

THE APPLICATION OF PHASE EQUILIBRIUM DATA TO CERTAIN ASPECTS OF CLAY MINERALOGY¹

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ABSTRACT

The recent interest in the determination of the phase diagrams for many systems involving water as one component has been in those systems which are of greatest importance to clay mineralogy.

The importance of both published and more recent work on synthesis of the clay is demonstrated in the ability to prepare chemically pure, mineralogically homogeneous kaolinites, montmorillonites, micas, and chlorites. The stability and identification of the clay minerals are discussed in relation to some of the major problems of clay mineralogy. Some of the chief objections to data obtained by the usual hydrothermal techniques are treated at length.

INTRODUCTION

During the past four or five years, much phase-equilibrium work has been done in systems involving water as one component and most of it is in those systems which are of greatest interest to clay mineralogists. A survey of the work done to date will show that the systems studied include, compositionwise, several of the major problems in clay mineralogy. The recent work includes the systems:

$Al_2O_3-H_2O$ (Ervin and Osborn, 1951), with the relationships between gibbsite, boehmite, diaspore, and corundum.

$Al_2O_3-SiO_2-H_2O$ (Roy and Osborn, 1952a), treating the stability of the kaolinite family, the endellite-halloysite relationship, the formation of pyrophyllite, the existence of a new layer silicate hydralsite, etc.

$MgO-SiO_2-H_2O$ (Bowen and Tuttle, 1949), treating the serpentine and talc synthesis and stability.

$MgO-Al_2O_3-SiO_2-H_2O$ (Roy, 1952; Yoder, 1952), involving the saponitic magnesium montmorillonites, beidellitic aluminum montmorillonites, chlorites, antigorites, etc. One important aspect of this system is treated in detail in a later paper in this volume (Nelson and Roy, 1954).

$Na_2O-Al_2O_3-SiO_2-H_2O$ (Sand, Roy and Osborn, 1953), chiefly of interest in this context owing to the montmorillonite-mica relationship.

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$K_2O-Al_2O_3-SiO_2-H_2O$ (Roy and DeVries, 1952; Yoder and Eugster, 1953), dealing with the illite-muscovite problem, and stability of muscovite.

In addition, a study of the composition, temperature and pressure limits of formation of the basic clay groups has been initiated in our laboratories. The study of the two-layer kaolinite has been completed (Roy and Roy, 1953) and that of the three-layer montmorillonite-mica is well advanced. Some work has been done with the chlorites (Roy, 1952; Nelson and Roy, 1954) in this connection, but a more extensive study is in the initial stages now.

Very recently Yoder and Eugster (1953) have studied the solid solution and stability relations between various typical micas, including the phlogopite-muscovite and phlogopite-annite series. We are currently concerned with the substitution in disilicic micas.

SYNTHESIS OF CLAY MINERALS

One of the most obvious and immediately useful results of these investigations — although actually a “by-product” of the phase studies — has been the synthesis of almost all the clay minerals. Moreover, in contrast to most other mineral synthesis work, especially of the hydrated minerals, these minerals can be grown to as large or larger sizes than their natural counterparts. It is, of course, well known that these are not the earliest syntheses of the clay minerals; several workers have synthesized some of them before. Of the earlier work that of Noll (1944) deserves especial recognition as well as that of Ewell and Insley (1935). However, most investigators did not work with either closely controlled compositions — frequently adding “mineralizing agents” — or under well-defined conditions of temperature and pressure. With the rapid strides that have been made in clay mineralogy in the last several years, one of the most serious handicaps to the refinement of the values for various properties of these minerals is the absence of “pure” samples. With the recently acquired knowledge, it is now possible, therefore, to make a clay which is not only chemically pure but also mineralogically a single phase and morphologically homogeneous. It is relatively easy to make the phases “chemically pure”, but mineral homogeneity requires a much greater degree of knowledge and experimental skill. It is further possible to synthesize clays with controlled and definite amounts of isomorphous substitution. Indeed for the study of fundamental properties it is possible to synthesize a clay structure containing ions which are more “desirable” from a certain viewpoint. For example, Ga^{3+} can be made to replace Al^{3+} in several structures, or Mg^{2+} can be completely replaced by Ni^{2+} in others, making unequivocal structure determinations by x-ray methods somewhat easier.

The status of synthesis of the various clay minerals and groups is as follows:

Kaolinite family

Of this family, only kaolinite itself can be made reproducibly: it does not appear to be possible to synthesize either nacrite or dickite under any of the experimental conditions tried so far (the failure being tentatively assigned to too low pressures). Attempts to repeat the scattered reported syntheses of these phases have always been unsuccessful. Identification of the product when it is very fine grained also renders uncertain the differentiation between the polymorphs. Neither endellite nor therefore halloysite has been synthesized as yet.*

Kaolinite can be made from simple mixtures of fine-grained or "amorphous" forms of alumina and silica but forms much better when coprecipitated gels are used. It yields well-developed hexagonal flakes with properties essentially identical to those of typical natural kaolinite (for other details on preparation, etc., see Roy and Osborn, 1952).

It is of considerable interest that kaolinite stands as the only example of a dioctahedral two-layer silicate structure which can be synthesized or occurs naturally. Protracted efforts to make analogues containing very similar ions such as Fe^{3+} , Ga^{3+} and Cr^{3+} , met with no success. Kaolinite does not admit appreciable amounts of Mg^{2+} into its lattice.

Montmorillonoids

Under this term are included all the "expanding" three-layer silicates except the vermiculites. This family of minerals demonstrates especially well the usefulness of the method. It has been found possible to synthesize a montmorillonite ranging in composition of end members from pure alumina-silica-water to pure magnesium-silica-water—thus embracing both the beidellites and the saponites and all the typical "montmorillonites." The alumina-silica end member provides an example of an expanding structure with *all* the charge-unbalance residing in the tetrahedral layer. Montmorillonites containing other ions in the exchange positions derived from the above montmorillonites have, of course, been made. Other divalent ions such as Ni^{2+} and Zn^{2+} also enter the sheets themselves; the only univalent ion which enters the structure is Li^+ and this yields hectorite which forms as beautiful flat laths. Thus it is possible to synthesize a montmorillonite of a chosen composition—let us say one with a certain substitution ratio of Mg for Al in the octahedral layer—and obtain a product (with proper care) which appears homogeneous both to x-rays and under the electron microscope.

* At temperatures near 100°C , recent runs of some months duration yielded a phase amorphous to x-rays, but having a single-crystal electron diffraction pattern ($hk0$ projection) more similar to halloysite than to kaolinite. However, the crystals were too small to discern whether the distinctive tubular habit of halloysite was actually present.

Micas

The syntheses of muscovite (Yoder and Eugster, 1953), paragonite (Sand, Roy and Osborn, 1953), and phlogopite (Eugster and Yoder, 1953) are relatively easy and their equilibrium decompositions have been studied. These authors have also studied possible solid solution between phlogopite and muscovite. Talc, also a nonexpanding three-layer structure, is synthesized very easily, and also permits a great variety of ions to replace the Mg^{2+} or Si^{4+} (Roy and Roy, 1953). On the other hand the dioctahedral analogue of talc, pyrophyllite, is relatively difficult to prepare and also unique with respect to ionic substitution. No substitution appears to take place between talc and pyrophyllite.

Serpentines and the Related Aluminous Serpentines (Septechlorites)

This group of minerals is not always classified under the clays but since chrysotile, the end member, is the trioctahedral counterpart of kaolinite, there is good reason for doing so. Moreover, as a result of our work on the alumina-containing phases, we have every reason to believe that these minerals probably are common constituents of soils. In this group, a whole range of isomorphous substitutions have been demonstrated for both the tetrahedrally and octahedrally coordinated ions. They may be replaced partly or completely by Ni^{2+} or Ge^{4+} separately or simultaneously. The substitution of Al^{3+} in both positions gives rise to a series of solid solutions having the two layer silicate structure with a 7A series of reflections ranging in composition from chrysotile to amesite. (See p. 335 this volume.) Further detailed investigation of the influence of isomorphous substitutions on various typical clay properties is necessary.

Chlorites

The last group of layer silicates is that involving four layers—the chlorites. As a result of synthetic work (Roy, 1952; Nelson and Roy, 1954) it has been possible to improve considerably our understanding of the composition of these minerals. It has been shown that the 7A series of aluminous serpentines, called septechlorites above, are polymorphic variations of the “true” 14A chlorites and that there are complete though separate isomorphous series extending from the chrysotile (penninite in the case of the 14A series) to the amesite composition. In nature minerals originally classed as “chlorites” may prove to be of either the 7A or 14A type. Here again, in the synthetic phases chosen ions may be introduced into either octahedral or tetrahedral positions. Ions such as Ni^{2+} and Cr^{3+} are being currently studied in this connection, the latter being common in nature.

THE STABILITY OF THE CLAY MINERALS

The main purpose of phase equilibrium studies is to determine the stability of the phases with changes of composition, temperature, and pressure. Of course, in these studies one is concerned with *equilibrium*

processes and products (not always easily defined), and while this approach has the advantage of absolute reproducibility and significance, the techniques are such that they probably cannot be used immediately by all workers studying clays. However, these stability data do provide fundamental information necessary to explain not only the genesis of clays in nature, but also their behavior under conditions imposed on them by industrial or laboratory use. The equilibrium data also provide useful clues and guides in the use of nonequilibrium data which may be more easily obtainable. The relation of recent studies under hydrothermal conditions to earlier ones under "dry" conditions is quite clear. The earlier studies applied to the same systems only at much higher temperatures where no hydrated phases were stable. At lower temperatures, at which hydrated phases must be considered and reactions are very slow, water is used both as a mineralizer and as a component. The "dry" equilibrium diagrams have proved their usefulness in the ceramic applications of the clay minerals, and similar usefulness for the hydrothermally determined diagrams is to be expected.

Composition as the Dominant Variable

One of the most general conclusions and perhaps self-evident propositions is the fact that the over-all composition of the starting materials will be the dominant factor in determining the clay minerals which will form. Composition greatly outweighs the effect of temperature, pressure, pH, etc. Thus, if the formation of clays in fresh-water and marine conditions is considered, the total composition of the system immediately determines the fact that in the former, no magnesium-potassium-bearing phase such as montmorillonite could be formed in appreciable amounts. And so it happens that the chemical analysis of the whole "clay system" being studied becomes of paramount importance. Knowing the chemical composition and the pressure-temperature relationships among the phases from the investigations already made, one is able to predict the mineralogical composition. Not only is this true of equilibrium, but since in the study of these systems the probable metastable assemblages are also encountered, one can also say something of the assemblages which might occur if the rocks do not appear to have reached equilibrium. In any event, since the easiest part of the study is the investigation of the actual mineralogical content of the clay assemblage, the phase data combined with the chemical analysis will permit the checking of the mineralogical analysis and avoid absurd or impossible results. A case in point may be cited in the occurrence of septechlorites (7A series chlorites) in soils: up to the present it is almost certain that on the basis of the x-ray patterns these minerals have been labeled kaolinite. A glance at the phase diagram would tell us whether any particular assemblage could indeed have contained kaolinite: and if this method is combined with a total chemical analysis one could unambiguously eliminate either the septechlorite or the kaolinite as a possibility.

In this connection mention should also be made of the oft-invoked factor of pH. That pH can play a determinative role especially in the extreme ranges is very probable, but whether or not it actually does when invoked is another matter. For example, let us consider the usual connotations of a "basic" environment. From the phase equilibrium point of view the environment is different and "basic" owing mainly to the presence of "basic" ions such as K^+ , Na^+ , Ca^{2+} rather than to a high pH. Thus, if there were in nature a strongly basic (high pH) solution, it would immediately react with the common amphoteric oxides present to give rise to neutral or perhaps slightly basic solutions, and the environment would really differ from before only by the amount of basic ions present — i.e., only in total chemical composition.¹ Precisely the same is true of the acid environments except that in this case the mineralogy of anion substitution and new compound formation is a much less investigated field. This is not to say that actual hydrogen ion concentrations other than $pH=7$ do not exist in nature, nor to deny their possible importance in controlling especially minor changes in phase assemblages such as favoring one polymorph or enhancing some metastability, but rather to point out that extremes of pH can only very rarely exist in nature and then not for long in contact with common rocks in large amounts. One of the best reasons for minor changes in pH, and one that we have attempted to use in the laboratory, is the presence of organic bases or acids. In these cases, the other fraction of the molecule attached to the H^+ or $(OH)^-$ does not enter the solid phases and a more or less constant environment can be maintained.

One important aspect of the phase data is the determination of the extent and limits of isomorphism in a structure, i.e., the extent of solid solution in a particular phase. This knowledge, of course, is essential also in determining the phase assemblages from the chemical composition and in demarcating the compositional areas in which one, two or more phases are stable together. Thus, the montmorillonites present a very rare instance of quaternary solid solutions, in which the same (structurally speaking) phase can be formed from compositions differing in any or all of the four component oxides. On the other hand, we have in kaolinite a mineral which is very intolerant to substitution even by very similar ions; similar to kaolinite are talc and pyrophyllite. Chrysotile permits substitution in its lattice along only a single binary join in a quaternary system; and the chlorites permit extensive solid solution but with only relatively few ions.

Stability with Temperature

The maximum and minimum temperatures of formation (i.e., stability) of the common clay minerals *in the presence of an excess of water* are listed in round figures (Table 1) for a pressure of 1000 atmospheres of

¹ It has been called to the author's attention that a similar argument has been presented earlier by Millot (1949, p. 277-279, 287-288).

TABLE 1. — DATA ON SYNTHESIS OF CLAY MINERALS

Mineral	Minimum (if any)	Maximum	Reference
Kaolinite	<R.T. ¹	400°C	Roy & Osborn, 1952a
Nacrite, Dickite			
Halloysite	<R.T.	400°C	Roy & Osborn, 1952a
Endellite (Halloysite 4H ₂ O)	<R.T.	200°C	Roy & Osborn, 1952a
Montmorillonites (Change with composition) in:			
a) Na ₂ O-Al ₂ O ₃ -SiO ₂ -H ₂ O	<R.T.	250-450°C	Sand, Roy & Osborn, 1953
b) MgO-Al ₂ O ₃ -SiO ₂ -H ₂ O	<R.T.	300-460°C	Roy, 1952
Pyrophyllite	400°C	575°C	Roy & Osborn, 1952a
Talc	300°C	780°C	Bowen & Tuttle, 1950
Muscovite	<R.T.?	675°C	DeVries & Roy, 1952 Yoder & Eugster, 1953
Paragonite	250°C	650°C	Sand, Roy & Osborn, 1953
Phlogopite	<R.T.	1000°C	Eugster & Yoder, 1953
Chrysotile	<R.T.?	500°C	Bowen & Tuttle, 1950
Septechlorites	<R.T.?	650°C (metastably) 400°C (stably)	Nelson & Roy, 1954 Roy, 1952
Clinochlore	400°C?	680°C	Yoder, 1952
Hydralsite (2Al ₂ O ₃ • 2SiO ₂ • H ₂ O)	400°C	450°C	Roy & Osborn, 1952a
Gibbsite	<R.T.	120°C	Ervin & Osborn, 1951
Boehmite	120°C	280°C	Ervin & Osborn, 1951
Diaspore	280°C	400°C	Ervin & Osborn, 1951

¹ Room Temperature.

water. The nature and limitations of these data are discussed in the next section. The data shown in Table 1 were compiled from work at The Pennsylvania State University and the Geophysical Laboratory of the Carnegie Institution of Washington.

The usefulness of these data is not as easy to tabulate, since there are undoubtedly many fields of application of which we are unaware. However, it is obvious that these data give us some definite points on a temperature-pressure scale with which to connect theories of the genesis of clay minerals. The "hydratability" of minerals such as talc, pyrophyllite, and paragonite bears on their presence or absence in soils. The stability differences among the various montmorillonite compositions should find immediate application in the field of stabilizing bentonite drilling-muds which encounter conditions of high temperature and high pressure.

The question of relative stability of septechlorites and chlorites at low temperatures is closely connected with their occurrence in low-rank clay-bearing horizons.

OTHER CLAY PROBLEMS AFFECTED BY
PHASE EQUILIBRIUM DATA*Octaphyllitic-Heptaphyllitic Substitution*

The question as to whether or not isomorphous substitution may take place between the dioctahedral (heptaphyllitic) and trioctahedral (octaphyllitic) end members of a type structure has always been of great interest. The data show that this type of substitution is almost negligible in the case of the joins kaolinite-chrysotile, and talc-pyrophyllite. Within the montmorillonite group compositions lying on the join from a pure $\text{MgO-SiO}_2\text{-H}_2\text{O}$ member to a pure $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ member can be made to yield a single (?) montmorillonite phase. However, owing to the several different possible rearrangements, especially between the base-exchange and structural positions, one cannot immediately say whether this is necessarily substitution of the type in question. In the phlogopite-muscovite series the solid solution in the fluorine micas has been shown to be very limited (Eitel, 1945) and in the hydroxyl analogues it is also limited at high temperatures, although conceivably more extensive at low temperatures (Yoder and Eugster, 1953).

Static and Dynamic Heating Methods

While the phase changes occurring when the clays are heated "dry" have been the subject of intensive investigation by ceramists for several decades, during the past few years static heating has been increasingly used as a method of identification of clays. The new phase equilibrium data provide new light on these changes. They enable us to determine when, if at all, the dry reaction has reached equilibrium. They indicate the possibility of firing a ceramic body hydrothermally several hundred degrees below the usual temperatures. Furthermore, these data not only enable one to predict in part the sequence of phase changes on heating the clays but also indicate the possible phase assemblages to be expected, thus avoiding the mistakes which may be found in the recent literature.

The equilibrium data also provide checks on the use of differential thermal analysis data in the determination of any thermodynamic parameters of the clay phases. These data tell us what the equilibrium products of a reaction should be and also provide the means to obtain equilibrium values for the decomposition temperature, heat of reaction, etc.

Base-Exchange Capacity and Other Properties

In the study of the base-exchange capacity values of montmorillonites one insoluble problem faces the experimentalist dealing with natural minerals and that, of course, concerns the purity of the sample. It is not yet established, for instance, whether or not the base-exchange capacity varies with substitution in the various layers. Synthetic samples with fairly rigid chemical purity and superior mineral homogeneity should

provide much better standards. For a study of the "expansion" of the structure with organic bases these same samples would also provide a controlled series with the "seat of charge" varying from all in the tetrahedral to all in the octahedral layer, the total charge also being variable. The use of synthetic clays with different ions of varying polarizability within the sheets would also provide the means to check the effect of intra-layer bonds on the exchange capacity and other properties. The notoriously difficult process of assigning frequencies in the infra-red to bonds in complex structures such as silicates may also be helped by using completely substituted clays and empirical methods.

LIMITATIONS ON THE APPLICATION OF PHASE EQUILIBRIUM DATA TO GEOLOGICAL PROBLEMS

Unfortunately it is necessary to qualify any remarks on phase equilibrium data applied to systems of interest to clay mineralogists with some statement regarding the applicability and limitations of such data. Normally phase equilibrium data are sufficiently well-established that they do not need to be hedged about. However, in most hydrothermal systems the data themselves need considerable interpretation. Some of these basic problems will be dealt with in the following paragraphs.

The Question of Attaining Equilibrium

The problem usually encountered in dealing with phase equilibrium in oxide systems is that of sluggishness of reaction making it difficult to reach equilibrium. If this is true of the high temperature region, let us say above 1000°C, it becomes infinitely more difficult in the region below, say, 500°C in which most reactions of interest to clay mineralogists take place. An excellent example may be cited from the system MgO-Al₂O₃-SiO₂-H₂O investigated by both Roy (1952) and Yoder (1952). One may heat a mixture of the clinocllore composition at 600°C and 10,000 psi for 25 days, and on examination the product is found to contain a 7A two-layer phase analogous to kaolinite. One can hardly be blamed for thinking that equilibrium has been attained. However, if the same run were continued for another week or two it would be found that the 7A phase had started to disappear and a 14A chlorite of the same composition started to form, showing that the latter was the stable phase and the former had persisted metastably for several hundred hours. In this case the structural rearrangement is relatively small, but another striking example is found in the system alumina-silica-water. Ehlers (1953) has reported, for instance, that in several runs in this system with a 1:2 Al₂O₃:SiO₂ ratio he obtained quartz and corundum together. He repeated the work making runs of up to 60 days in length and could not obtain any other results. As a matter of fact, Roy and Osborn (1952) have shown that there are seven possible phases which make such an assemblage only metastable — and in this study of the system we have shown how at

equilibrium the assemblage changes with temperature, the correct mineral sequence at moderate pressures being kaolinite, hydralsite + pyrophyllite, pyrophyllite + andalusite, quartz + andalusite, quartz + mullite, and even at the highest temperature cristobalite + mullite. In this case the starting materials were the source of the trouble. These two examples merely show the difficulty of obtaining equilibrium in these systems of importance to clay mineralogy, and, therefore, the care which must be exercised in the attaining and use of the results.

An objection which can be raised in connection with several of the reactions studied hydrothermally is that in actual point of fact equilibrium has not been approached from both sides of the reaction. This is especially true of the simple binary systems involving the sesquioxides and water. In most cases it has been found, for example, that it is impossible to convert the anhydrous oxide into a hydrate by a direct process. Similarly one cannot make the monohydrates revert to the trihydrate by any kind of treatment in the stability range of the latter. While this is a serious flaw in the data, many other arguments can be used to show the reasonableness of the interpretation given. Thus, for example, while even a five-month "grinding" of corundum at 10,000 psi and 375°C fails to give diaspore, the following lines of evidence suggest that diaspore is nevertheless the stable phase in this range:

- i. Gibbsite or boehmite if heated under appropriate conditions to 375°C will yield this phase.
- ii. An "amorphous" or metastable form of Al_2O_3 will transform to diaspore under these conditions.
- iii. The limit is indicated by runs in which, for example, the low temperature or amorphous phases yield diaspore at, say 395°C even after several weeks, whereas at 400°C (5° higher) corundum is formed in a few hours.

Metastable Persistence of Phases

Allied to the above phenomena but distinct from them are the questions of metastability and persistence of phases. Several examples of this are well known and they have considerable importance in the relation of phase equilibrium data to geological observations. These are cases in which the equilibrium assemblages have been determined and in which, owing to the conditions of the experiment, other phases are observed. The best known case, of course, is that of cristobalite. It is well known and established both by direct experiment and from thermodynamic calculations that quartz is the stable form of silica up to 867°C; but in almost all our runs, even of several weeks duration, silica appears first as cristobalite. Its occurrence in nature even in the vicinity of quartz does not disprove the validity of the diagram for the silica system but is merely a commentary on the importance of metastability. Thus the occurrence of diaspore at room temperature does not invalidate the equilibrium diagram for the system

$\text{Al}_2\text{O}_3\text{-H}_2\text{O}$; it only indicates that diasporite persists metastably. Similarly boehmite in the presence of excess water is also metastable at room temperature, a common condition in several millions of tons of sedimentary rock. On the other hand, not every phase assemblage is likely to persist metastably outside its stability range. It is especially rare to find an assemblage persisting to temperatures higher than the equilibrium one for any but the shortest time. For this reason the stability maxima of the phases which have been studied are of considerably greater importance in geological applications. Thus, under usual geological conditions and pressures of say 1-2000 atmospheres, 400°C is undoubtedly the maximum temperature of persistence of kaolinite as 575°C is the maximum for pyrophyllite.

The Region of Water-Deficiency and the Effect of Inert Pressure

The concept of the water-deficient region is quite essential to a proper understanding of phase equilibria in the presence of water; the idea was treated in a most lucid manner by Bowen and Tuttle (1949). Many misconceptions regarding this persist, especially concerning the relation between the "water-deficient" areas and the effect of "inert" pressure. Any set of equilibrium assemblage triangles for a three-component system involving water provide a simple example. Thus in Figure 1 are shown three triangles representing the equilibrium assemblages at three temperatures in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$. The water-deficient regions in the three triangles are outlined by QMKDC in IV, QMHMu in V, and OPHMu in VI. It is quite obvious that within these regions lie all the three-phase assemblages which do not involve water as one phase. Owing to the experimental methods which have to be used to date, it is not possible to make runs in the area in which water is not a phase. As a matter of fact, the gross compositions of all the runs are always very near the water apex, and must, of course, lie within a triangle with water as a corner, or within a tetrahedron with water as an apex (in a four-component system). Thus, consider a triangle such as pyrophyllite-andalusite-diasporite (in triangle IV.); each of the two-phase assemblages and the three-phase assemblage are very common in nature. Experimentally however, one cannot realize this assemblage at all; since if a mixture of, say, the andalusite composition is taken with an excess of water, the products move into the triangle kaolinite + diasporite + water. Abortive attempts to work in these regions have, of course, been made using such devices as sealed platinum tubes containing the total desired composition. What needs to be stressed here is only the fact that theory foresees these regions of water deficiency in which the present experimental methods are useless, and that the existence of several common assemblages in nature which cannot be duplicated should therefore be expected. Before leaving the point it should be mentioned that the water-deficient regions

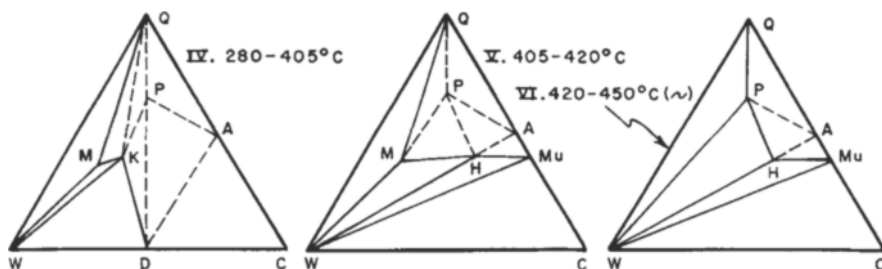


FIGURE 1.—Sequence of phase-equilibrium triangles showing compatible stable phases in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at a pressure of 10,000 psi. The areas “behind” the solid lines (looking from the water apex) constitute in each case the water-deficient region; they are defined by the joins QMKDC, QMHMu, and QPHMu, in triangles IV, V, and VI respectively.

consist therefore of an assemblage which can be considered as a “dry” system.

The quite different problem of inert pressure is conveniently discussed in terms of Figure 2. Figure 2a shows a simple representation of a phase diagram in the form of a cube — or a series of planes parallel to the back face ABCD. The diagram ABCD (see Fig. 2d) is a typical p-t representation for a three-component system. The “x” axis represents “t” as is usual, and the “z” axis total pressure. The “y” axis represents increasing partial pressure of water, so that on the ABCD face all the pressure is water pressure, on the intermediate planes the partial pressure of water decreases and on the front face we have no water at all, let us say all N_2

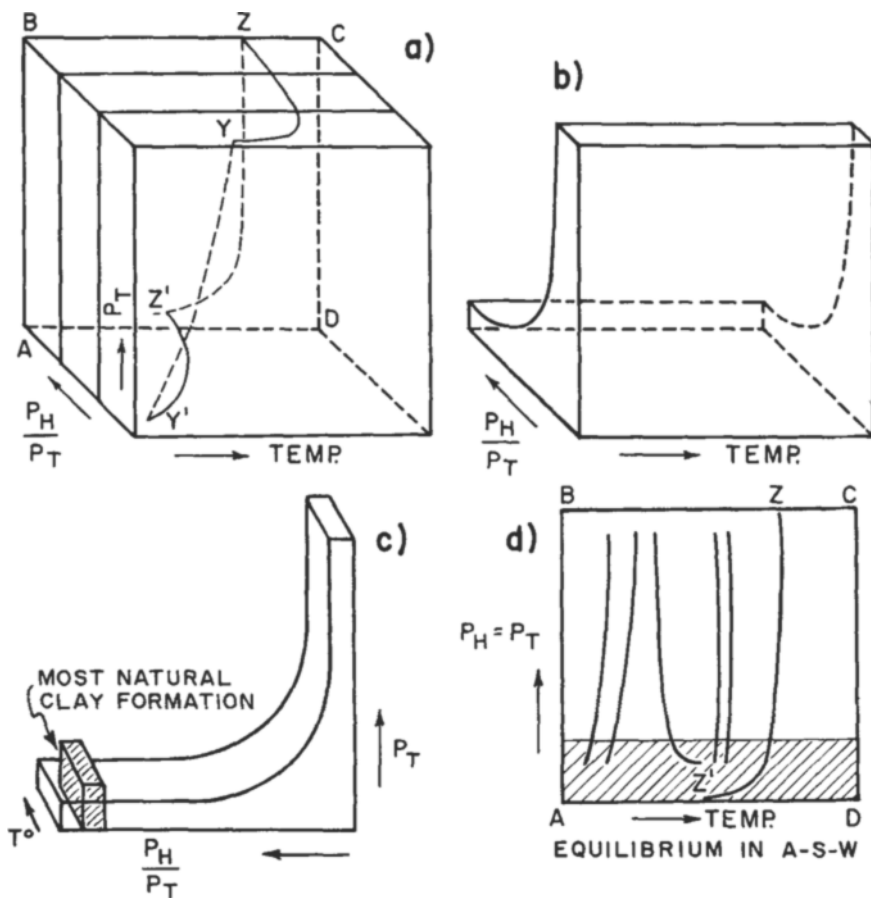


FIGURE 2. — A three-dimensional representation of p-t curves for the system alumina-silica-water illustrating the effect of change of partial pressure of water on the system.

a) Schematic cubical phase diagram, the three axes being temperature, total pressure (P_T) and $\frac{\text{partial pressure of water } P_H}{\text{total pressure } (P_T)}$. The latter variable varies from 0 on the front face to 1 on the back face ABCD. ABCD, the rear face of the cube, is a typical p-t diagram for say a three component system with water as one component. The planes parallel to ABCD and approaching the front are similar diagrams determined under particular conditions where $\frac{P_H}{P_T}$ is held at some fixed fraction throughout the pressure range. ZZ' is a typical univariant curve and Z'Y, Y'Y, YZ represent the changes likely to occur if P_T and $\frac{P_H}{P_T}$ are varied together (see text).

b) Shows an approximate volume (see text) of the cube shown in part a) in which the univariant curves determined on the back face are most likely to be drastically changed in both position and slope.

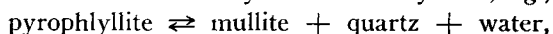
c) The same volume as in b) showing also the region in this diagram in which most natural clay minerals form.

d) Univariant curves for the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (Roy and Osborn, 1952) plotted as determined on P-T diagram where $P_H = P_T$, i.e., on the back face of the cube in a). The shaded area shows the only fair extent of overlap between the experimental work and the probable region of natural clay formation.

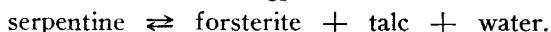
pressure. All published hydrothermal work to date refers only to the face ABCD. A criticism of recent hydrothermal phase equilibrium studies which is partly justified contends that while one may continue to extend the "z" axis upwards to attain the greater pressures supposedly encountered within the earth, one does not actually simulate natural conditions since in nature there could be great pressures and at the same time relatively low partial pressures of water. It is further claimed that this would radically alter the equilibrium relationships. Some comments on this criticism are listed below to show that no dramatic changes should be expected in phase assemblages except at very low partial or total pressures of water.

a) It is, of course, obvious that no difference would be made to any reaction which does not involve water itself as a phase in the reaction being studied. Thus, the transition boehmite-diaspore will be affected by pressure strictly according to the Clausius-Clapeyron relation whether that pressure be H_2O , N_2 , rocks, Coca-Cola or anything else that does not enter the solid phases. Similarly the relations among the anhydrous aluminosilicates will not be affected by changing the partial pressure of water; i.e., the shape and position of the univariant curves showing the dependence of such reactions on temperature and pressure will be unchanged in going from the front face to the back face of Figure 2a.

b) In reactions such as the dehydration of a hydrate, e.g.,



or



One recognizes that there must be a very great difference between the positions of the p-t curves for these reactions when the front and back faces are compared, the temperatures being much lower in the former. From this there also emerges the important point that the *maximum* temperature of persistence of a hydrated phase has been definitely determined when its p-t curve has been studied by current experimental methods.

A survey of the several p-t curves of this type which have already been determined shows that pressure changes from 5000 psi to 30,000 psi water pressure do not make a very marked difference in the stability maximum; the change is frequently of the order of 10-20°C (and reflects, of course, the shape of the compressibility curve of water and the relative incompressibility of the solid phases). With this knowledge it is not difficult to predict that the only region within the cubical diagram (Fig. 2a) in

which we may expect major changes in the position of the p-t curve will be those in which the partial pressure of water falls below approximately this same value. In Figure 2d is shown very approximately the shapes for the p-t curves in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ as they would appear with a linear pressure scale extending to 30,000 psi. One curve ZZ' — the uppermost with respect to temperature — for the dehydration of pyrophyllite has been shown in greater detail and extrapolated to lower pressures than those for which actual data are available. The shaded area shows the region of most clay-mineral formation and a part of this area in Figure 2d may be called the area of "drastic change". The changes in the curve ZZ' may now be followed within the cube. On the top surface, the line ZY traces the path of the decomposition temperature of pyrophyllite (with the total pressure maintained at the maximum, say 30,000 psi) as the partial pressure of water is lowered. Simple reasoning suggests a shape for ZY as shown, resembling ZZ' on the P-T face ABCD, and in fact being somewhat steeper than the latter. That is to say that at a total pressure of 30,000 psi one would not expect major changes in the decomposition temperatures of hydrates until one reached the very low partial pressure (say some hundreds of psi) region. By similar reasoning one can speculate on the shape of YY' and Z'Y'. Z'Y' lies on a total pressure plane (parallel to top and bottom faces of the cube) where the pressure lies within the region of "drastic change". Y and Y' also lie on a plane within this region, but one which is parallel to and very close to the front face of the cube. The slopes of YY' and Y'Z' will be much more gradual. One can, therefore, construct an approximate volume of "drastic change" as has been done in Figure 2b. It is unnecessary to point out that this volume and the curves such as ZY and YY' are not quantitative but merely diagrammatic representations of generalized conclusions. The volume shown gives us only an idea of the region into which the experimental data obtained so far cannot be extrapolated. Finally, one can see that there is no particular connection between the region of water deficiency and the effects of "inert" pressure. Water-deficient composition regions can exist in quaternary and ternary systems in any part of the cube from the back face to the front; only the front face is an entirely water-deficient region. However, it should be mentioned that equilibria between phases which lie in the water-deficient region are not affected by movement from back to front in the cube, as others, of course, can be.

Fortunately, with regard to clay minerals, there is for all intents and purposes always an excess of water, and total pressure is nearly all water pressure. The same volume as in Figure 2b is shown turned around in Figure 2c and in addition we show a probable volume in which most clay minerals form (excepting some micas and chlorites). Most of them probably form under conditions which can be represented essentially on the back face of the cube. The volume shown is a little displaced for convenience. However, although the clay minerals can form in a relatively

low-pressure region, this is not always the case, since a burial of a mere one-half mile is shown as the height of the highest pressure of the region of "drastic change". It is not unlikely that many sediments have been formed or re-formed at pressures greater than this. In Figure 2d is shown the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system, and the shaded area is the one of greatest interest to genetic clay mineralogy. It will be seen that our data have not been extended to very low pressure areas, but that nevertheless many of the data are directly applicable to the stability of clay minerals. It also indicates that the phase equilibrium data should be extended to lower water pressures to be of greater value to the clay mineralogist.

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DISCUSSION

R. E. Grim. — Have you been able to synthesize apparent tubular forms of halloysite?

Rustum Roy. — No, I omitted to mention that we cannot claim to have synthesized tubular endellite or halloysite. We keep trying, however, and we believe it is possible that we have made it and not recognized it. This is because we have rejected the products of all runs which appeared to be amorphous to x-rays. However, at the low temperatures at which endellite is stable, runs of even several months duration yield products which are not crystalline to x-rays. Recently we have been using single crystal electron-diffraction techniques and have obtained very interesting data on several so-called amorphous products encountered in clay mineralogy. On examining some of the products from our low-temperature runs we do find that the intensity distribution is decidedly more like that of halloysite than that of kaolinite examined under the same conditions. However, the percentage of what may be called "tubes," even by a prejudiced viewer, was seen to be very small in the electron microscopic observations.