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THE THERMODYNAMIC STATUS OF COMPOSITIONALLY-VARIABLE CLAY MINERALS: A DISCUSSION

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Abstract—According to Lippmann (1977, 1982) wide compositional variations and excess enthalpies of mixing calculated with electrostatic models imply that clay minerals of variable composition are disequilibrium solids. However, recent ATEM analyses of illite samples indicate compositional homogeneity of single illite grains and limited compositional variations in sedimentary basins. Moreover, Lippmann's electrostatic model may be inadequate inasmuch as it neglects polarization energy which is known to be a significant component of lattice energy even in dominantly ionic structures. Contrary to the assumptions of Lippmann, I/S minerals have also been shown to undergo Ostwald ripening.

May *et al.* (1986) reported that smectites do not reversibly control equilibria and further argued that conceptual and experimental deficiencies inherent in the solubility method prevent the attainment and demonstration of equilibrium in experiments with complex aluminosilicates of variable composition. However, equilibrium may be assumed if: (1) steady states are approached from both under- and oversaturation, (2) the slopes of univariant lines representing mineral-solution equilibria are rational over a wide range of solution compositions and temperature, and (3) results are reproducible in experiments of long duration. Recent solubility studies of smectites, chlorites, and illites meet these criteria indicating that clay minerals of variable composition are true phases capable of attaining equilibrium.

Key Words—Illite, Montmorillonite, Thermodynamic status, Excess lattice energy, Solubility, Compositional variation.

INTRODUCTION

Owing to the compositional complexity and wide range of solid solubility of nonstoichiometric clay minerals (e.g., smectite, illite), their thermodynamic status is a long-standing mineralogical problem. The issues in question include whether: (1) complex aluminosilicates of variable composition are true thermodynamic phases (Lippmann, 1977, 1982); (2) illites and smectites are stable or metastable phases (Jiang *et al.*, 1990); (3) equilibria involving these minerals can be determined by the solubility method (May *et al.*, 1986).

Lippmann's (1977, 1982) concept of the thermodynamic status of clay minerals underscores many of these current questions. Lippmann (1977) reasoned that the fractional subscripts in the structural formulae of illites and montmorillonites preclude derivation of solubility products for these minerals inasmuch as valid solubility products may only be derived for phases with fixed chemical compositions and nonfractional subscripts. According to him, the solubility of these solid solutions must be defined in terms of the partial solubility products of end-member components. In view of the large number of such end-member minerals required to define the solubility products, Lippmann (1977, 1982) further speculated that these clay minerals must be disequilibrium solids that form by precipitation from extremely supersaturated solutions; thus, their wide range of compositional variations do not reflect crystal chemical constraints. Assuming that the magnitudes of electrostatic excess lattice energies calculated for the paragonite-muscovite and muscovite-pyrophyllite systems suggest a significant solid miscibility gap at low temperatures, Lippmann (1982) also speculated that the formation of illites and montmorillonites under low temperature conditions must imply their metastability. In this contribution, we will argue that these theoretical considerations are misconceived and that recent empirical developments suggest that these clay minerals are true thermodynamic phases.

Jiang *et al.* (1990) documented the coexistence of nearly stoichiometric pyrophyllite and muscovite in metapelites and therefore argued that their observation provides a direct confirmation for the metastability of illite (Lippmann, 1982). However, this interpretation has recently been questioned by Loucks (1991) who examined variations in the molar proportions of structurally bound water as a function of interlayer site occupancy. Loucks' (1991) analysis suggests that the projection of illite compositions onto the simple binary join muscovite-pyrophyllite is incorrect, which in turn

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calls into question the basic premise of the disequilibrium/metastable model of illite. The illite compositions he used were obtained from bulk (wet) chemical analyses which do not consider the multi-phase nature of most natural illitic samples (Środoń, 1984). Because the apparent excess charge often encountered in recalculating bulk chemical analyses of clay minerals may reflect the presence of more than one illitic phase, Loucks' analysis is not definitive. Nonetheless, it may well be that illites and smectites are metastable phases which for kinetic reasons form in preference to coarse-grained micas at low temperatures ($T < 300°C$). If clay minerals are metastable phases, the determination of their metastable equilibrium would still be useful inasmuch as such phases form commonly in nature and thus carry vital petrogenetic information by virtue of their metastability (Lippmann, 1982).

Finally, May *et al.* (1986) reported the irreversibility in $pH\text{-}1/3pAl^{3+}$ vs. $pSiO_{2(aq)}$ space of their smectite (three Hawaiian Vertisols and two bentonite samples) dissolution experiments. In the experiments with bentonite samples, gibbsite appeared to control Al level whereas amorphous aluminum hydroxides appeared to precipitate in the Hawaiian soil samples. In order to explain these irrational solubility data, May *et al.* (1986) presented a hypothetical solubility model for an idealized montmorillonite in the ternary system $(AlFe)Si_4O_{10}(OH)_2$-$(AlMg_{3/2})Si_4O_{10}(OH)$-$H_2O$. According to them, kinetic restrictions and incongruent dissolution preclude equilibrium solubility of complex aluminosilicates of variable composition along a solution saturation curve; they also suggest that the irreversible solubility indicated by their data is somewhat analogous to stoichiometric saturation (Thorstensen and Plummer, 1977). However, stoichiometric saturation does not imply irrational solubility behavior. Rather, owing to kinetic restrictions, a fixed composition of a compositionally-variable mineral may equilibrate during a short term geologic process (natural or laboratory). Thus, compositional complexity alone cannot preclude the dissolution of a solid solution to a point of thermodynamic equilibrium. The critical question, therefore, becomes whether solubility controlling phases can be identified in solubility experiments with natural clay minerals. We will show, based on recent dissolution and solution equilibration data, that clay minerals of variable compositions equilibrate with fixed compositions under isothermal, isobaric conditions.

THEORETICAL CONSIDERATIONS

The wide ranges of compositional variations characteristic of natural illites and montmorillonites (Figure 1) provided the primary basis for the disequilibrium/metastable model of Lippmann (1982). According to him, this variability is unexpected for low temperature minerals especially in view of the smaller range

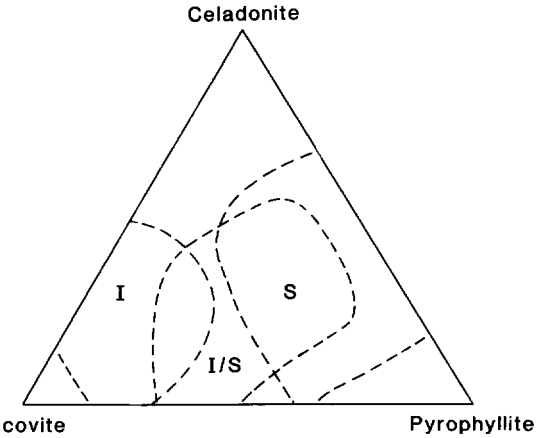


Figure 1. Muscovite, pyrophyllite, celadonite diagram showing wide range of compositional variations obtained by bulk analysis (I, illite; I/S, mixed-layer illite/smectite; S, smectite; Weaver and Pollard, 1973).

of solid solutions exhibited by higher temperature systems; that is, comparable range of stable solid solutions in the paragonite-muscovite and pyrophyllite-muscovite systems are expected above the relevant solvus temperatures (600° and 800°C, respectively). Below these temperatures, mutual solubility of the end members is negligible unless the system is characterized by a solvus having a lower critical point. The latter condition requires that the heat of mixing be exothermic (see Figures 2–5; Lippmann, 1982).

In order to determine whether these clay minerals are characterized by exothermic energy of mixing, Lippmann (1982) calculated excess lattice energies using the equation

$$H^M = -M/r$$

where

H^M = electrostatic enthalpy of mixing,
M = Madelung energy, and
r = cation-anion distance.

For a regular solid solution model, the theoretically-calculated maximum excess lattice energy (H^M) for the paragonite-pyrophyllite system (17.9 KJ/mol) is equal to G^E (excess Gibbs energy of mixing). Based on this value of G^E, he suggested that the equilibrium miscibility between paragonite and pyrophyllite is negligible over a wide temperature range varying from surface to metamorphic conditions. Inasmuch as the composition of Na montmorillonite may be projected into the paragonite-pyrophyllite system and experimental heat of hydration of Na montmorillonite (18.4 KJ/mol) does not account for the effect of water adsorption on the surfaces, Lippmann (1982) concluded that hydration is not sufficient to render the mixing of paragonite and pyrophyllite overwhelmingly exothermic. According to this analysis, the necessary thermodynamic con-

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Table 1. Comparison of experimental and calculated lattice energies (KJ/mol) for some alkali halides.[1]

Salt	Experimental	Calculated[2]	Calculated[3]
LiF	1034	1008	1033
LiCl	840.1	811.3	845.2
NaF	914.2	902.0	915.0
NaCl	770.3	755.2	777.8
KF	812.1	797.5	813.4
KCl	701.2	687.4	708.8

[1] Data from Huheey (1983); [2] Calculated with a purely ionic model; [3] Calculated with electrostatic model with corrections for polarization and repulsion between nearest and next nearest neighbor.

straints required to explain compositional variations in clay minerals (e.g., illite, montmorillonite) are not satisfied. In further support of this conclusion, he noted that excess lattice energies calculated for dominantly ionic compounds (oxides, halides, sulfides, and carbonates; Urusov, 1975) are always endothermic.

A critical flaw in the above thermodynamic model is the undue emphasis placed on electrostatic lattice energies. In the development of the electrostatic model of Urusov (1975), the excess enthalpy of mixing is a sum of the effective ionic (Madelung) and covalent contributions. Because differences in the ionic character of the end member components of the solid solution are not well known (Urusov, 1975), only the Madelung component is considered, making this a purely electrostatic model. Excess enthalpies of mixing calculated in this manner may have some heuristic values, especially for simple compounds. Even for such simple compounds, however, mutual solubility of the components increases with increasing complexity of composition and structure of the solid solution (Urusov, 1975). Moreover, silicate minerals are not purely ionic solids and thus the excess electrostatic lattice energy function cannot be used to determine the thermodynamic status of clay minerals. In fact, successful *ab initio* models of the thermodynamic properties of silicate minerals correct for polarization and other nonionic interactions (Price *et al.*, 1987; Lasaga, 1980). Considering that the effects of these corrections were neglected in Lippmann's model, the conclusion that the difference between calculated electrostatic excess lattice energy and the measured heat of hydration (Na montmorillonite) implies that the paragonite-pyrophyllite mixing reaction is not overwhelmingly exothermic, is questioned. Indeed, the extension of Urusov's (1975) model to silicates is debatable inasmuch as electrostatic lattice and binding energies calculated for predominantly ionic compounds are usually more positive than empirical values; the difference is reconciled using contributions from other factors, notably polarization energies (Table 1).

The fundamental assumption of Lippmann's model is that the properties of well-crystallized phyllosilicates

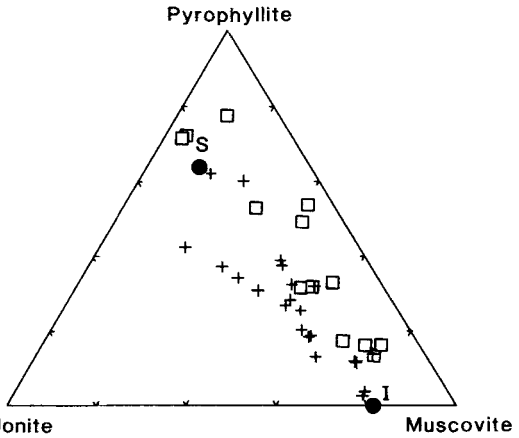


Figure 2. Muscovite, pyrophyllite, celadonite diagram comparing the restricted range of clay mineral compositions determined by ATEM analysis of single crystals (crosses, Inoue *et al.*, 1987, in Lanson and Champion, 1991) with compositions determined from solution equilibration experiments (squares, Aja *et al.*, 1991b). S, smectite; I, illite.

may be used to rigorously model the corresponding properties (e.g., chemistry, thermochemistry) of clay minerals. Clearly, the important pedagogic value of this practice is reflected in its widespread use. However, a simple mixing model of these well-crystallized end member minerals cannot provide a conclusive test of the thermodynamic status of these clay minerals. Tardy and Fritz (1981) demonstrated that solubility products of illites and montmorillonites modelled after these well-crystallized end member micas are too low (stable) to explain clay mineral stability fields. Other models for mixing these end members have not accurately predicted the relative stabilities of dioctahedral clay minerals in both natural (Aagaard and Helgeson, 1983) and experimental solutions (Aja *et al.*, 1991a). Furthermore, the compositional space theoretically possible for 2:1 layer clay minerals should be very large if clay mineral compositions are modelled after these well-crystallized micas. Recent ATEM studies of natural illite samples have, however, shown that: (1) the overall range of clay mineral chemistries for hydrothermal samples is limited (Figure 2), and (2) significant compositional variations are not observed for different samples from a particular sandstone formation (Warren and Curtis, 1989). Thus, only a small fraction of this theoretical compositional range is realized in nature owing, in part, to (1) the existence of certain stability restrictions (Giggenbach, 1985), (2) the limited compositions of natural water solutions and (3) the presence of other mineral phases.

Finally, recognizing that the stability of all clay minerals are decreased by their fine grain sizes, Lippmann (1982) further maintained that clay minerals do not undergo Ostwald ripening and thus must have formed by non-equilibrium nucleation from highly supersat-

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urated solutions. Ostwald ripening is the process of recrystallization, in which dissolution and growth of a mineral occurs simultaneously in a system containing crystallites having a wide range of particle sizes. The driving force for grain coarsening is the minimization of surface energy by dissolving small particles and growing larger ones. Because Ostwald ripening is the basic process of aggrading neomorphism over a wide range of geologic conditions for minerals (Baronnet, 1982), the disequilibrium solid model would be supported by an inability of clay minerals to undergo ripening. However, recent morphological studies suggest that sericites (Eberl *et al.*, 1990) and I/S clay minerals (Inoue *et al.*, 1988) do undergo Ostwald ripening, contrary to the assumptions of Lippmann (1982). Moreover, Ostwald ripening in these minerals is apparently not precluded by the relatively low temperatures and low solubilities involved.

SOLUBILITY EXPERIMENTS

May *et al.* (1986) have presented a formidable list of conceptual and experimental deficiencies that they believe prevent the unequivocal demonstration of equilibrium for clay minerals of variable compositions in solubility studies. These include: (1) lack of proof of the attainment of equilibrium where equilibrium has been inferred from extrapolation of solute activities to infinite time; (2) use of acidic equilibrating solutions in which minerals may be unstable; (3) use of inappropriate analytical techniques which neglect the role of ion speciation especially for Al^{3+}; (4) erroneous identification of solubility-controlling mineral species; and (5) uncertainties in the role of exchangeable cations in smectites. These criteria and limitations have been used to evaluate the results and conclusions of recent solubility experiments on natural clay minerals.

Chlorite

Four natural chlorites, having fractional subscripts in their formulae were equilibrated with solutions near neutral pH at 25°C by Kittrick (1982, 1984a). X-ray diffractometry showed all samples to be monomineralic, crystalline, and devoid of impurities. Criteria for the attainment of equilibrium were the close approach to the same steady-state values of $pH\text{-}1/2pMg^{2+}$ and pH_4SiO_4 from under- and supersaturation as well as agreement between successive analyses and between duplicated samples in experiments of widely varying duration (7 to 793 days). Concentrations of Al, Fe, and silica in solution were buffered by the addition of excess gibbsite, hematite, or kaolinite, respectively (Figure 3). The slopes of solubility lines derived from mass action constraints were used to estimate the compositions of the solubility-controlling phases (Kittrick, 1982). The compositions thus estimated were compatible with those of the chlorites used as starting materials in the experiments and not with potential solid solution end members (e.g., brucite or talc). Thus, neither fractional subscripts in the chemical formula nor the particular experimental techniques used in this study prevented the attainment of equilibrium.

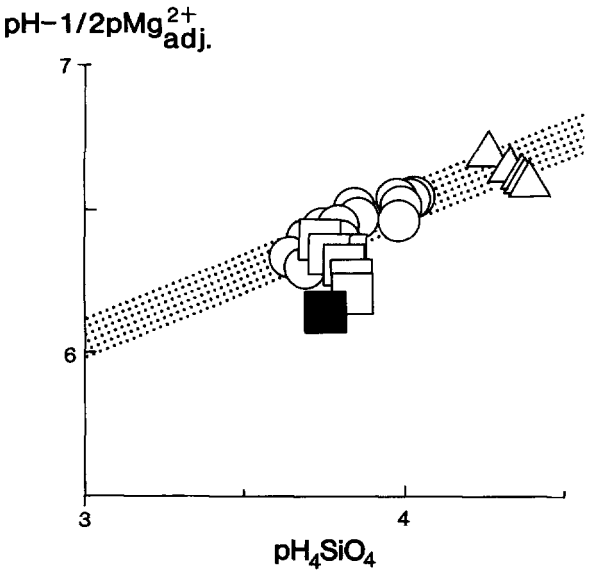


Figure 3. Adjusted solution compositions after equilibration with assemblages containing Vermont Chlorite. Circles: chlorite, kaolinite, hematite. Triangles: chlorite, gibbsite, hematite, kaolinite. Squares: chlorite, gibbsite, hematite. Solution compositions lie on line (shaded) having the predicted slope (Kittrick, 1982).

Smectite

In 1971, Kittrick equilibrated smectite and smectite/kaolinite mixtures in solutions of low pH (2.74–3.48) over a period of 3 to 4 years and concluded that equilibrium was controlled by a smectite having a composition approaching that of the starting Belle Fourche montmorillonite (BF) $[K_{0.92}(Si_{7.57}Al_{0.43})(Al_{3.15}Mg_{0.61}Fe_{0.28})O_{20}(OH)_4]$. Despite the relatively long duration of these experiments, the starting smectite appeared to have maintained its structural integrity.

Because the experiments of Kittrick (1971) were conducted in acid solutions and the role of exchangeable ions was not considered, this study may be questioned in the light of the criticisms of the solubility method by May *et al.* (1986). However, in more recent experiments of much shorter duration (1–8 weeks), the solubilities of K-saturated (Peryea and Kittrick, 1986; Kittrick and Peryea, 1988) and Mg-saturated (Kittrick and Peryea, 1989) [<0.2 and 0.2–5 μm particle size fractions (PSF), respectively] BF montmorillonite were measured in high (approx. 8.7) and low to high pH (3.26–8.16) suspensions, respectively.

For experiments in a K-saturated system, the dissolution of the BF montmorillonite in the presence of kaolinite, goethite, and magnesite may be expressed by the reaction (Kittrick and Peryea, 1988):

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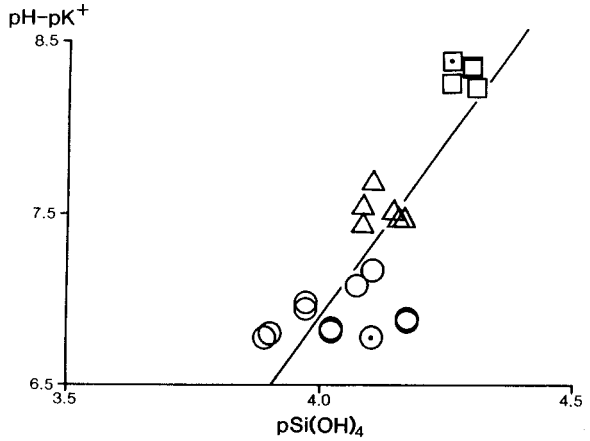


Figure 4. Compositions of final solutions equilibrated with BF (K-saturated), magnesite, and kaolinite. Squares, triangles and circles show experiments in 1.0 M K^+, 0.10 M K^+, 0.01 M K^+ solutions, respectively. Dot indicates overlapping points. Slopes of experimental and predicted line are 4.19 ($R^2 = 0.81$) and 4.34, respectively (Kittrick and Peryea, 1988).

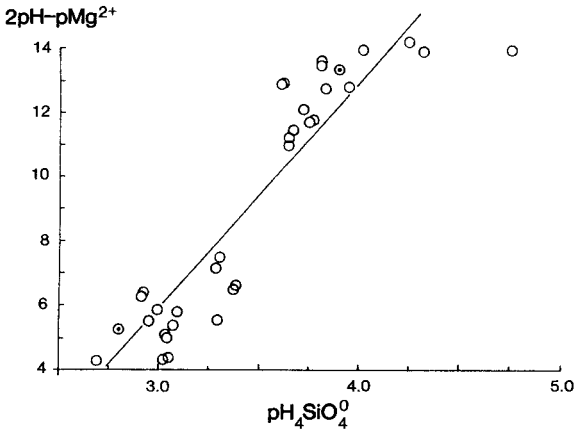


Figure 5. Compositions of final solutions equilibrated with BF (Mg-saturated), gibbsite, and geothite in 0.01 M $MgCl^2$. Slopes of experimental and predicted boundaries are 6.99 + 1.09 (2σ; $R^2 = 0.83$) and 6.99, respectively (Kittrick and Peryea, 1989).

$$\text{smectite} + 4.34H_2O + 0.61CO_{2(g)} + 0.92H^+(aq) = 1.79 \text{ kaolinite} + 0.28 \text{ goethite} + 0.61 MgCO_3 + 3.99 Si(OH)_4 + 0.92 K^+$$

Thus, if the interlayer potassium is a structural component of the smectite (i.e., monophase structure model), log a_{K^+}/a_{H^+} will vary as a function of log $a_{SiO_{2(aq)}}$ whereas if the exchangeable cation is not a structural component (i.e., charged structure model), only pH will be a function of log $a_{SiO_{2(aq)}}$. Comparison of the data of Peryea and Kittrick (1986) indicates a much better match to the monophase structure model (Figures 1 and 2; Kittrick and Peryea, 1988). Moreover, the slope of the best fit line on log a_{K^+}/a_{H^+} *vs* log $a_{SiO_{2(aq)}}$ diagram (−4.19, $R^2 = 0.81$) closely approximates the slope (−4.34) predicted for the BF (Figure 4).

Solubility data for Mg-saturated BF montmorillonite in the presence of gibbsite and goethite also define a linear relationship having a slope close to that predicted for the monophase structure model (Figure 5). Kittrick and Peryea (1989) also attempted similar experiments using CMS (Clay Minerals Society) standard smectite SWY-1. This study was unsuccessful apparently due to the excess silica in the starting material.

A comparison of Figures 4 and 5 reveals that the data from 0.01 M $MgCl_2$ and from 0.01 M KCl experiments show more scatter relative to those at higher KCl concentrations (0.10 and 1.0 M KCl). Apparently, ion saturation in the exchangeable cation site was not attained in the experiments conducted with dilute solutions. In the 0.01 M KCl solution experiments, for instance, Kittrick and Peryea (1988) estimate a 75% K saturation of the exchangeable site. Nonetheless, the equilibrium boundary obtained from solubility measurements in dilute solutions show the same ion relationships as those from experiments in higher ionic strength solutions which is unexpected for the charged structure model (Kittrick and Peryea, 1988).

On balance, recent solubility studies involving smectite demonstrate that equilibrium (probably metastable) can be attained and that interlayer cations behave as an integral part of the smectite structure. None of the conceptual and experimental problems anticipated by May *et al.* (1986) are in evidence in these latter studies. However, most smectite samples contain significant amounts of impurities which may interfere with solubility studies (Kittrick and Peryea, 1989). Thus, experiments with natural smectite samples that yield uninterpretable solubility data may reflect the presence of impurities rather than experimental and conceptual deficiencies.

Illite

Because of the complexity of illite and I/S-bearing assemblages, solution equilibration experiments of several natural illites (Beavers Bend, Goose Lake, Marblehead, and Silver Hill illites) have recently been conducted (Aja, 1991; Aja *et al.*, 1991a, 1991b; Rosenberg *et al.*, 1990; Sass *et al.*, 1987; Kittrick, 1984b). The solution equilibration procedures employed in these studies differ from direct dissolution studies (e.g., May *et al.*, 1986; Kittrick and Peryea, 1989) in that the chemical composition of actual solubility-controlling phases were calculated from the slopes of univariant lines on activity diagrams (see Nordstrom and Munoz, 1985; p. 246–250). Because the stoichiometry of the solubility-controlling phase is thus not based on bulk chemical analyses, errors resulting from the presence of impurities in these natural samples are avoided. Inasmuch as the attainment of equilibrium was demonstrated by reversing solute activities along univariant phase boundaries, the problems associated with inferring equilibrium conditions from extrapolations

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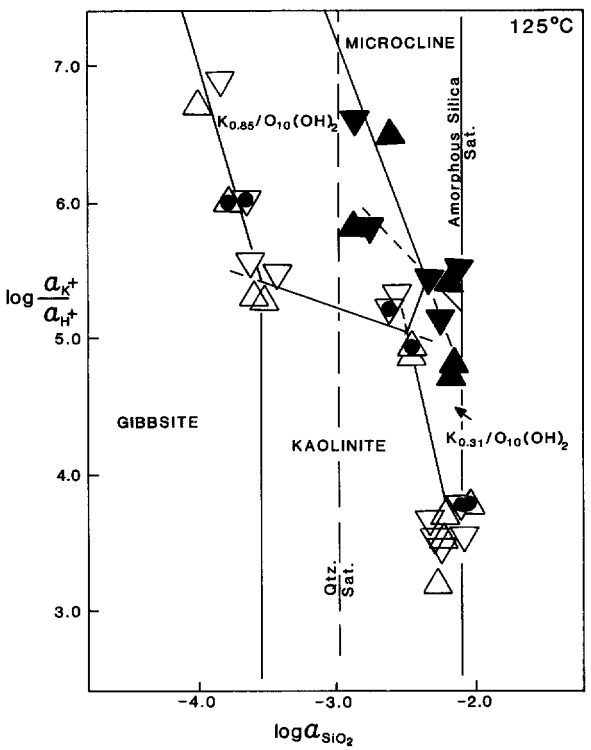


Figure 6. Isothermal, isobaric activity diagram (log a_{K^+}/a_{H^+} *vs* log a_{SiO_2}) for the system K_2O-Al_2O_3-SiO_2-H_2O at 125°C (Aja *et al.*, 1991a). Open (2.0 M KCl solutions) and partially-open (0.2 M solutions) triangles, excess kaolinite; solid triangles, excess microcline. Top and bottom apices of triangles indicate direction of approach to equilibrium (Aja *et al.*, 1991a).

of solute concentrations as time functions (Lafon, 1978) were avoided.

Equilibrium relationships observed in experiments with Marblehead illite are illustrated using an isothermal, isobaric activity diagram constructed at 125°C (Figure 6). The compositions of the solubility-controlling phases were calculated from the slopes of the univariant boundaries with kaolinite. Using compositions deduced in this manner, it was shown that the observed relationships are topologically consistent (Aja *et al.*, 1991a). Furthermore, the existence of natural analogues of these solubility-controlling phases have also been documented (Rosenberg *et al.*, 1990).

The illites used in the studies (Beavers Bend, Goose Lake, Marblehead, and Silver Hill illites) come from a wide variety of geologic environments (Mankin and Dodd, 1963; Gaudette, 1965; Gaudette *et al.*, 1966; Hower and Mowatt, 1966; Güven, 1972; Grim and Bradley, 1939) and have different crystallinities and crystal sizes (Hooper and Rosenberg, unpublished data). Despite these differences, only five mica-like phases were found to control solubility in the presence of kaolinite and microcline over the pressure-temperature interval investigated (Figure 7).

In general, the attainment of equilibrium in solubility experiments may be assumed if: (1) the same steady state can be approached from both under- and oversaturation; (2) the slopes of univariant lines representing mineral-solution equilibria are rational over a wide range of solution compositions and temperatures; and (3) results are reproducible in experiments of long duration (Aja and Rosenberg, 1991). These conditions appear to have been met in the recent solubility studies discussed above and, thus, provide empirical evidence that clay minerals of variable compositions are true thermodynamic phases. We conclude, therefore, that illites and smectites may dissolve to a point of thermodynamic equilibrium in solubility experiments.

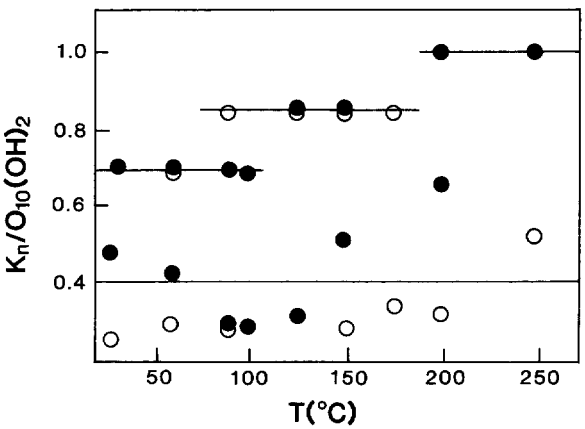


Figure 7. Temperature dependence of the compositions of illitic solubility-controlling phases in the presence of kaolinite and quartz between 25 and 250°C. Filled circles, Marblehead illite; open circles, Goose Lake, Beavers Bend, and Silver Hill illites (Aja, 1991).

CLAY COMPOSITIONAL VARIATION

As previously noted, the extensive compositional variation reported for natural illites, smectites, and I/S (e.g., Hower and Mowatt, 1966; Meunier and Velde, 1989; Merino and Ransom, 1982) provided the basis for the disequilibrium solid model. It has, however, become apparent that earlier bulk chemical analyses did not resolve single illite crystals (Ransom and Warren, 1989). Indeed, recent ATEM studies of natural illite samples have shown that: (1) individual crystals from geothermal basins are compositionally homogenous (e.g., Lonker *et al.*, 1990) and (2) the overall compositional range appears to be more limited than previously presumed (Figure 2). Where differences in compositions have been observed for samples from different sandstone formations, they reflect differences in the chemistry of the coexisting pore fluids (Warren and Curtis, 1989). Inasmuch as the disequilibrium solid model requires clay minerals to show extensive compositional variations at both the sub-microscopic and macroscopic levels (May *et al.*, 1986; Lippmann, 1982), these observations contradict this model.

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Unlike illite, natural smectites are characterized by charge heterogeneity (e.g., Talibudeen and Goulding, 1983) and a much more variable particle morphology (Güven, 1988). This may merely reflect kinetic effects and environmental conditions or it may imply that smectite solubility and authigenesis cannot be treated by equilibrium models as suggested by May *et al.* (1986). However, if the model of Lippmann is unrealistic, as proposed here, then theoretical justification for classifying smectites as disequilibrium solids does not exist and empirical observations may provide important insights. Several studies of authigenesis (e.g., Badault and Risacher, 1983) and synthesis of homogenous smectites (see Güven, 1988) show that smectite precipitation occurs under restricted solute concentrations (e.g., pH, pMg, $pSiO_2$) suggesting the existence of stability fields. Perhaps, the chemical/structural heterogeneity and the presence of amorphous silica characteristic of natural smectites reflect low temperatures and hydrological constraints (i.e., during their recrystallization from natural glass).

In the solubility experiments discussed previously, equilibrium was controlled by phases of invariant compositions under isothermal, isobaric conditions. In the case of chlorite and smectite experiments, solubility was controlled by phases having chemical compositions identical to that of the bulk starting material. Although the various starting illites used in the experiments were neither monomineralic nor from the same locality, limited numbers and compositions of solubility-controlling phases were observed. This reflects internal buffering of the experimental system and further implies the existence of certain free energy minima. Nevertheless, phases whose compositions vary from those synthesized in experimental systems may crystallize in natural waters inasmuch as natural water systems are likely to be buffered externally.

CONCLUSIONS

Complex clay minerals of variable composition including chlorites, illites, and smectites have been shown empirically to attain equilibrium in solubility experiments and, therefore, should be considered to be true thermodynamic phases. Solution equilibration experiments which permit reversals of mineral-solution equilibria provide a means for calculating the chemical composition of solubility controlling phases. The occurrence of relatively homogenous natural illites and the limited number and compositions of phases observed during solution equilibration strongly suggest that natural illites are not disequilibrium solids but true phases capable of attaining stable or metastable equilibrium. Furthermore, smectite often occurs as a lower temperature phase relative to illite or mixed-layer I/S in diagenetic sequences and in hydrothermal alteration assemblages. If these clay minerals are indeed inhomogeneous disequilibrium solids, then no correlations would be expected between physicochemical parameters and mineral paragenetic sequences.

The appearance of fractional subscripts in the structural formulae of clay minerals of variable composition was the original basis for questioning the application of solubility methods to these minerals (Lippmann, 1977). However, the use of fractional components is merely a convention. The solubility products of compositionally-complex minerals can provide valid measures of solid solution-aqueous phase interactions (e.g., Glynn and Reardon, 1990).

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