

## SOIL MINERALS IN THE $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ SYSTEM AND A THEORY OF THEIR FORMATION\*

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**Abstract**—An attempt has been made to assemble the best thermodynamic information currently available for soil minerals in the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system at 25°C and 1 atm. Montmorillonite is included by considering its aluminum silicate phase. Diagrams are presented so that the stability of the minerals can be visualized in relation to the ionic environment. Although the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system is a very simple one compared to soils and sediments, the stability diagrams depict a mineral stability sequence and mineral pair associations that are in good agreement with natural relations.

According to the stability diagram, mineral pairs that can form in intimate association are gibbsite-kaolinite, kaolinite-montmorillonite, and montmorillonite-amorphous silica. Forbidden pairs are amorphous silica-kaolinite, amorphous silica-gibbsite, and montmorillonite-gibbsite. The formation of intimate mixtures of three or more of these minerals is also forbidden. The stability diagrams predict ion activity relationships that are in reasonable agreement with those obtained from soils and sediments.

Amorphous silica probably limits high silica levels, with montmorillonite also forming at high silica levels. Kaolinite forms at intermediate and gibbsite at low silica levels. These minerals in turn probably control the activity of aluminum ions at a level appropriate to the pH. The formation of gibbsite, kaolinite, montmorillonite and amorphous silica appears to be controlled by a combination of kinetics and equilibria. That is, the kinetic dissolution of unstable silicates appears to control the  $\text{H}_4\text{SiO}_4$  level. The new mineral(s) most stable at that  $\text{H}_4\text{SiO}_4$  level appear to precipitate in response to solution equilibria.

### INTRODUCTION

IT HAS been shown that the composition of the ocean depends upon the composition of river waters, which in turn depends upon the ground waters whose composition depends upon the minerals they contact (Mackenzie and Garrels, 1966; Bricker and Garrels, 1967; Stumm and Leckie, 1967). The objective of this paper is to contribute to the knowledge of mineral formation in soils and sediments. The general hypothesis of this paper is that the ground water-mineral system is a two-way street. That is, not only do minerals help determine the composition of ground waters, the composition of the ground waters also determines the course of mineral formation in the soil or sediment.

There are too many important minerals that form in soils and sediments to consider them all at once, yet is very difficult to understand the formation of a single mineral in isolation from others that compete for the same elements. The necessary

compromise is to consider only those minerals that seem most important in competing for a limited group of elements. The  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system at 25°C and 1 atm has been chosen for two reasons. First, it is a relatively simple system, yet contains minerals that make up large percentages of many soils and sediments. Second and most important, stability information is available for the minerals that need to be considered.

The organization of this paper involves an initial discussion of individual mineral stabilities within several mineral groups. The stability relations between minerals in these groups are displayed in a series of diagrams. Next, a single mineral from each group is selected for inclusion in a stability diagram representing the whole  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system. Finally, the apparent applicability of the simple  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system to the much more complicated soil system is considered.

### AMORPHOUS SILICA AND QUARTZ

Quartz is an important mineral because it is so abundant in soils and sediments. The determination of quartz solubility has been difficult, partly because of the influence of more soluble particles adhering to a quartz surface which may itself have more soluble regions. When these more soluble

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substances are removed chemically, a fundamental problem in determining quartz solubility remains. The problem appears to derive from the high activation energy required to alter the Si—O—Si bond (Stöber, 1967). This results in a very slow dissolution rate and a negligible precipitation rate for quartz at room temperature. The negligible precipitation rate prevents the establishment of a true thermodynamic equilibrium at room temperature. Perhaps the best procedure is to determine quartz solubility at higher temperatures, where dissolution and precipitation rates are appreciable, and to extrapolate these values to room temperature. Siever (1962) has extrapolated high temperature data of his own, together with those of Kennedy (1950), Fournier (1960) and van Lier (1959), and obtained a solubility for quartz at 25°C of 10.8 ppm SiO<sub>2</sub> or 1.80 × 10<sup>-4</sup> M. An independent extrapolation of their own data by van Lier, DeBruyn and Overbeek (1960) confirms this

value, which is indicated by the quartz solubility line in Fig. 1 (upper left) intersecting the abscissa at a pH<sub>4</sub>SiO<sub>4</sub> of 3.74 (the ordinate of this diagram is explained later).

The very slow dissolution rate and the negligible precipitation rate of quartz at room temperature resulting from the high activation energy of the Si—O—Si bond have two very important consequences in the weathering of quartz. The very slow dissolution rate means that quartz will be relatively "resistant to weathering" and the negligible precipitation rate means that quartz is unlikely to control any silica equilibria. One result is that many silica equilibria are controlled at silica levels considerably in excess of quartz solubility, some by amorphous silica.

Essentially, amorphous silica is an unstable intermediate that accumulates because it precipitates more readily than quartz (much amorphous silica is produced biochemically from undersaturated

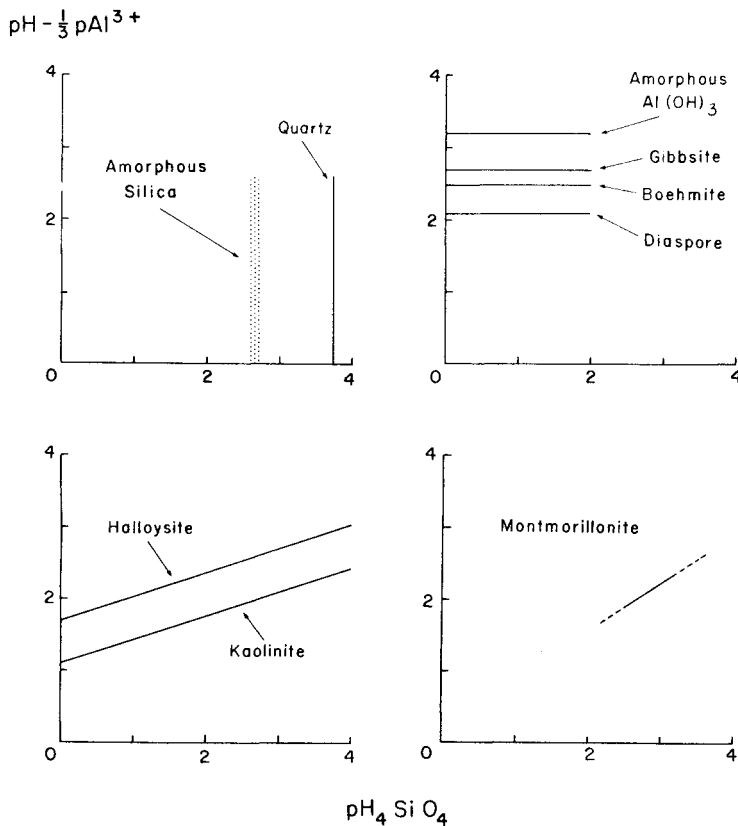


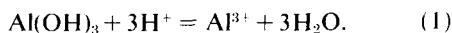
Fig. 1. Stability diagrams for some minerals in the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system at 25°C and 1 atm. The area above or to the left of the solubility lines represents supersaturation, whereas the area below or to the right represents undersaturation.

solutions) and yet converts to more stable forms slowly (for example, opal in sea water that has not altered to quartz in over 60 million yr, Rex, 1967). The exact solubility of amorphous silica is difficult to determine. There is a tendency for samples to remain supersaturated indefinitely, probably because the precipitation reaction, although much faster than for quartz, is still slow on the time scale of laboratory experiments. As with quartz, the best approach appears to be high temperature equilibration with subsequent extrapolation to room temperature. Morey, Fournier and Rowe (1964) found the data of both Hitchen (1935) and Kitahara (1960) fit the same straight line, which extrapolates to 115 ppm at 25°C. The room temperature dissolution data of Morey *et al.* (1964) for amorphous silica indicate an initial supersaturation followed by a very slow approach to equilibrium at 115 ppm  $\text{SiO}_2$ . This same value is obtained from supersaturated hot spring waters (but only after months or years of equilibration and only in alkaline solutions, where precipitation seems to be more rapid).

Most solubility values for amorphous silica range between 115 and 140 ppm  $\text{SiO}_2$  (Alexander, Heston and Ihler, 1954; Krauskopf, 1956). The writer has had a montmorillonite sample in contact with a solution of 151 ppm  $\text{SiO}_2$  for over 3 yr at pH 2.74, with no apparent tendency for the concentration of  $\text{SiO}_2$  to decrease. The range in values from 115 to 150 ppm  $\text{SiO}_2$  probably represents the same range of concentrations that can be supported by amorphous silica in soils and sediments, hence its solubility is given as a range from  $\text{pH}_4\text{SiO}_4$  of 2.60 to 2.72 in Fig. 1 (upper left).

#### ALUMINUM HYDROXIDE AND OXYHYDROXIDES

Consider the dissolution of aluminum hydroxide



The equilibrium constant,  $K$ , equals  $\text{Al}^{3+}/(\text{H}^+)^3$ , assuming the activity of aluminum hydroxide and water is unity. Taking negative logarithms,  $\text{pK} = \text{pAl}^{3+} - 3\text{pH}^+$ , Rearranging and dividing by 3 to permit direct use of experimental pH values,  $\text{pH} - \frac{1}{3}\text{pAl}^{3+} = -\frac{1}{3}\text{pK}$ . This is the equation of a straight line of slope zero and an intercept of  $-\frac{1}{3}\text{pK}$  on the ordinate in Fig. 1 (upper right). The quantity  $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ , related to the chemical potential of aluminum hydroxide (Schofield and Taylor, 1955) is sometimes referred to as the aluminum hydroxide potential. It is a convenient way of representing two variables on one ordinate.

*Amorphous aluminum hydroxide.* From (1),

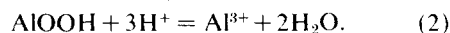
$$\Delta G_r = \Delta G_{\text{Al}^{3+}} + 3\Delta G_{\text{H}_2\text{O}} - 3\Delta G_{\text{H}^+} - \Delta G_{\text{Al}(\text{OH})_3(\text{amorph.})}$$

where  $\Delta G_r$  is the standard free energy of reaction. The  $\Delta G$  of amorphous aluminum hydroxide is approximately  $-271.9$  kcal per mole\*, so that  $\Delta G_r = -115.0 + 3(-56.7) - 3(0.0) - (-271.9) = -13.2$  kcal. From the equation  $\Delta G_r = 1.36 \text{ pK}$ ,  $\text{pK} = -13.2/1.36 = -9.7$  and  $-\frac{1}{3}\text{pK} = 3.2$ , which is the point of intersection of the amorphous aluminum hydroxide solubility line with the ordinate in Fig. 1 (upper right).

Because most mineralogical identification techniques require crystalline material, there is little direct evidence to indicate that amorphous aluminum hydroxide is an important constituent in soils and sediments. Amorphous aluminum hydroxide is commonly the first solid phase to form during the precipitation of aluminum hydroxides and oxyhydroxides in the laboratory and one might anticipate similar results in the field. However, previous work of Frink and Peech (1962) and computations by the author from the data of Pierre *et al.* (1932) have seldom indicated a value of  $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$  for soil solutions as high as that supported by amorphous aluminum hydroxide. This does not necessarily mean that amorphous aluminum hydroxide is not present in these soils, but it does indicate that, if present, it does not control the aluminum hydroxide potential.

*Gibbsite*, also  $\text{Al}(\text{OH})_3$ , is a common constituent of soils and sediments.† A range of stabilities between amorphous aluminum hydroxide and well-crystallized gibbsite has been reported, apparently depending upon the crystallinity of the gibbsite. Well-crystallized gibbsite is much less soluble than amorphous aluminum hydroxide, with a  $\Delta G$  of  $-274.2$  kcal per mole (Kittrick, 1966a). From (1) we may compute  $\Delta G_r$  for the dissolution of gibbsite to be  $-10.9$  kcal and  $-\frac{1}{3}\text{pK}$  to be 2.7 as indicated in Fig. 1 (upper right).

*Boehmite.* The oxyhydroxides of aluminum appear to be even less soluble than the hydroxides, although their variation in stability with crystallinity is not well established. Consider the equation



As before,  $\text{pH} - \frac{1}{3}\text{pAl}^{3+} = -\frac{1}{3}\text{pK}$ . The  $\Delta G$  for boehmite is given as  $-217.5$  kcal per mole by Latimer (1952) and by Fyfe and Hollander (1964).

\*The source of thermodynamic values not otherwise indicated is Appendix 2 of Garrels and Christ (1965).

†Bayerite, also  $\text{Al}(\text{OH})_3$ , has a slightly different structure from that of gibbsite. It can be synthesized in the laboratory and with a  $\Delta G$  of about  $-274.0$  kcal per mole (Hem and Roberson, 1967), it appears to be about as stable as gibbsite. Because it appears to be rare (Wayman, 1963) or nonexistent (Federickson, 1952) in nature, it need not be considered in this investigation.

A recent NBS Technical Note (Wagman *et al.* 1968) gives it as  $-218.2$  kcal per mole. Using the most recent value,  $\Delta G_r = -115.0 + 2(-56.7) - 3(0.0) - (-218.2) = -10.2$  kcal,  $pK = -10.2/1.36 = -7.50$ , and  $-\frac{1}{3}pk = 2.5$ , as shown in Fig. 1 (upper right).

*Diaspore.* Wagman *et al.* (1968) indicate the  $\Delta G$  of diaspore to be  $-220$  kcal per mole of  $AlOOH$  (Fyfe and Hollander, 1964, give  $-219.5$  kcal). From (2)  $\Delta G_r$  is computed to be  $-6.2$  kcal and  $-\frac{1}{3}pk$  to be 2.1 for diaspore, as shown in Fig. 1 (upper right). Thus, diaspore appears to be the most stable mineral of the group.\*

*Relative stabilities and the influence of time.* All explanations for the distribution of the aluminum hydroxides and oxyhydroxides in soils and sediments ultimately depend upon what one believes their relative stability to be. A typical compilation of data on the hydroxides and oxyhydroxides published a few years ago indicated boehmite and diaspore to be of approximately equal stability, with gibbsite more stable than either. The recent work previously cited has provided more accurate data, especially for gibbsite, indicating the stability sequence, amorphous aluminum hydroxide < gibbsite < boehmite < diaspore.†

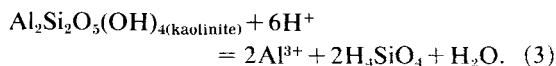
Considering that gibbsite is less stable than boehmite or diaspore and yet is much more common in such geologically-young features as soils, it appears that on a geologic timescale gibbsite is a metastable fast-former that alters to more stable forms relatively slowly. The product of the laboratory dehydration of gibbsite is normally boehmite rather than the more stable diaspore (Deer, Howie and Zussman, 1962). A similar sequence appears to take place with time in nature where Bridge

(1952) observes that gibbsite predominates in Cenozoic bauxites, with some admixture of boehmite. Bauxites of Mesozoic age are principally boehmite, with some admixture of gibbsite, especially in the younger Mesozoic. Diaspore deposits appear to be generally confined to the Paleozoic.

Factors determining the alteration rate from amorphous aluminum hydroxide to gibbsite to boehmite to diaspore may be such things as local climate and associated substances with catalytic properties. These factors are unlikely to be uniform over the earth or over vast time periods. Thus, in spite of a few exceptions noted by Bridge and by Keller (1964) in the time sequence, the present correlation of thermodynamic stability and time seems remarkably good.

### KAOLINITE

Consider the equation



Assuming the activity of water and kaolinite is unity,  $pK = 2pAl^{3+} + 2pH_4SiO_4 - 6pH^+$ , and  $pH - \frac{1}{3}pAl^{3+} = \frac{1}{3}pH_4SiO_4 - \frac{1}{6}pK$ . This is the equation of a line of slope  $\frac{1}{3}$  with an intercept of  $-\frac{1}{6}pK$ .

For the most crystalline kaolinite encountered so far,  $\Delta G = -903.8$  kcal per mole (Kittrick, 1966b). Taking  $\Delta G_{H_4SiO_4}$  to be  $-313.0$  kcal per mole (computed from the data of van Lier *et al.*, 1960; Wise, *et al.*, 1963), from (3),  $\Delta G_r = 2(-115.0) + 2(-313.0) + (-56.7) - 6(0.0) - (-903.8) = -8.9$  kcal. Then  $pK = -8.9/1.36 = -6.5$  and  $-\frac{1}{6}pK = 1.1$ , which is the intersection of the kaolinite solubility line of slope  $\frac{1}{3}$  with the ordinate in Fig. 1 (lower left).

As a first approximation, it is assumed that the lower limit of crystallinity for kaolinite may be represented by the halloysite of Barany and Kelley (1961), from a deposit near Bedford, Indiana. Adding  $-15.0$  kcal per mole to their calorimetrically-determined value, to take into account a revised heat of solution for quartz, one obtains  $-898.6$  kcal per mole for the  $\Delta G$  of halloysite.\*

\*The other mineral that might be considered in this group is corundum. There are indications that it forms in small amounts in bauxite deposits (Keller, 1964). With a  $\Delta G$  of  $-378.2$  kcal per mole of  $Al_2O_3$  (Wagman, *et al.*, 1968), the intersection of its solubility curve with the  $pH - \frac{1}{3}pAl^{3+}$  ordinate in Fig. 1 (upper right) is 2.7. Thus, the stability of corundum is essentially identical to that of highly crystalline gibbsite. It may form at the same time in nature as gibbsite, but at a much slower rate. A correspondingly slower rate of alteration may explain its persistence in nature, even after gibbsite has altered to more stable minerals.

†Reesman and Keller (1968) present extensive original  $\Delta G$  data on the high-alumina and clay minerals. Their paper should be consulted, but for experimental or computational reasons their  $\Delta G$  values for minerals may not be directly comparable to those used in this paper. For example, for a more direct comparison one would have to use the same values for  $Al(OH)_4^-$  and  $H_4SiO_4$  in the computations.

\*Nacrite and dickite are two minerals with identical formulas, and structures basically similar to kaolinite. Both are relatively rare and are thought to be of hydrothermal origin. The  $\Delta G$  of dickite is  $-902.4$  kcal per mole (Barany and Kelley, 1961, corrected for the revised heat of solution of quartz). Thus dickite is somewhat less stable than crystalline kaolinite at  $25^\circ C$ , but much more stable than halloysite.

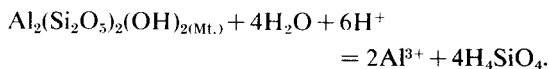
For the dissolution of halloysite according to equation (3),  $\Delta G_r = -10.4$  and  $-\frac{1}{6} \text{pK} = 1.7$ , resulting in the solubility line in Fig. 1 (lower left). It can be seen that halloysite is unstable relative to crystalline kaolinite.

Values of  $\Delta G$  down to  $-902.5$  kcal per mole were found to be due to kaolinite of proportionately lesser crystallinity than the material that gave  $-903.8$  kcal per mole (Kittrick, 1966b). However, many kaolinite samples contained small X-ray-amorphous particles whose stability ranged down to  $-899.2$  kcal per mole, approximately that of the halloysite from Bedford, Indiana. Thus, there not only appears to be a gradation from halloysite to crystalline kaolinite for samples from different sources, but also, a similar gradation within a sample from a single source. Based upon structural and field evidence, it has often been suggested that kaolinite may form from halloysite. Similarly, the stability evidence strongly suggest that halloysite is a fast-forming metastable precursor to crystalline kaolinite.

#### MONTMORILLONITE

Montmorillonite cannot be completely defined in the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system, because it contains at least one other element. However, because it often occurs associated with kaolinite and particularly with amorphous silica, it would be of great value to represent montmorillonite on the same ordinates chosen for the minerals previously discussed. This may be done as a first approximation by considering the other element(s) (usually Mg) in montmorillonite as an impurity substituting for aluminum in what is essentially an aluminum silicate with the pyrophyllite formula  $\text{Al}_2(\text{Si}_2\text{O}_5)_2(\text{OH})_2$ .

Consider the following dissolution equation for montmorillonite (Mt.)



Assuming the activity of water to be unity,  $\text{pK} = 2\text{pAl}^{3+} + 4\text{pH}_4\text{SiO}_4 - 6\text{pH}^+ - \text{pMt.}$ , and  $\text{pH} - \frac{1}{3}\text{pAl}^{3+} = \frac{2}{3}\text{pH}_4\text{SiO}_4 - \frac{1}{6}(\text{pK} + \text{pMt.})$ . This is the equation of a line of slope  $\frac{2}{3}$  whose intercept is  $-\frac{1}{6}(\text{pK} + \text{pMt.})$ .

The intercept of the montmorillonite solubility line in the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system will depend upon the activity of the aluminum silicate phase in the particular montmorillonite in question, but the slope of the solubility line will be  $\frac{2}{3}$  if an aluminum silicate phase of the indicated composition is controlling the equilibrium. A solubility line of approximately two-thirds slope has been found for

three montmorillonites.\* Thus, to a first approximation at least, the solubility line for the aluminum silicate phase of montmorillonite may be displayed as shown in Fig. 1 (lower right).

#### STABILITY DIAGRAM

Having established the stabilities of some common soil minerals in the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system, the next step is to compare their stabilities in a single diagram. Such a diagram would be applicable to soils and sediments where the minerals considered control the activity of  $\text{H}^+$ , or  $\text{Al}^{3+}$ , or  $\text{H}_4\text{SiO}_4$ , or some combination of the three. In a strict thermodynamic sense, the only two minerals that need be displayed on the stability diagram are quartz and diaspore. Amorphous silica, montmorillonite, kaolinite and gibbsite are all thermodynamically unstable fast-forming intermediates relative to quartz and diaspore. However, amorphous silica, montmorillonite, kaolinite and gibbsite predominate on the time scale of weathering of most soils and sediments and thus, it is *their* relative stabilities that are displayed in Fig. 2.

#### Phase relationships

The composition of each phase, P, in the present system can be expressed by the three components, C, which are  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{H}_2\text{O}$ . A given stability line in Fig. 2 represents two phases, the mineral and solution. According to phase rule,  $F = C + 2 - P$ , so there are three degrees of freedom, F in the system. By limiting ourselves to the weathering environment we fix two degrees of freedom (temperature and pressure), so that  $F = C - P$ . Thus each stability line in Fig. 2 has only one degree of freedom. That is, for a selected value of  $\text{pH}_4\text{SiO}_4$  there is a single equilibrium value of  $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$ , and *vice versa*.

Where two minerals are at equilibrium with the same solution in Fig. 2, we have a three-phase system with no degrees of freedom. Thus the point where two solubility lines cross represents an invariant point. The values of both  $\text{pH}_4\text{SiO}_4$  and  $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$  are fixed for that mineral pair. This has been demonstrated experimentally for the

\*The montmorillonites used were from Belle Fourche, South Dakota, from Otay, California, and from Aberdeen, Mississippi. The solubility of the 0.2–5  $\mu$  fraction after Fe-removal treatment was determined from under-saturation and from supersaturation. (Kittrick, J. A. Montmorillonite stability from solubility measurements in the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system at 25°C and 1 atm. Presented before Div. S-9, American Society of Agronomy Meetings, Nov. 12, 1968. New Orleans, La.)

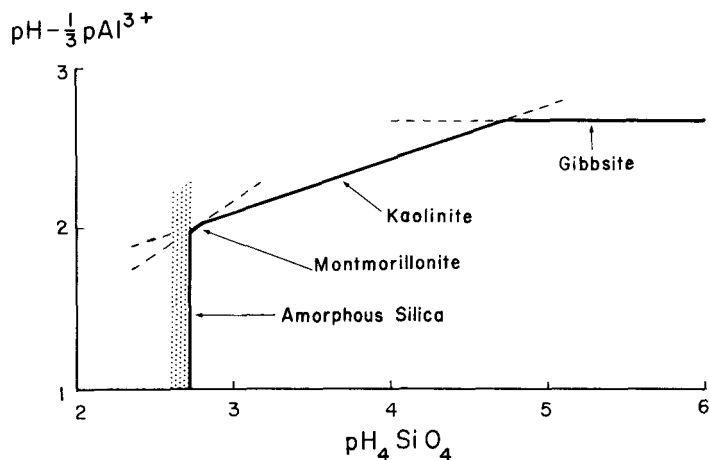


Fig. 2. Composite stability diagram for some minerals in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$  system at  $25^\circ\text{C}$  and 1 atm. The stability line of each mineral is solid where it is the most stable mineral of the group.

gibbsite-kaolinite pair (Kittrick, 1967) and for the montmorillonite-kaolinite pair.\* In the present system, no more than two minerals can be in equilibrium at a time and they must be minerals whose solubility lines intersect.

#### *Ion activity relationships*

The interpretation of Fig. 2 is strongly influenced by the choice of ordinates. Subject to later justification,  $\text{pH}_4\text{SiO}_4$  has been chosen as the independent variable, and  $\text{pH} - \frac{1}{3}\text{pAl}^{3+}$  as the dependent variable. Thus, for a given activity of  $\text{H}_4\text{SiO}_4$  in Fig. 2, the most stable mineral supports the lowest aluminum hydroxide potential. Where a given mineral is the most stable of the group, its solubility line is shown solid. The metastable extension is shown dotted. A solution composition above or to the left of the solid line is supersaturated with respect to at least one mineral, whereas a point below or to the right indicates undersaturation.

Notice the change in mineral stability with change in silica activity in Fig. 2. At the far left the system is supersaturated with respect to amorphous silica. As the  $\text{H}_4\text{SiO}_4$  activity decreases ( $\text{pH}_4\text{SiO}_4 > 2.7$ ), montmorillonite briefly supports the lowest aluminum hydroxide potential and is the most stable mineral. Kaolinite becomes

more stable than montmorillonite at a  $\text{pH}_4\text{SiO}_4$  of about 2.8 and then kaolinite supports the lowest aluminum hydroxide potential until the silica activity decreases to a  $\text{pH}_4\text{SiO}_4$  of about 4.7. In the low silica environment above  $\text{pH}_4\text{SiO}_4$  of 4.7, the most stable mineral of the group is gibbsite.

The logarithmic scale in Fig. 2 tends to obscure the real extent of the stability range of the minerals involved. Silica concentrations in natural waters are normally reported in terms of ppm  $\text{SiO}_2$ . In these terms, the stability range for amorphous silica in Fig. 2 is approximately 150 ppm  $\text{SiO}_2$  and higher, the stability range for montmorillonite in Fig. 2 is from about 150 to 96 ppm  $\text{SiO}_2$ , the stability range for kaolinite is from about 96 to 1 ppm  $\text{SiO}_2$ , and the stability range for gibbsite is from 1 to 0 ppm  $\text{SiO}_2$ .

#### **APPLICATION OF THE STABILITY DIAGRAM TO THE WEATHERING OF SOILS AND SEDIMENTS**

The essential correctness of the  $\Delta G$  values for amorphous silica, kaolinite and gibbsite is indicated by agreement between values derived from independent measurement methods (measurement of solubilities compared to measurement of enthalpy and entropy changes). Since  $\Delta G$  for montmorillonite has been measured only by solubility methods so far, its validity must be evaluated by a comparison with natural relations.

Since the Al ion species is pH dependent, it would be reasonable to have the ordinate in Fig. 2 in terms of an Al ion species that is dominant in the pH range where most weathering occurs. That is approximately within a pH unit of 7. At the present time there is little definite that can be

\*The montmorillonites used were from Belle Fourche, South Dakota, from Otay, California, and from Aberdeen, Mississippi. The solubility of the 0.2-5  $\mu$  fraction after Fe-removal treatment was determined from undersaturation and from supersaturation. (Kittrick, J. A. Montmorillonite stability from solubility measurements in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$  system at  $25^\circ\text{C}$  and 1 atm. Presented before Div. S-9, American Society of Agronomy Meetings, Nov. 12, 1968, New Orleans, La.)

said about the dominant Al ion species in the near-neutral pH range, except that it is polynuclear. This does not affect the *validity* of the equations or the graph derived from them. They hold at any pH, for however much of the total Al is  $\text{Al}^{3+}$ .

The *applicability* of the equations and the graph cannot be checked by direct analysis of soil solutions in the near-neutral pH range, because it is not possible to determine what portion of the total Al in solution is  $\text{Al}^{3+}$ . This drawback is more theoretical than actual, because most of the minerals support too little Al and certainly too little  $\text{Al}^{3+}$  in solution to measure in the near-neutral pH range. For example, the  $\text{pAl}^{3+}$  supported by amorphous aluminum hydroxide at pH 7 will be 11.4. Much lower levels of  $\text{Al}^{3+}$  will usually be supported by the other minerals. Fortunately, the applicability of Fig. 2 (and the applicability of mineral stabilities derived from equilibrium thermodynamics) to the weathering of soils and sediments can be tested by a comparison of predicted quantities with what is known of natural mineral relations. The considerable amount that is known about the mineral structures, their reactions, and especially their field relationships, will be a great advantage in such a comparison.

#### *Phase relationships*

General agreement between Fig. 2 and field relationships is indicated by the fact that as the  $\text{H}_4\text{SiO}_4$  activity decreases, one proceeds through stages 9 (montmorillonite), 10 (kaolinite), and 11 (gibbsite) of the weathering sequence of Jackson *et al.* (1948). The minerals in the weathering sequence are adjacent and in the proper order.

A much more detailed comparison of theory with nature is permitted by mineral associations. The only minerals in Fig. 2 that can form in intimate association with one another are those adjacent to invariant points. Permitted associations are gibbsite-kaolinite, kaolinite-montmorillonite, and montmorillonite-amorphous silica. Non-permitted associations are gibbsite-montmorillonite, gibbsite-amorphous silica, kaolinite-amorphous silica, and three or more of these minerals.\*

\*Keep in mind the dependence of these associations upon the minerals selected for inclusion in the diagram. For example, if a situation exists where quartz (or a dehydrated silica phase of similar solubility) forms, then kaolinite-quartz is a permitted pair and montmorillonite has no stability area at all. The fact that montmorillonite is widespread indicates that this is not a common occurrence. If a situation exists where diaspore forms readily, then diaspore-montmorillonite is a permitted association and diaspore-kaolinite is forbidden, or vice versa, the stability line intersections are too close to state definitely. As mentioned previously, if quartz and diaspore both form readily, then none of the other minerals are stable.

By consulting a review article such as Jackson and Sherman (1953), it can be seen that some of the permitted associations are very common particularly montmorillonite-kaolinite and gibbsite-kaolinite. However, in order to prove the positive assertion, that the diagram in Fig. 2 holds for weathering in soils and sediments, one must show that the proper associations always occur. The negative assertion permits a simple, much more sensitive test, because only one exception is required. The author knows of no associations where non-permitted minerals have definitely been shown to precipitate in intimate mixture, but it is frequently a difficult thing to determine if minerals have formed in place or are merely a mechanical mixture transported from other locations. Where such a determination is possible, investigators can readily check the applicability of Fig. 2 to mineral weathering.

#### *Ion activity relationships*

It must be recognized at the outset that for several reasons the ion activity levels depicted in Fig. 2 can only be considered approximate. For example, the stability line for each mineral will vary somewhat depending upon the crystallinity of the mineral. Further, the lines represent the stability of mineral specimens as determined by dissolution and other methods. These methods determine the ion activities that the mineral specimen will support. Similar minerals may not necessarily *precipitate* in nature at exactly these ion activity levels. An important uncertainty still exists in some of the mineral stability determinations and also in some of the thermodynamic values required to compute  $\Delta G$  values for these minerals. For example, the gibbsite and kaolinite  $\Delta G$  values used in this paper are dependent upon the  $\Delta G$  of  $\text{Al}^{3+}$ , which may have to be revised.

As more is learned about the stability of these minerals, their stability lines will be placed more exactly. It would be unwise at this time to insist upon detailed agreement between ion activity levels indicated in Fig. 2 and those found in natural situations. Fortunately, the theory of mineral formation developed from Fig. 2 will depend much more upon the general geometry of the graph than upon the exact placement of solubility lines.

*Aluminum hydroxide potential as the dependent variable.* The selection of  $\text{pH} - \frac{1}{3} \text{pAl}^{3+}$  as the dependent variable was based upon the geochemistry of Al. Al is usually concentrated at the site of weathering. The activity of ionic Al (as opposed to Al complexed by organic substances) appears to be controlled at very low levels in natural waters. More Al appears in acid than in neutral waters, so the control is evidently pH-

dependent. The precipitation of new minerals containing Al is the most likely reason for the concentration of Al at the site of weathering. These new minerals are probably responsible for the pH-dependent control of Al at low levels. It is likely that the aluminum hydroxide potential in soils and sediments often depends upon which of the minerals in Fig. 2 is controlling it. Thus, the aluminum hydroxide potential is the logical choice as the dependent variable in Fig. 2.

In order to compare aluminum hydroxide potential levels predicted in Fig. 2 with those found in nature, determinations of the latter must definitely be equilibrium measurements and must be made where mineralogical determinations indicate one or two of the minerals in Fig. 2 are forming. So far as the author is aware, none of the available data meet these requirements. It is encouraging to note, however, that much of the rather limited aluminum hydroxide potential data on soils and sediments do fall in the range indicated in Fig. 2 (see for example Lindsay, Peech, and Clark, 1959).

*H<sub>4</sub>SiO<sub>4</sub> as the independent variable.* Whatever controls H<sub>4</sub>SiO<sub>4</sub> in solution is extremely important, because as the independent variable, the activity of H<sub>4</sub>SiO<sub>4</sub> determines which of the minerals in Fig. 2 will precipitate. The control of mineral precipitation by the H<sub>4</sub>SiO<sub>4</sub> activity is in accord with field observations which suggest that H<sub>4</sub>SiO<sub>4</sub> levels are an important factor in secondary mineral formation in soils and sediments. For example, high H<sub>4</sub>SiO<sub>4</sub> levels appear to be required for montmorillonite formation (Jackson, 1964; Wildman, Jackson and Whittig, 1968).

The control of H<sub>4</sub>SiO<sub>4</sub> activity seems likely to be mostly a matter of kinetics (see for example, Wollast, 1967). This should involve the rate of dissolution of unstable silicates, the rate of removal of H<sub>4</sub>SiO<sub>4</sub> from the water (along with most of the Al from solution) by precipitation of new minerals, and the rate of movement of H<sub>4</sub>SiO<sub>4</sub>-bearing waters out of the system. Acquaye and Tinsley (1965) have shown that in some soils at least, the level of H<sub>4</sub>SiO<sub>4</sub> is seasonal and may be strongly influenced by plant uptake.

Most soils and sediments contain unstable primary minerals that have a high ratio of Si to Al (such as olivines, pyroxenes, amphiboles and feldspars), whose dissolution rate could control the H<sub>4</sub>SiO<sub>4</sub> level. Where appreciable primary minerals are not present (absent initially, or weathered out completely, or perhaps weathered out in the finer size fractions), the dissolution of a secondary silicate such as montmorillonite or kaolinite may control the H<sub>4</sub>SiO<sub>4</sub> level that determines which mineral of a lesser Si content will form. This mechanism would require that

normal weathering proceed from minerals of high silica content to minerals of low silica content. Considering the silica-containing minerals in the weathering sequence of Jackson *et al.* (1948), this appears to be exactly the case.

According to Fig. 2, the H<sub>4</sub>SiO<sub>4</sub> levels over which gibbsite, kaolinite and montmorillonite may form range from zero to about 150 ppm SiO<sub>2</sub>. Since the levels of H<sub>4</sub>SiO<sub>4</sub> in solution in soils and sediments are postulated to be kinetically controlled, a comparison of H<sub>4</sub>SiO<sub>4</sub> levels required in Fig. 2 with those found in nature is much easier than was a similar comparison for the aluminum hydroxide potential. The values for H<sub>4</sub>SiO<sub>4</sub> in nature do not have to be at equilibrium and no evidence for the concomitant formation of the minerals in Fig. 2 is required. The measured silica activity in solutions in contact with acid soils generally ranges from less than 1 ppm up to about 40 ppm SiO<sub>2</sub> (McKeague and Cline, 1963; Miller, 1967). Because amorphous silica is precipitated in at least some soils and sediments, the silica activity must exceed approximately 150 ppm SiO<sub>2</sub> at times. This may happen when the soil solution is concentrated by drying, but can also happen if enough acid is available to dissolve unstable primary minerals sufficiently.\* It is evident that the solution silica levels required in Fig. 2 have either been measured or are indicated indirectly in soils and sediments.

*Kinetics and weathering intensity.* Montmorillonite, kaolinite and gibbsite represent successive stages of increasing weathering intensity. If the stability of these minerals is dependent upon successively decreasing levels of H<sub>4</sub>SiO<sub>4</sub> activity in solution, which in turn are a matter of kinetics, then kinetics and weathering intensity should be related. As mentioned previously, there are at least four factors that appear to be important in determining solution H<sub>4</sub>SiO<sub>4</sub> levels, (1) the rate of dissolution of unstable silicates, (2) the rate of precipitation of stable silicates, (3) the rate of movement of H<sub>4</sub>SiO<sub>4</sub>-bearing solutions out of the system and (4), the rate of plant uptake. Rates (1), (2) and (4) and their variation from place to

\*Two eastern Washington loess samples (Palouse C, Thatuna C) and an interbasaltic sediment containing abundant primary minerals were equilibrated to determine the silica activities they would support. 30-1g samples were treated for 2 months with water to which HCl was added to maintain approximately the same pH which had been used to determine the stabilities of montmorillonite, kaolinite and gibbsite (pH 3.2-3.5). The first solution analysis showed 245 to 275 ppm SiO<sub>2</sub>. Five months later there were 209-218 ppm SiO<sub>2</sub>, still supersaturated with respect to amorphous silica.



place are largely unknown, but rate (3) can be inferred from rainfall and drainage data.

As shown by Jackson *et al.* (1948), high rainfall is one of the characteristics of the more intense weathering situations where gibbsite forms. Thus, large amounts of water might pass through the system so rapidly as to permit only a low silica activity from the dissolution of unstable silicates. Further, relatively intense weathering may have already removed most of the more reactive silicates or their finer size fractions, which would also help to keep the silica activity low.

Jackson *et al.* also suggest impeded drainage to indicate a less intense weathering situation. The common association of montmorillonite with impeded drainage suggests a longer contact time between solution and unstable soil minerals, resulting in the higher  $\text{H}_4\text{SiO}_4$  activities required for montmorillonite stability. High  $\text{H}_4\text{SiO}_4$  activities could also be maintained by relatively static solutions in gas vesicles in minerals such as volcanic glass, with which montmorillonite is commonly associated. Montmorillonite may actually serve as a geologic indicator mineral of silica levels at near-saturation with respect to amorphous silica.

If the  $\text{H}_4\text{SiO}_4$  activity is largely a matter of kinetics as suggested, areas where the minerals of Fig. 2 form do not necessarily have to be widely separated in time and space. If mineral stability depends in part upon rate of water movement, then different minerals may be stable during different seasons, or in closely adjacent parts of the landscape where different drainage conditions prevail (for example, Sherman and Uehara, 1956). In any event, it is evident from natural relations that kinetics and weathering intensity are related.

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**Résumé**—On a tenté de rassembler toutes les informations thermodynamiques actuellement disponibles sur les minéraux terrestres dans le système  $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$  à 25°C et 1 atm. La montmorillonite y est incluse compte tenu de sa phase de silicate d'aluminium. Des diagrammes sont présentés de façon à ce que la stabilité des minéraux puisse être représentée en relation avec l'environnement ionique. Bien que le système  $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$  soit très simple par comparaison aux sols et sédiments, les diagrammes de stabilité décrivent une séquence de stabilité minérale et des associations minérales paires qui sont en accord avec les relations naturelles.

Selon le diagramme de stabilité, les paires minérales qui peuvent se former en association intime sont gibbsite-kaolinites, kaolinites-montmorillonites, et silice amorphe montmorillonite. Les paires interdites sont les silices amorphes kaolinites, silices amorphes gibbsites, kaolinites montmorillonites, et silices amorphes montmorillonites. La formation de mélanges intimes de 3 ou plus de ces minéraux est également interdite.

Le diagramme de stabilité prédit des rapports d'activité ionique en accord raisonnable avec ceux obtenus à partir des sols et des sédiments. Les silices amorphes limitent probablement des niveaux de silice élevés, avec de la montmorillonite se formant également à ces mêmes niveaux de silice. Les kaolinites se forment à des niveaux intermédiaires et les gibbsites à des niveaux de silice très bas. A leur tour, ces minéraux contrôlent probablement les activités des ions d'aluminium à un niveau approprié au pH. La formation de gibbsite, de kaolinite, de montmorillonite et de silice amorphe paraît être contrôlée par une combinaison de cinétique et d'équilibre. C'est à dire que la dissolution cinétique de silices instables semble contrôler le niveau  $\text{H}_4\text{SiO}_4$ . Le nouveau minéral le plus stable à ce niveau  $\text{H}_4\text{SiO}_4$ , semble précipiter en réponse à la solution d'équilibre.

**Kurzreferat**—Es wurde versucht, die besten derzeit erhältlichen thermodynamischen Daten für Bodenminerale im  $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$  System bei 25°C und 1 Atmosphäre zu vereinigen. Montmorillonit wurde unter Berücksichtigung seiner Aluminiumsilikatphase miteingeschlossen. Aus den beigefügten Kurvenbildern lässt sich die Beständigkeit des Minerals in Bezug auf die Ionenumgebung beurteilen. Obwohl das  $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$  System im Vergleich mit Böden und Ablagerungen ein sehr einfaches ist, zeigen die Beständigkeitskurven eine Mineralbeständigkeitsfolge und Mineralpaarungen, die gut mit natürlichen Verhältnissen übereinstimmen.

Gemäss den Beständigkeitskurven können folgende Mineralpaare in enger Association geformt werden: Gibbsit-Kaolinit, Kaolinit-Montmorillonit und Montmorillonit-amorphe Kieselsäure. Verboten sind Paare von amorpher Kieselsäure-Kaolinit, amorpher Kieselsäure-Gibbsit und Montmorillonit-Gibbsit. Die Bildung enger Mischungen von drei oder mehr dieser Minerale ist ebenfalls ausgeschlossen. Die Beständigkeitskurven weisen auf Ionenaktivitätsbeziehungen hin, die recht gut mit den aus Boden- und Ablagerungsproben erhaltenen übereinstimmen.

Amorphe Kieselsäure schliesst wahrscheinlich hohe Kieselsäureniveaus aus während Montmorillonite auch bei hohen Kieselsäureniveaus geformt werden. Kaolinit bildet sich bei mittleren, und Gibbsit bei niedrigen Kieselsäureniveaus. Diese Minerale bestimmen wahrscheinlich die Aktivität der Aluminiumionen a einem dem pH entsprechenden Niveau. Die Bildung von Gibbsit, Kaolinit, Montmorillonit und amorpher Kieselsäure scheint durch eine Kombination von Kinetik und Gleichgewichten bestimmt zu werden, d.h. die kinetische Auflösung unbeständiger Silikate scheint das  $\text{H}_4\text{SiO}_4$  Niveau zu bestimmen. Die neuen auf diesem  $\text{H}_4\text{SiO}_4$  Niveau beständigsten Minerale scheinen durch die Lösungs-gleichgewichte zur Ausfällung gebracht zu werden.

**Резюме**—Сделана попытка собрать наиболее достоверные термодинамические данные для минералов почв, образующихся в системе  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  при 25°C и 1 атм. Монтмориллонит включен в связи с его алюмосиликатной составной частью. Диаграммы даны так, чтобы можно было составить представление о стабильности минералов в зависимости от их ионного окружения. Хотя система  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  очень проста в сравнении с почвами и осадками, диаграммы эти изображают и последовательность стабильности и парные ассоциации минералов в хорошем согласии с природными соотношениями.

В соответствии с диаграммами стабильности, пары минералов, образующих тесные ассоциации, таковы: гиббсит—каолинит, каолинит—монтмориллонит, монтмориллонит—аморфный кремнезем. К запрещенным парам относятся: аморфный кремнезем—каолинит, аморфный кремнезем—гиббсит и монтмориллонит—гиббсит. Образование тонких смесей из трех (или более) минералов также запрещено. Диаграммы стабильности позволяют предсказать соотношения активности ионов, удовлетворительно согласующиеся с найденными при изучении почв и осадков.

Аморфный кремнезем, вероятно, ограничивает верхний предел активности кремнезема, причем монтмориллонит образуется также при высокой активности кремнекислоты. Образование каолинита происходит при промежуточных, а образование гиббсита—при низких уровнях активности кремнезема. Эти минералы, вероятно, в свою очередь контролируют активность ионов алюминия в соответствии со значением pH. Образование гиббсита, каолинита, монтмориллонита и аморфного кремнезема, как кажется, контролируется совместным влиянием и кинетики и равновесия, т.е. кинетика растворения неустойчивых силикатов, по-видимому, контролирует уровень активности  $\text{H}_4\text{SiO}_4$ ; новый минерал или минералы, которые наиболее устойчивы при этом уровне активности  $\text{H}_4\text{SiO}_4$ , по-видимому, осаждаются в соответствии с равновесными отношениями в растворе.