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SOIL MINERALS IN THE SYSTEM Al_2O_3–SiO_2–H_2O: PHASE EQUILIBRIUM MODEL

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Abstract—Mineralogical reactions in the system Al_2O_3–SiO_2–H_2O 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 Al_2O_3–SiO_2–H_2O 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 Al_2O_3–SiO_2–H_2O 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.

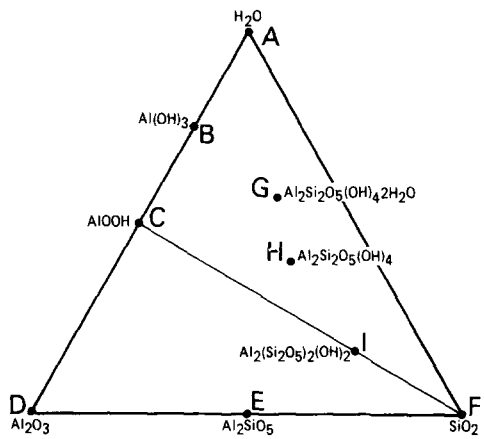


Fig. 1. The system Al_2O_3–SiO_2–H_2O showing the compositions of phases. A—water; B—gibbsite, bayerite, nordstrandite; C—boehmite, diaspore; D—corundum; E—andalusite, sillimanite, kyanite; F—quartz; G—halloysite; H—kaolinite, dickite, nacrite; I—pyrophyllite.

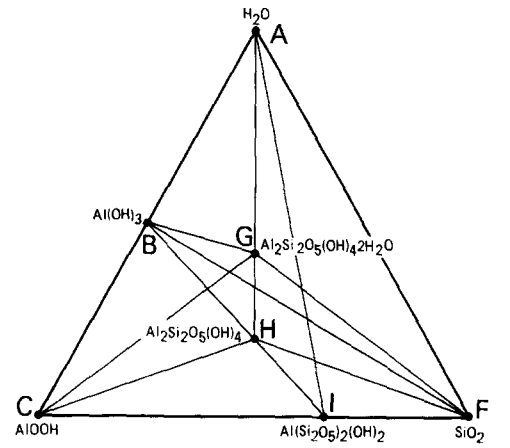


Fig. 2. The compositional triangle AlOOH–SiO_2–H_2O with all possible tie lines drawn. For phase identification refer to the caption of Fig. 1.

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 AlOOH–SiO_2–H_2O. Figure 2 shows this system with all possible tie lines drawn in. The topology of the diagram indicates a possible mineralogical reaction in one of four ways:

(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);

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Table 1. 113 possible reactions in the system $AlOOH–SiO_2–H_2O$

(a)	$Al(OH)_3 = Al(OH)_3$	(3 reactions)
(b)	$AlOOH = AlOOH$	(2 reactions)
(c)	$Al_2Si_2O_5(OH)_4 = Al_2Si_2O_5(OH)_4$	(3 reactions)
(d)	$Al_2Si_2O_5(OH)_4 2H_2O = Al_2Si_2O_5(OH)_4 + 2H_2O$	(3 reactions)
(e)	$Al(OH)_3 = AlOOH + H_2O$	(6 reactions)
(f)	$Al_2(Si_2O_5)_2(OH)_2 = 2AlOOH + 4SiO_2$	(2 reactions)
(g)	$2Al_2Si_2O_5(OH)_4 = Al_2(Si_2O_5)_2(OH)_2 + 2Al(OH)_3$	(9 reactions)
(h)	$Al_2Si_2O_5(OH)_4 = 2AlOOH + 2SiO_2 + H_2O$	(6 reactions)
(i)	$Al_2Si_2O_5(OH)_4 = Al(OH)_3 + AlOOH + 2SiO_2$	(18 reactions)
(j)	$2Al_2Si_2O_5(OH)_4 = Al_2(Si_2O_5)_2(OH)_2 + 2AlOOH + 2H_2O$	(6 reactions)
(k)	$Al_2Si_2O_5(OH_4).2H_2O = 2Al(OH)_3 + 2SiO_2 + H_2O$	(3 reactions)
(l)	$Al_2Si_2O_5(OH_4).2H_2O = 2AlOOH + 2SiO_2 + 3H_2O$	(2 reactions)
(m)	$2Al_2Si_2O_5(OH)_4.2H_2O = Al_2(Si_2O_5)_2(OH)_2 + 2AlOOH + 6H_2O$	(2 reactions)
(n)	$Al_2Si_2O_5(OH)_4.2H_2O + 2SiO_2 = Al_2(Si_2O_5)_2(OH)_2 + 3H_2O$	(1 reaction)
(o)	$Al_2Si_2O_5(OH)_4.2H_2O + AlOOH = 3Al(OH)_3 + 2SiO_2$	(2 reactions)
(p)	$Al_2Si_2O_5(OH)_4.2H_2O + 2AlOOH = Al_2Si_2O_5(OH)_4 + 2Al(OH)_3$	(18 reactions)
(q)	$2Al(OH)_3 + 4SiO_2 = Al_2(Si_2O_5)_2(OH)_2 + 2H_2O$	(3 reactions)
(r)	$2Al(OH)_3 + 2SiO_2 = Al_2Si_2O_5(OH)_4 + H_2O$	(9 reactions)
(s)	$Al_2Si_2O_5(OH)_4 + 2SiO_2 = Al_2(Si_2O_5)_2(OH)_2 + H_2O$	(3 reactions)
(t)	$Al_2(Si_2O_5)_2(OH)_2 + 6Al(OH)_3 = 2Al_2Si_2O_5(OH)_4.2H_2O + 4AlOOH$	(6 reactions)
(u)	$Al_2(Si_2O_5)_2(OH)_2 + 2Al_2Si_2O_5(OH)_4.2H_2O = 6Al(OH)_3 + 8SiO_2$	(3 reactions)
(v)	$2Al_2(Si_2O_5)_2(OH)_2 + Al_2Si_2O_5(OH)_4.2H_2O = 3Al_2Si_2O_5(OH)_4 + 4SiO_2$	(3 reactions)

(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 $Al_2Si_5O_3(OH)_4$ 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 ΔG_f 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 $-117{\cdot}8 \pm 1{\cdot}9$ 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 consistent with halloysite being a metastable phase under earth-surface conditions.

Thermodynamic examination of pyrophyllite-bearing reactions (based on $\Delta G_{f25°C}$ 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*

Table 2. Free energies of formation of soil minerals in the system $Al_2O_3–SiO_2–H_2O$, at 25°C and 1 atm total pressure

	$\Delta G_{f25°}$, 1 atm (in kcal/gfw)	Source
Water	$-56{\cdot}688 \pm 0{\cdot}020$	Robie and Waldbaum (1968)
Quartz	$-204{\cdot}646 \pm 0{\cdot}410$	Robie and Waldbaum (1968)
Gibbsite	$-273{\cdot}486 \pm 0{\cdot}310$	Robie and Waldbaum (1968)
Diaspore	$-219{\cdot}5 \pm ?$	Parks (1972)*
Boehmite	$-218{\cdot}7 \pm ?$	Parks (1972)*
Halloysite	$-898{\cdot}419 \pm 0{\cdot}910$	Robie and Waldbaum (1968)
Kaolinite	$-902{\cdot}868 \pm 0{\cdot}960$	Robie and Waldbaum (1968)

* The uncertainty in these two values 'may be larger than 1 Kcal' (footnote to Table 3, Parks, 1972).

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al., 1962, p. 117). Between 300 and 500°C it is readily produced with kaolinite and boehmite, an assemblage suggestive of reaction (j). Roy and Osborn's (1954) experiments in the system Al_2O_3–SiO_2–H_2O enabled them to construct 700 kg/cm^2 compatibility triangles that show pyrophyllite as a phase in the H_2O absent region of the triangle at temperatures above 280°C and as a phase in the H_2O 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_2O, 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_2O 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. 3 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_2O_3–SiO_2–H_2O (Polzer, Hem and Gabe, 1967) at 25°C and 1 atm pressure show that gibbsite will only precipitate at very low SiO_2 concentrations. At a concentration of $30{\cdot}0 \times 10^{-5}$ moles SiO_2/l. it is replaced

Table 3. The four reactions considered in determining the low pressure, low temperature diagram of Fig. 4

(e)	$Al(OH)_3$	=	AlOOH	+	H_2O
	gibbsite		boehmite		
(h)	$Al_2Si_2O_5(OH)_4$	=	2AlOOH	+	$2SiO_2$ + H_2O
	kaolinite		boehmite		
(i)	$Al_2Si_2O_5(OH)_4$	=	$Al(OH)_3$ + AlOOH	+	$2SiO_2$
	kaolinite		gibbsite boehmite		
(r)	$2Al(OH)_3$ + $2SiO_2$	=	$Al_2Si_2O_5(OH)_4$	+	H_2O
	gibbsite		kaolinite		

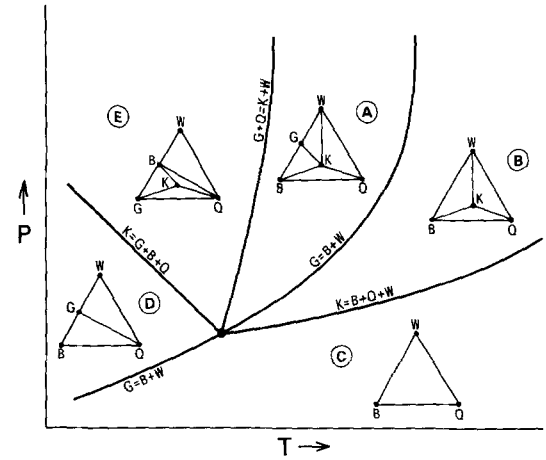


Fig. 3. Pressure (P)—temperature (T) diagram for the system AlOOH–SiO_2–H_2O at relatively low pressures and temperatures. Earth-surface conditions (25°C, 1 atm total pressure) fall within segment A of the diagram.

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 $\Delta G_{f25°C}$ 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.

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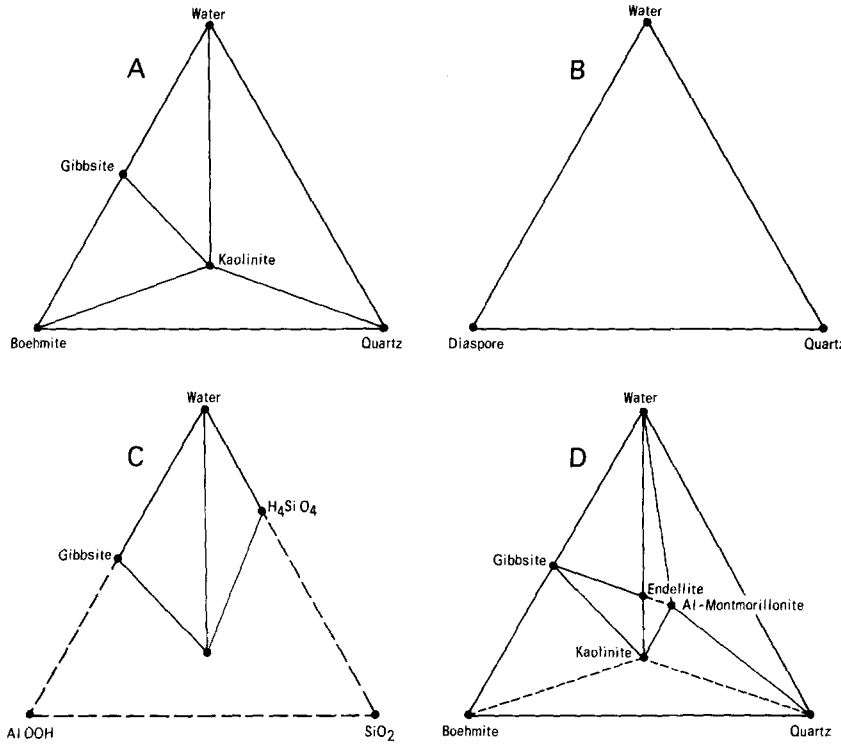


Fig. 4. Four versions of the system AlOOH–SiO_2–H_2O at low pressures and temperatures. A—Chesworth (this paper); B—Kittrick (1969); C—Garrels and Christ (1965); D—Roy and Osborn (1954). A, B and C pertain to conditions of 25°C and 1 atm total pressure. D is said by its authors to pertain to pressures down to at least 140 kg/cm^2 and temperatures below 130°C.

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_2O 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

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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 granodiorite relatively high in quartz. Thus the higher the silica content of the system the more the clay mineralogy approaches that which would be expected in a silica-oversaturated environment, e.g. kaolinitic assemblages. On the other hand in quartz-free environments gibbsitic assemblages are found. The one discordant 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 discordancy is an important one and should be emphasized. The presence of gibbsite as an early product of weathering 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, *Compositions 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 weathering 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 compatible assemblages. In the system under consideration, 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 vermiculites for example. Thus montmorillonite is common in the clay fraction of podsols (Brydon *et al.*, 1968). However, 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 AlOOH–SiO_2–H_2O 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, K_2O and Na_2O need be added.

On the basis of evidence from Australian soils (Chesworth, 1973a), weathering trends converge on the system SiO_2–Al_2O_3–Fe_2O_3–H_2O of which the three component system under consideration is an important part. The closer this 'residua system' (Chesworth, 1973b) is approached the more the soil–clay fraction tends to be made up of combinations of gibbsite, kaolinite and quartz (together with an iron oxide or hydroxide). Compositions distantly removed from this end point are dominated by other clay minerals (Fig. 5). In other words, in soils where the clay fraction has a composition that can be fairly well approximated by the system AlOOH–SiO_2–H_2O, the clay mineral assemblages tend to be dominated by phases that are stable in the 25°C, 1 atm cross-section of that system (Fig. 4a).

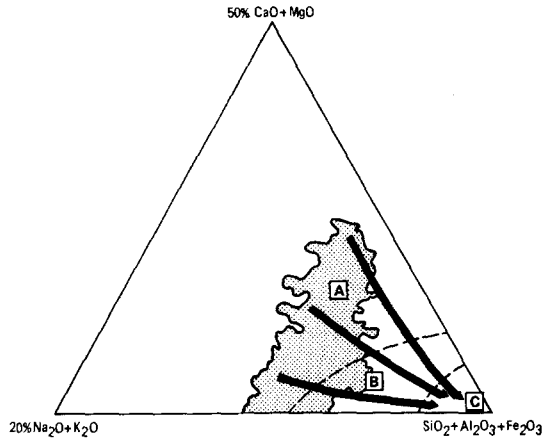


Fig. 5. Generalized weathering trends from the field of the common igneous rocks (stippled area) towards the residua system of weathering. The clay fraction of weathered materials in field A is dominated by primary silicates, smectites, randomly interstratified clay minerals and possibly vermiculites: that of weathered materials in field B by smectites and illites: and that of weathered materials in field C, by aluminum and iron oxides and hydroxides and kaolinite. Only compositions within field C can be usefully approximated by the system AlOOH–SiO_2–H_2O, and to do this the iron oxides or hydroxides must be treated as indifferent phases.

CONCLUSION

The configuration of the system AlOOH–SiO_2–H_2O at 25°C and 1 atm total pressure has been worked out from a basis of experimental work and the application of the Gibbs Phase Rule and the topological techniques of Schreinemakers. The result (Fig. 4a) differs markedly from other workers' versions, in particular 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 appropriate 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 significant role in systematizing studies of the genesis of igneous and metamorphic rocks.

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