SOIL MINERALS IN THE SYSTEM $\text{Al}_2\text{O}_3$-$\text{SiO}_2$-$\text{H}_2\text{O}$: PHASE EQUILIBRIUM MODEL

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Abstract—Mineralogical reactions in the system $\text{Al}_2\text{O}_3$-$\text{SiO}_2$-$\text{H}_2\text{O}$ are examined and an isothermal, isobaric cross-section of the portion of the system applicable to soil genesis, is determined. The relevance of the cross-section to soil mineralogy is discussed.

INTRODUCTION

Kittrick (1969) examined the stability of a number of soil minerals in the system $\text{Al}_2\text{O}_3$-$\text{SiO}_2$-$\text{H}_2\text{O}$ at 25°C and 1 atm total pressure by a method based principally on solution chemistry. One of his conclusions was that: "In a strict thermodynamic sense, the only two minerals that need be displayed on the stability diagram are quartz and diaspore" (Kittrick, 1969, p. 161). If this were true, the application of the principles of phase equilibrium to soils would be an exercise in futility for even in those soils with a clay mineralogy of a composition that falls completely within this system, the assemblage quartz-diaspore is virtually unknown. Consequently, in this paper stability relations are re-examined from the standpoint of the Phase Rule and using the methods of Schreinemakers.

To apply the concepts of phase equilibrium to the natural world involved a number of simplifications the most important of which are choice of components and choice of conditions. Kittrick's (1969) reasons for the choices that he made are equally applicable to the present case. The system $\text{Al}_2\text{O}_3$-$\text{SiO}_2$-$\text{H}_2\text{O}$ at 25°C and 1 atm total pressure is firstly: "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" (Kittrick, 1969, p. 157). It is worth adding that this choice of pressure-temperature conditions offers a reasonable model for the surface of the earth.

The important soil phases found within the ternary system are water, quartz, gibbsite, boehmite and kaolinite. Less common ones are bayerite, nordstrandite, dickite, nacrite and halloysite. Minerals of this system not known to form under earth-surface conditions are corundum, diaspore, pyrophyllite and andalusite, kyanite and sillimanite (Fig. 1).

Of the minerals mentioned all those known to be authigenic in soils are confined to the compositional triangle $\text{AlOOH}$-$\text{SiO}_2$-$\text{H}_2\text{O}$ with all possible tie lines drawn. For phase identification refer to the caption of Fig. 1.

Fig. 1. The system $\text{Al}_2\text{O}_3$-$\text{SiO}_2$-$\text{H}_2\text{O}$ showing the compositions of phases. A—water; B—gibbsite, bayerite, nordstrandite; C—boehmite, diaspore; D—corundum; E—andalusite, sillimanite, kyanite; F—quartz; G—halloysite; H—kaolinite, dickite, nacrite; I—pyrophyllite.

(a) by a coincidence of two phases at a single point (e.g. boehmite and diaspore); (b) by colinearity of three phases (e.g. water–halloysite–kaolinite);
Table 1. 113 possible reactions in the system AI0(OH)-SiO2-H2O

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
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<tbody>
<tr>
<td>(a)</td>
<td>Al(OH)3 = Al(OH)3</td>
</tr>
<tr>
<td>(b)</td>
<td>AIOOH = AIOOH</td>
</tr>
<tr>
<td>(c)</td>
<td>AI2Si2O5(OH)4 = AI2Si2O5(OH)4</td>
</tr>
<tr>
<td>(d)</td>
<td>AI2Si2O5(OH)42H2O = AI2Si2O5(OH)4 + 2H2O</td>
</tr>
<tr>
<td>(e)</td>
<td>AI(OH)3 = AIOOH + H2O</td>
</tr>
<tr>
<td>(f)</td>
<td>AI2Si2O5(OH)4 + 2AIOOH = 2AI0(OH)3 + 2SiO2</td>
</tr>
<tr>
<td>(g)</td>
<td>2AI2Si2O5(OH)4 = AI2(OH)3 + 4AIOOH + 2SiO2</td>
</tr>
<tr>
<td>(h)</td>
<td>2AI2Si2O5(OH)4 = 2AI2Si2O5(OH)4 + 2H2O</td>
</tr>
<tr>
<td>(i)</td>
<td>AI2Si2O5(OH)4 + 2AIOOH = 2AI2Si2O5(OH)4 + 2H2O</td>
</tr>
<tr>
<td>(j)</td>
<td>AI2Si2O5(OH)4 + 2AI2Si2O5(OH)4 + 2H2O</td>
</tr>
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</table>

(c) by a crossing of tie lines (e.g. kaolinite–water and gibbsite–quartz);
(d) by one phase lying within a triangle formed by
three other phases (e.g. halloysite in the triangle
gibbsite–quartz–water).

Application of these criteria to Fig. 2 yields 113 possible reactions (Table 1) not all of which will be considered for reasons given below.

Firstly, gibbsite alone of the Al(OH)3 polymorphs (reaction a) and kaolinite of the AI2Si2O5(OH)4 polymorphs (reaction c) are sufficiently well known thermodynamically or in soils, to merit attention.

Secondly, reactions involving diaspore, halloysite or pyrophyllite are ignored for reasons revealed in the next three paragraphs.

The polymorphic transition Boehmite = Diaspore (reaction b) cannot be assessed on the basis of free energy data (Table 2) because the ΔGf values for the two phases are not precise enough. Principally on the authority of Kennedy (1959) diaspore is taken to be the phase stable at low pressure even though it has never been formed at 1 atm (whereas boehmite has). Kennedy’s argument rests on the negative slope of the solid–solid transition curve, such a slope being distinctly unusual for reactions of this kind. However, later workers suggest a positively sloped transition curve (Torkar and Krischner, 1963) which offers no obstacle to regarding boehmite as the phase stable at low pressure. Furthermore, reaction (a) has been reversed at 1 atm (unpublished results), a finding that is again consistent with the stability of boehmite at low pressure.

The reaction halloysite = kaolinite + 2 water (reaction d) defines the upper stability limit of halloysite. The free energy change of the reaction is $-1178 \pm 1.9$ Kcal at 25°C and 1 atm total pressure. Thus at the surface of the earth halloysite can be expected to dehydrate, yielding kaolinite. This reaction has in fact been accomplished in the laboratory at atmospheric pressure, though it has never been reversed, a fact that is again consistent with halloysite being a metastable phase under earth-surface conditions.

Thermodynamic examination of pyrophyllite-bearing reactions (based on ΔGf values for pyrophyllite from Zen (1972)) is inconclusive. It is generally accepted however, that pyrophyllite is not synthesised at atmospheric pressure much below 300°C (Deer et
Soil minerals in the system Al$_2$O$_3$–SiO$_2$–H$_2$O

Al., 1962, p. 117). Between 300 and 500°C it is readily produced with kaolinite and boehmite, an assemblage suggestive of reaction (i). Roy and Osborn's (1954) experiments in the system Al$_2$O$_3$–SiO$_2$–H$_2$O enabled them to construct 700 kg/cm$^2$ compatibility triangles that show pyrophyllite as a phase in the H$_2$O absent region of the triangle at temperatures above 280°C and as a phase in the H$_2$O present region of the triangle above 420°C. A decrease in pressure to 140 kg/cm$^2$ did not do much to change the equilibria and in the absence of contrary data it is assumed that Roy and Osborn's (1954) results may serve as a guide to pressures as low as 1 atm.

Conclusion

In the system AlOOH–SiO$_2$–H$_2$O, only those reactions involving the phases water, quartz, gibbsite, boehmite and kaolinite need be considered. These are reactions (e), (h), (i) and (r) of Table 1, which are rewritten in Table 3 in terms of the appropriate polymorphs.

THE PRESSURE–TEMPERATURE (PT) DIAGRAM

Consider the general case of 5 phases at equilibrium in a three component system. By the Phase Rule, the equilibrium is invariant and may be represented on a PT diagram by a point. From the point, 5 univariant curves emanate, each representing equilibrium between 4 phases. Between any 2 univariant curves lies a divariant space in which 3 phases are at equilibrium.

Let the 5 phases of the invariant point be water, quartz, gibbsite, boehmite and kaolinite. In terms of these phases the system AlOOH–SiO$_2$–H$_2$O has one degenerate feature: the colinearity of water, gibbsite and boehmite. This type of system has been treated by Schreinemakers (1916, pp. 818–819) and his solution gives the sequence of univariant curves shown in Fig. 5 which is drawn so that the dehydration reactions have slopes of the right sense. The question that arises now is: which pair of univariant curves bracket the conditions of the earth's surface?

Gibbsite is stable up to temperatures of about 70°C or more (unpublished data) at 1 atm pressure so that the surface conditions are on the low temperature side of reaction (e). Furthermore, experiments in the system Al$_2$O$_3$–SiO$_2$–H$_2$O (Polzer, Hem and Gabc, 1967) at 25°C and 1 atm pressure show that gibbsite will only precipitate at very low SiO$_2$ concentrations. At a concentration of 300 x 10$^{-5}$ moles SiO$_2$/l. it is replaced by a phase with the morphology of tubular kaolinite. If in fact we assume this to be kaolinite then the tie line kaolinite–water would be stable under earth-surface conditions. That this is likely to be the case is confirmed by Kittrick's (1970) synthesis of kaolinite in an aqueous environment under similar earth-surface conditions. The conclusion is that earth-surface conditions lie on the high temperature side of reaction (r). In other words 25°C and 1 atm total pressure are bracketed by reactions (r) and (e). Thus the isothermal, isobaric phase diagram for a model of the surface of the earth is triangle A of Fig. 3.

Reaction (r) is also amenable to thermodynamic examination. It shows a negative free energy of reaction in the direction of kaolinite + water so that assemblages kaolinite + water + gibbsite and kaolinite + water + quartz are at divariant equilibrium at 25°C and 1 atm total pressure. The assemblages of triangle A are consistent with this.

A COMPARISON WITH OTHER WORKERS

Figure 4 enables the results of this paper to be directly compared with Kittrick (1969), Garrels and Christ (1965) and Roy and Osborn (1954).

Kittrick's diagram is based on $\Delta G_{25^\circ}$ values for minerals within the system. It is open to the criticism that the thermodynamic data are not sufficiently precise to enable unequivocal choices between alternatives to be made. This is especially emphasised by the fact that it appears likely that much of the thermodynamic data for aluminum bearing minerals may be out by as much as 3500 cal per mole of Al (Robie, 1973). Such a fact does not inspire much confidence in either Kittrick's reported limits of error, nor indeed in those reported in Table 2. A specific point covered in Chesworth (1972) is that Kittrick's contention that the aluminum hydroxides form a stability sequence with diaspore as the most stable, is not tenable.
Garrels and Christ (1965) show amorphous silica rather than quartz at the SiO$_2$ pole of their diagram. Kittrick (1969) also recognizes that amorphous silica rather than quartz will control any natural equilibria mainly because of kinetic reasons, i.e. the slow precipitation–dissolution rate of quartz itself. However amorphous silica is an ‘unstable intermediary’ (Kittrick, 1969, p. 158) so that it has no place on a phase equilibrium diagram. It is expected that amorphous silica-rich phases will age to yield quartz (Harder and Flehmig, 1970) and indeed quartz can form without the intervention of an amorphous stage (Mackenzie and Gees, 1971).

Finally, the results of Roy and Osborn (1954) are extrapolations from high pressure–temperature hydrothermal studies and as such must be used with caution. In particular it is worth noting that (a) endellite was never actually synthesized under any conditions and (b) Al-montmorillonite was only synthesized at temperatures in excess of 407°C and pressures in excess of 8000 psi. Thus it is difficult to justify the inclusion of these minerals on a low temperature, low pressure phase diagram.

**DISCUSSION**

There is a general feeling amongst soil scientists that soils, being so obviously in process of change, are not open to interpretations based on phase equilibrium. However, there is sufficient data available to show that the clay mineralogy of many soils is made up of assemblages that appear in the equilibrium diagram for AlOOH–SiO$_2$–H$_2$O at 25°C and 1 atm total pressure. To demonstrate this it is necessary firstly to point out that water is present as a separate phase in the vast majority of soils. Thus if any part of the phase diagram is applicable to soils it will be the water-present part, i.e. the part wherein the appropriate assemblages of divariant equilibrium are water + kaolinite + quartz and water + kaolinite + gibbsite. Here, no tie line exists between quartz and gibbsite which are therefore incompatible phases. Gardner (1970) reached the same conclusion on thermodynamic grounds though the precision of the thermodynamic parameters that he uses is not good enough to prove the point unequivocally.

A good demonstration of the approach to equilibrium mineralogy is provided by Delvigne’s (1965) data for weathering under tropical conditions. Specifically, he studied the weathering of plagioclase under tropical conditions and observed four sequences:

1st sequence: plagioclase → gibbsite
2nd sequence: plagioclase → gels → gibbsite
3rd sequence: plagioclase → gels → gibbsite + kaolinite
4th sequence: plagioclase → gels → gibbsite → kaolinite

For present purposes the sequence is less important than the end stage. The first two sequences are
obtained from the rock lowest in silica: norite. The
third sequence comes from an intermediate rock of a
charnockitic suite and a dolerite, both low in quartz,
whilst the last sequence is found in weathered grano-
diorite relatively high in quartz. Thus the higher the
silica content of the system the more the clay miner-
alogy approaches that which would be expected in a
silica-oversaturated environment, e.g. kaolinitic
assemblages. On the other hand in quartz-free environ-
ments gibbsitic assemblages are found. The one discord-
ant feature is provided by sequence 3 where gibbsitic
assemblages are found in rocks containing free quartz
As has been shown, the gibbsite + quartz pair is not
stable under earth-surface conditions. This discord-
dancy is an important one and should be emphasized.
The presence of gibbsite as an early product of weath-
ering of silica oversaturated rocks is probably a much
commoner phenomenon than is normally accepted
(see for example the important work of Dejou et al.,
1972).

A possible explanation for the appearance together
of incompatible phases is that local (Thompson, 1959)
or mosaic (Korzhinskii, 1959) equilibrium is more
likely than general equilibrium, in weathering systems.
Weathering proceeds mainly by surface reaction and
even in silica-oversaturated rocks such as granite there
exist minerals with surfaces that are relatively alumina-
rich and silica-poor, (see, e.g. Devore, 1962, p. 31, Com-
positions of Feldspar Surfaces). It is not inconceivable
that gibbsite might grow on such surfaces even though
free quartz were present in a different part of the rock.
The various and different mineral surfaces in a weath-
ering system would on this hypothesis be considered as
different domains of local equilibrium. The overall clay
mineralogy of a given weathered rock or soil would
then be expected to be a mixture of the possible com-
patible assemblages. In the system under considera-
tion, e.g. gibbsite, kaolinite and quartz could all be
found together.

There are of course other soils that contain other
suites of clay minerals; illites, smectites and vermicu-
lites for example. Thus montmorillonite is common in
the clay fraction of podsolos (Brydon et al., 1968). How-
ever, the clay fraction of such soils is not necessarily in
a state of mineralogical disequilibrium even though it
is dominated by phases other than those that appear
in the system AIOOH—SiO2—H2O at 25°C and 1 atm.
In fact it is inappropriate to discuss these soils in terms
of this system: more components, particularly CaO,
MgO, K2O and Na2O need be added.

On the basis of evidence from Australian soils (Ches-
worth, 1973a), weathering trends converge on the
system SiO2—Al2O3—Fe2O3—H2O of which the three
component system under consideration is an import-
ant part. The closer this ‘residua system’ (Chesworth,
1973b) is approached the more the soil—clay fraction
must be treated as indifferent phases.

Fig. 5. Generalized weathering trends from the field of
the common igneous rocks (stippled area) towards the residua
system of weathering. The clay fraction of weathered mater-
ials in field A is dominated by primary silicates, smectites,
randomly interstratified clay minerals and possibly vermicu-
lites: of weathered materials in field B by smectites and
ilites: and that of weathered materials in field C, by alu-
minate and iron oxides and hydroxides and kaolinite. Only
compositions within field C can be usefully approximated
by the system AIOOH—SiO2—H2O, and to do this the iron
oxides or hydroxides must be treated as indifferent phases.

CONCLUSION

The configuration of the system AIOOH—SiO2—
H2O at 25°C and 1 atm total pressure has been worked
out from a basis of experimental work and the appli-
cation of the Gibbs Phase Rule and the topological
techniques of Schreinemakers. The result (Fig. 4a)
differs markedly from other workers’ versions, in par-
ticular with those that rely on thermodynamic data.

There are strong reasons for doubting the published
thermodynamic data in this system though this does
not necessarily mean that the ‘phase rule model’ is the
best one. A good reason for believing that the diagram
developed here is closer to the truth than previous
attempts, is that soils with a clay-fraction of appro-
priate composition tend to contain combinations of
quartz, kaolinite and gibbsite in that fraction. This is
what would be predicted on the basis of Fig. 4a.

All this suggests that conventional techniques of
analysis of physico-chemical systems, utilizing the
phase rule, have an important part to play in studies
of the origin of soil. It is too early to predict where this
might lead but analogous techniques played a signifi-
cant role in systematizing studies of the genesis of
igneous and metamorphic rocks.

REFERENCES

Brydon, J. E., Kodoma, H. and Ross, G. J. (1968) Miner-
alogy and weathering of the clays in orthic podzols and
other podzolic soils in Canada: 9th Int. Soil Sci. Congress
Vol. 3, pp. 41—51.


Kennedy, G. C. (1959) Phase relations in the system $\text{Al}_2\text{O}_3 - \text{H}_2\text{O}$ at high temperatures and pressures. *Am. J. Sci.* 257, 563–573.


