of boehmite and diaspoire have grown at the expense of clay minerals, and everywhere in the diaspoire district, except possibly one mine, diaspoire has grown directly from the flint clays without an intervening stage of gibbsite.

Frederickson (1952) is explicit on this point; in discussing the clay deposits of Missouri and Pennsylvania he says, "Boehmite and diaspoire coexist in textural relationships that makes it doubtful that these rocks have been subjected to elevated temperatures and pressures."

Most interesting relations between boehmite and diaspoire are shown in the Mercer fire clay at North Central Pennsylvania (Bolger and Weitz, 1952). In this clay boehmite and diaspoire seem to be contemporaneous and are both growing at the expense of kaolin. Bolger and Weitz, who have examined the mineral relations of the Mercer fire clay deposits in detail, state, "It thus appears quite unlikely that abnormal pressure, abnormal temperature, or epigenic processes, either alone or in combination were responsible for the formation of the earliest diaspoire," and conclude that the Mercer diaspoire formed at the surface of the earth under conditions of lateritic weathering. Keller (1952) discussing the origin of Missouri high aluminum clays also emphasizes the very intimate mixture of boehmite and diaspoire.

It is gratifying that the evidence from the field and from the laboratory are not inconsistent. Diaspoire cannot be considered exclusively a high temperature or high pressure phase, and boehmite almost certainly has no field of stability in lateritic or other environments.

ACKNOWLEDGMENTS

Many people have aided in this investigation. Equipment was fabricated and kept in good repair by Lester Emarine. Don Lyon, Phillip LaMori and Edward Sharp aided in the experimental program. W. S. Fyfe and D. T. Griggs stimulated the writer's interest in this problem and discussed the problems of the interpretation of previously existing experimental data. This work has been supported by the Office of Naval Research, Nonr-233(28).

The manuscript has been critically read by V. T. Allen, J. R. Goldsmith, W. D. Keller, G. J. MacDonald and G. D. Robinson. Thanks are owing to these people for their many suggestions.

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