NOTES

THE THERMODYNAMIC STATUS OF COMPOSITIONALLY-COMPLEX CLAY MINERALS: DISCUSSION OF "CLAY MINERAL THERMOMETRY—A CRITICAL PERSPECTIVE"

Key Words—AEM, Compositionally-variable clay, HRTEM, Thermodynamic.

The thermodynamic status of compositionally-variable clay minerals is a controversial subject. In a recent discussion of this question, Essene and Peacor (1995) surmised that most clays are not distinct minerals or phases primarily because of their compositional heterogeneity. They further maintained that assemblages of clays in shales and mudstones are incompatible with the phase rule and thus, there is no basis for clay mineral geothermometry. Finally, they suggested that the experimental solubility data of illite conducted by Aja and co-workers (Aja 1989, 1991; Aja et al. 1991a, 1991b) are in violation of Schreinemakers' rules and therefore, indicate lack of equilibrium. However, most of these arguments are not new but represent a re-statement of the full consequences of the disequilibrium solid model of Lippmann (1977; 1982). Fundamental flaws inherent in the disequilibrium solid model have been extensively discussed by Aja and Rosenberg (1992) but were entirely ignored by Essene and Peacor (1995). Nonetheless, we welcome the opportunity to further clarify the implications of our solubility studies. In particular, we will show that the assertion that these solubility data violate Schreinemakers' rules is false and is based on an erroneous interpretation of our data.

The controversy surrounding the nature of clay minerals has been compounded by an obfuscation in terminologies. Specifically, the proponents of the disequilibrium solid model make no distinction between unstable and metastable phases. Metastable equilibria are quite common in chemical systems since reactions that may lower the energy state may be forestalled by activation energy barriers. To the extent that geochemists study natural systems, investigations of metastable equilibrium are inevitable, no less respectable and may indeed be particularly informative. For example, several research groups are currently conducting studies on the zeolite group of minerals (Aja 1995a; Murphy et al. 1995; Wilkin and Barnes 1995; Macinnis et al. 1995) despite the fact that they are metastable, fine-grained and compositionally heterogenous (Hemingway and Robie 1984; Broxton et al. 1987). In this context, metastability means that all gradients in temperature, pressure and composition of a system have not been eliminated. However, this does not preclude attainment of partial and/or local equilibrium in natural systems (Anderson and Crerar 1993). By contrast, metastability in the sense of Lippmann (1977, 1982) really implies instability. The basic tenet of the disequilibrium solid model is that compositional variations in clay minerals are not governed by either crystal chemical or equilibrium constraints. Therefore, the physical and chemical conditions responsible for formation of each clay mineral are unique and non-reproducible (May et al. 1986). A corollary to this postulate is that the behavior of compositionally-complex clay minerals in either experimental or natural systems are irreproducible and the relative stability of illites and smectites cannot be evaluated or predicted using thermodynamic arguments. We will show that these conclusions are untenable in light of available data on illite.

Finally, the distinction between the states of a system (stable, metastable, unstable) is only possible for systems that are well-known (Anderson and Crerar 1993). Clay-bearing systems are not very well-understood and a better knowledge of the nature of these systems will be gained by an objective assessment of all available evidence. Despite the flaws inherent in the disequilibrium solid model (Aja and Rosenberg 1992), Essene and Peacor (1995) have relied on this model in the interpretation of their high resolution and analytical electron microscopic (HRTEM, ATEM) observations. Regardless of the amount of care expended in execution of these TEM studies, such solid state studies cannot provide insights into the behavior of clay minerals in the presence of aqueous solutions. Such information, which can only be gained from direct solubility measurements, is particularly relevant given that clay minerals form in the presence of aque-

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ous solutions. Furthermore, HRTEM studies of natural clays from other research groups are at variance with the conclusions of Peacor and co-workers and appear to support inferences based on solubility measurements. Therefore, we will review implications of some recent HRTEM and ATEM studies in the context of the question under discussion.

RESULTS OF ILLITE
SOLUBILITY MEASUREMENTS

Natural illites (Marblehead = MH; Goose Lake = GL; Beavers Bend = BB; and Silver Hill = SH) and other naturally coexisting phases (kaolinite, gibbsite, quartz, microcline and amorphous silica) were equilibrated under hydrothermal conditions (T = 25 to 250 °C) using starting solutions of KCl/HCl and KCl/KOH and equal weights of mineral mixtures (illite + kaolinite). This mineral/water ratio was adopted to bring solutions to equilibrium rapidly. Experiments were conducted in pairs with identical solid mixtures and solutions of the same ionic strength (0.2–2.12 m) but with high and low values of K^+/H^+. The attainment of equilibrium was then tested by the reversibility of a_{K^+}/a_{H^+} and the reversibility of $a_{SiO_{2(aq)}}$. After the quench, the solid products were separated from solutions by immiscible displacement techniques (Kittrick 1983), and analyzed by X-ray diffractometry (XRD). The aqueous solutions were analyzed by flame atomic absorption spectrometry. The molalities of the experimental solutions were temperature corrected using Pitzer's approach, and depicted on isothermal, isobaric activity diagrams (Sass et al. 1987; Aja et al. 1991a, 1991b; Aja 1991).

Two alternative models were considered for the interpretation of the data. Within aqueous solutions, illite may behave either as a single phase solid-solution containing multiple components or as a multi-phase mineral (Garrels 1984). If the solubility controlling phases behave as discrete phases under isothermal, isobaric conditions, their compositions may be uniquely determined from numerical values of slopes of univariant phase boundaries. The validity of this approach derives from the Gibbs-Duhem relationship ($\Sigma_{i=1,n}n_id\mu_i = 0$). That is, changes in the slopes of univariant boundaries are predicated upon changes within chemical potential which then determine changes within the number of moles at equilibrium. Variations in the identity of solubility-controlling phases can be inferred by monitoring changes for the slope of reaction boundaries depicted on phase diagrams (such as activity-activity diagrams), if and only if, one of the coexisting solid phases has a variable composition. In our studies, kaolinite was equilibrated with illite. Therefore, changes in the stoichiometric coefficients of the illite ⇌ kaolinite reaction derive exclusively from changes in the composition of illite.

The compositions of the solubility-controlling phases observed in experiments with GL, SH and BB are identical to those observed in experiments with MH (Aja and Rosenberg 1992). Furthermore, the compositions of illites formed from solution equilibration experiments in which the starting mixtures consisted of muscovite and kaolinite (Yates 1993; Yates and Rosenberg 1993, 1995) are entirely consistent with those inferred exclusively on the basis of solution chemistry by Aja and co-workers. Moreover, the compositions of the illitic phases grown during muscovite-kaolinite equilibration experiments were based on both solution chemistry and AEM analyses.

EQUILIBRIUM VS.
NON-EQUILIBRIUM

The criticisms by Essene and Peacor (1995) of our illite solubility studies revolve around the following points: 1) phase boundaries for the stability field of illite in temperature vs. pH-pK$^+$ space (Figure 1) violate Schreinemakers' 180° rule; 2) measured pH-pK$^+$ and pH-0.5pMg^{2+} values may be controlled by exchangeable or absorbed cations, dissolution of fine crystallite fractions or reactions with surface layers only; 3) a stability field for gibbsite and/or boehmite was shown between 25 to 150 °C instead of that of diaspore, and the stability field of pyrophyllite was not shown in our diagrams; and 4) run products were not characterized by AEM and STEM.

Figure 2 represents an attempt by Essene and Peacor (1995) to correct the phase relations shown in Figure 1 for their perceived violation of Schreinemakers' 180° rule. Several problems are apparent with this reconstruction. In the first instance, Essene and Peacor (1995) failed to recognize that Figure 1 is a summary diagram on which equilibrium conditions for 3 different phases [muscovite, endmember illite and illite(0.69K)] have been projected. An appreciation of this fact ought to show that the perceived violation merely reflects errors in the construction of Figure 1 rather than any inadequacy of the experimental data. Figure 3 shows rational phase boundaries which are consistent with the experimental data and in accord to Schreinemakers' 180° Rule. The univariant boundaries proposed by Essene and Peacor (Figure 2) have apparently been chosen arbitrarily without regard to current knowledge of phase equilibria in the system $K_2O-Al_2O_3-SiO_2-H_2O$. In their diagram (Figure 2), the thermal stabilities of muscovite and illite are inverted, which clearly contradicts phase relationships in both Figure 1 and the actual experimental data (Aja et al. 1991a; Figure 2) on which Figure 1 is based. Furthermore, consideration of experimental and theoretical studies in this system (Hemley 1959; Montoya and Hemley 1975; Sverjensky et al. 1991) indicates that univariant boundaries involving micaceous phases are curvilin-
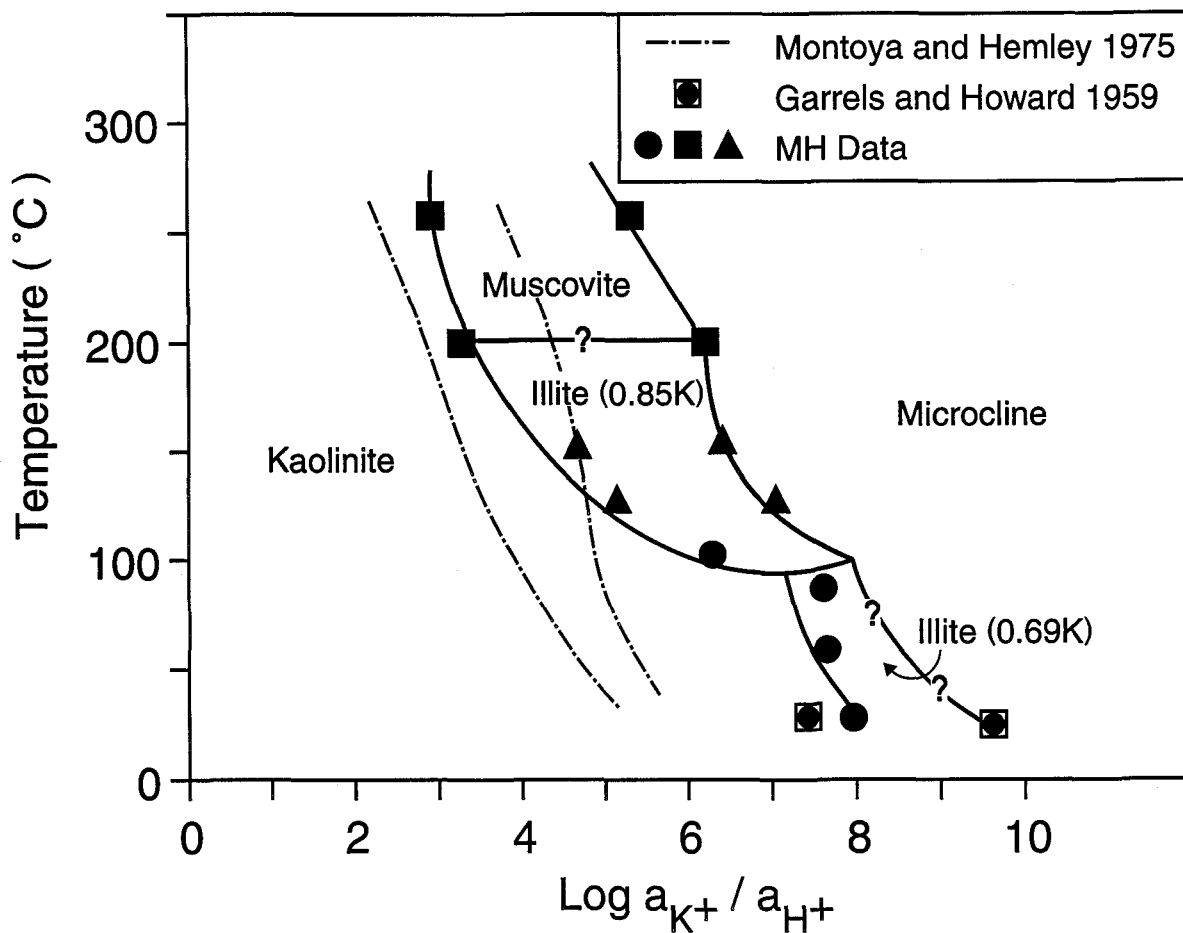
Figure 1. Temperature $-\log a_{K^+}/a_{H^+}$ diagram showing phase relationships in the system K_2O-Al_2O_3-SiO_2-H_2O in the presence of quartz. Key: Squares = equilibrium ion activities for muscovite; Triangles = endmember illite; Circles = ISII; and Question marks = uncertain boundaries (Aja et al. 1991a).

ear in temperature—log [K⁺]/[H⁺] space. The degree of curvature increases with decreasing temperature, which implies a shift of the equilibrium to more acidic conditions at higher temperatures. Since illitic materials are mica-like, a similar disposition of these univariant boundaries is to be expected although illitic phases equilibrate in less acidic aqueous solutions than does muscovite. These observations are consistent with the notion that illites are similar to muscovite and yet also distinct phases. Therefore, the topology of the univariant boundaries proposed by Essene and Peacor (1995) and shown in Figure 2 is misleading and fictitious. Ultimately, this question has become moot owing to the fact endmember illite is apparently stable beyond 250 °C (Aja 1995b; Yates and Rosenberg 1995) as shown in the revised phase diagram (Figure 4).

The second objection to our studies by Essene and Peacor (1995) is that the measured pH-pK⁺ and pH-0.5pMg²⁺ values may be controlled by exchangeable or absorbed cations, dissolution of fine crystallite

fractions, or reactions with surface layers only. We reject this argument on several grounds. The question of whether K is a structural or exchangeable cation is the primary reason why the measurements were conducted in decade solutions. An exchangeable K⁺ model implies that K⁺ does not participate in phase equilibria and therefore reactions involving illite should not depend on K⁺ activity in solution. Thus, illite phase boundaries in ion activity diagrams would vary with $\log(1/a_{H^+})$ rather than with $\log(a_{K^+}/a_{H^+})$. Results of our experiments show that a_{K^+} varies inversely with a_{H^+} in both 0.2 and 2.0 M runs implying that K⁺ does take part in reactions. If the alternative were true, K⁺ activity would not differ from its initial value and results of the 2.0 M runs would have plotted approximately one log unit below that of the 0.2 M runs. Evidently, interlayer cations behave as structural components during solution equilibration experiments (Kittrick and Peryea 1988, 1989). Moreover, a strong correlation exists in the distribution trends of data points (between isothermal, isobaric pH-0.5pMg²⁺ vs.
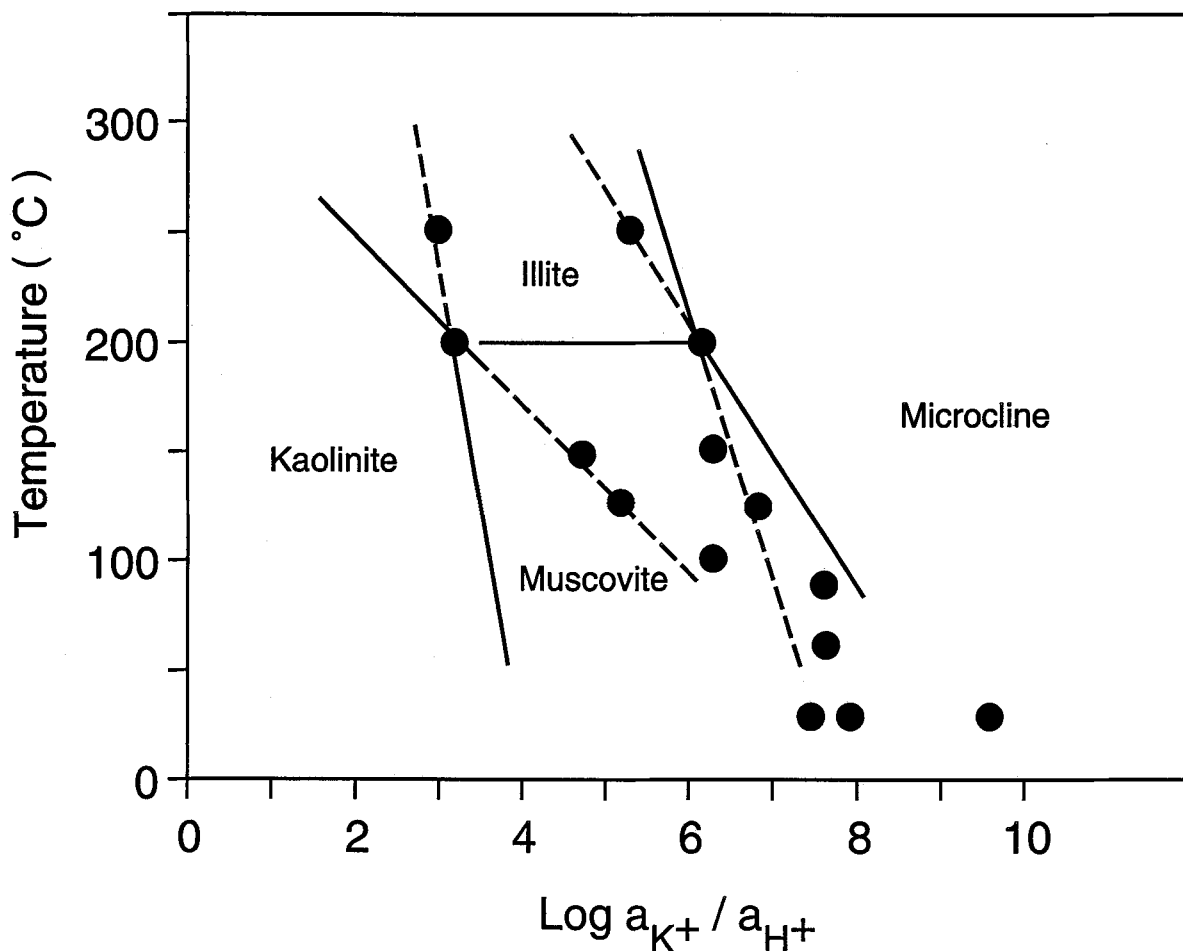
Figure 2.   Reconstruction of phase equilibria in Figure 1 suggested by Essene and Peacor (1995). Note that the distinctions made in the initial diagram for the different equilibria were completely neglected by the authors without any justification.

$pSiO_{2,aq}$ and $pH-pK^+$ vs. $pSiO_{2,aq}$ diagrams) over a wide temperature range, and an inverse relationship also exists between either $pH-pK^+$ or $pH-0.5pMg^{2+}$ and $pSiO2_{aq}$ (Aja et al. 1991a, 1991b). Nevertheless, Essene and Peacor (1995) speculated that Mg^{2+} was either an exchangeable cation or was adsorbed on clay surfaces in experiments with MH and we believe, this speculation is baseless. In our experiments with MH (and other illites), part of the pre-treatment included K-saturation by soak-washing with 1.0 M KCl solutions and exchangeable cations can usually be dislodged by such treatment. Furthermore, adsorption processes of alkali and alkaline earth cations (on mineral surfaces) are dominated by outer-sphere mechanisms and are thus strongly dependent on ionic-strength (Parks 1990). If our solution equilibration data were dominated by adsorption phenomenon rather than by phase equilibria, the internal topological consistency and the predictable correlation between different isothermal, isobaric diagrams (Aja et al. 1991a, 1991b; Aja and Rosenberg 1992) become problemat-

ical since these are trends that can only be rationalized by phase equilibrium arguments. The notion that some nebulous, poorly understood processes might be controlling these concise solubility trends (as implied by Essene and Peacor 1995) is therefore difficult to justify.

The third issue raised by Essene and Peacor (1995) is that it is inappropriate to omit the stability fields of pyrophyllite and diaspore from the diagram. Although diaspore is the most stable aluminum oxyhydroxide, it did not appear in our experiments at low temperatures ostensibly due to kinetic restrictions (Hemley et al. 1980). Conversely, the authors are apparently not aware that pyrophyllite becomes a stable phase only at $T \geq 300\ ^\circ C$ (Sverjensky et al. 1991), well above the temperature range investigated (Aja et al. 1991a). Furthermore, it did not appear as a metastable phase in our experiments.

The criticism that the solid products of our experiments were not characterized by STEM is a valid one, and we are fully aware of the importance of solid state
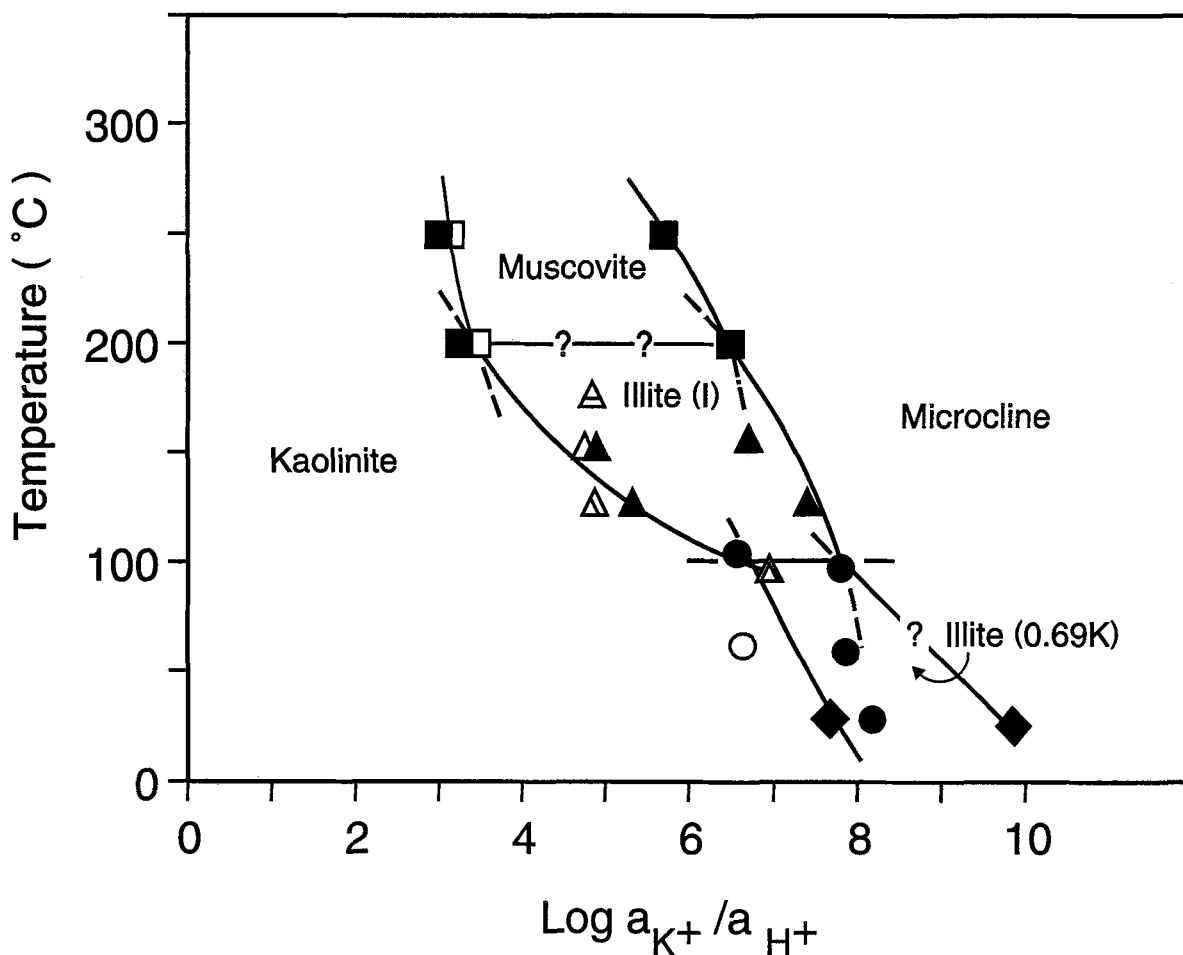
Figure 3. Temperature $-\log a_{K^+}/a_{H^+}$ diagram showing phase relationships in the system K_2O-Al_2O_3-SiO_2-H_2O in the presence of quartz. Positions of phase boundaries have been drawn to conform with Schreinemakers rules. Key: Squares = equilibrium ion activities for muscovite; Triangles = endmember illite; Circles = ISII; Solid symbols = data points from experiments with MH illite; Open symbols = data points from experiments with GL illite; Diamonds = data points from Garrels and Howard (1959); and Question marks = uncertain boundaries. The uncertainty in the location of the illite $\rightleftharpoons$ muscovite boundary (question marks) reflects the difficulty in distinguishing between endmember illite and endmember muscovite compositions from the slopes of univariant boundaries in isothermal, isobaric pH-pK$^+$ vs. pSiO$_{2,aq}$ diagrams.

studies (Aja 1995b). However, we disagree with Essene and Peacor (1995) that meaningful phase equilibrium relationships cannot be deduced from solution chemistry. Solid products of these illite-bearing experiments have now been analyzed by AEM (Yates 1993; 212–214). Yates' results are consistent with those based on the chemistry of coexisting solutions. Furthermore, Primmer et al. (1993) who conducted experiments similar to ours (Aja et al. 1991a) found illite compositions inferred from solution chemistry and from AEM analyses of coexisting solid products to be in close agreement. The compositions of solid products of muscovite-kaolinite experiments (Yates 1993; Yates and Rosenberg 1993, 1995), which were analyzed by AEM are also consistent with the compositions inferred from solution chemistry. Not only do the latter experiments document the growth of illite, they

also suggest that muscovite-kaolinite assemblage is not stable at T < 300 °C in agreement with observations in natural environments (McDowell and Elders 1980).

TEM CHARACTERIZATION OF CLAY MINERALS

Within the last 15 years, numerous electron microscope investigations have been conducted of illite, smectite and illite/smectite minerals. Early high resolution transmission electron microscopic investigations of illite/smectite (Ahn and Peacor 1986; Klimentidis and Mackinnon 1986; Yau et al. 1987) suggested that smectite and illite layers could not be differentiated owing to the dehydration and collapse of smectite layers under the electron beam. However, computer simulation of microscope images (Guthrie and Veblen
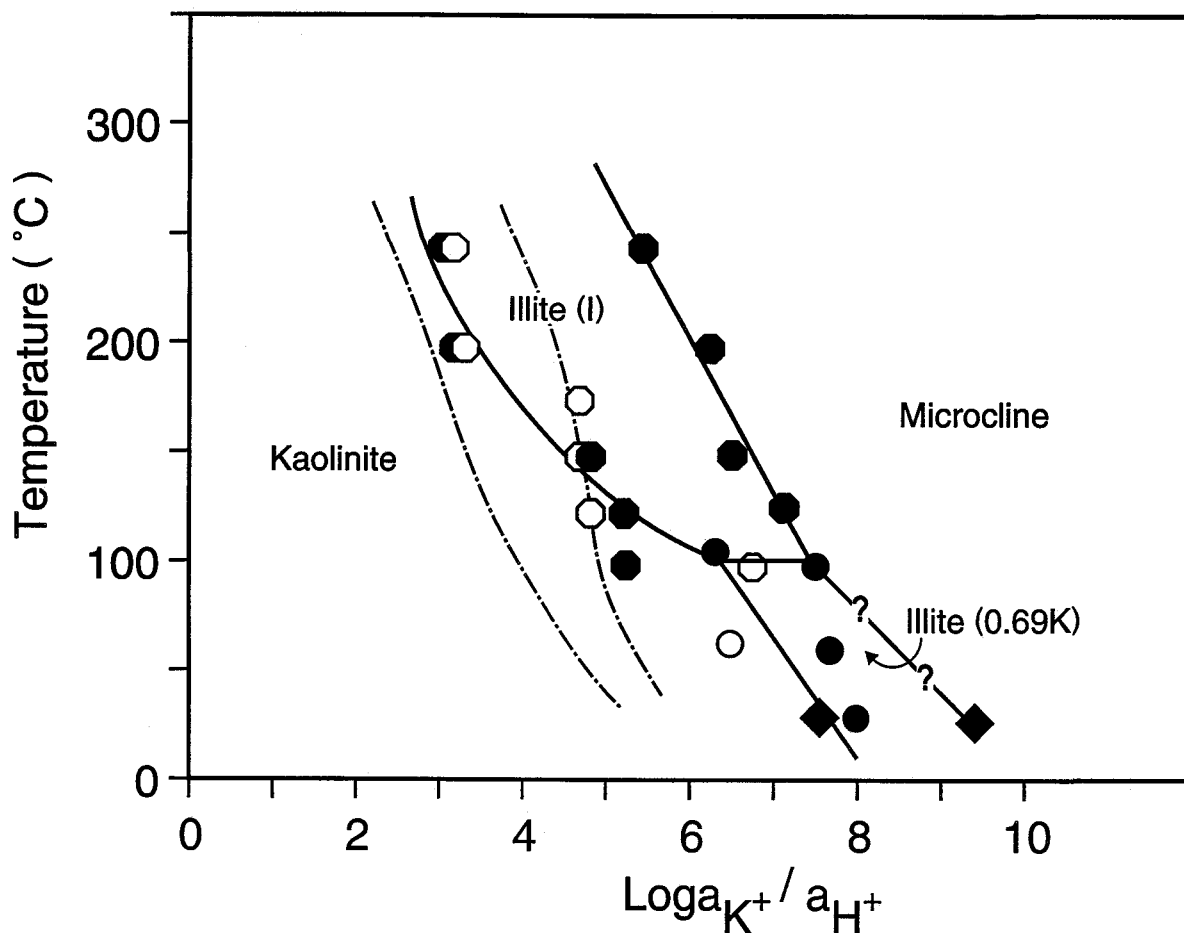
Figure 4.   Revised temperature $-\log a_{K^+}/a_{H^+}$ diagram showing phase relationships in the system K_2O-Al_2O_3-SiO_2-H_2O in the presence of quartz. The lower limit of muscovite stability is unknown but probably lies between 250 and 300 °C. The solubility-limiting phases are endmember illite and illite (0.69K). Key: Hexagons = equilibrium ion activities for endmember illite; Circles = equilibrium ion activities for ISII [illite (0.69K)]; Solid symbols = data points from experiments with MH illite; Open symbols = data points from experiments with GL illite; Diamonds = data points from Garrels and Howard (1959); Question marks = uncertain boundaries owing to lack of data; and Dot-dashed boundaries = the field of muscovite stability predicted by Montoya and Hemley (1975).

1989, 1990) demonstrated that illite and collapsed smectite layers produce lattice fringes with different contrast under appropriate focus conditions. In subsequent HRTEM studies (Ahn and Buseck 1990; Jiang et al. 1990; Veblen et al. 1990; Amouric and Olives 1991), illite and smectite layers showing varying degrees of ordering could be differentiated. Veblen et al. (1990) also noted that I/S layer stacking obtained by XRD compares favorably with HRTEM results. A limitation of computer image simulation experiments is the presumption of a certain structural model (of illite and smectite). Therefore, this constrains the results of the investigations.

An alternative approach to TEM study of clay materials (Vali et al. 1991, 1994) combines ultramicrotomy, n-alkylammonium exchange with HRTEM observation. The primary advantages of this technique is that n-alkylammonium loading is dependent on layer charge of the clay material and the clay-solvent complex is stable under the electron beam. HRTEM examination of clays treated in this manner shows the existence of at least three different layer types and is consistent with the multi-phase nature of illites suggested by our solubility studies (Vali et al. 1991). However, because ATEM analysis of the different components are not provided by Vali and co-workers, further exploration of the correlation between independent solubility and HRTEM data must await additional studies.

The implication of these TEM studies for the nature of clay minerals is one of the unresolved fundamental questions. Essene and Peacor (1995) maintain that a wide variety of diagenetic clays are comprised of complex submicroscopic intergrowths of minerals such as

smectite, chlorite and/or illite. According to them, this heterogeneity is also reflected in the chemistry of the layers and thus confirms the disequilibrium solid model of all compositionally-complex 2:1 clay minerals (Lippmann 1977, 1982). However, several problems are attendant on this conclusion. First of all, the true extent of compositional variability of 2:1 layer clays is much smaller than the possible range of compositions (Aja and Rosenberg 1992). Secondly, a credible alternative to the presumption of intrinsic instability exists that rationalizes real compositional variations in terms of environmental constraints (Aja and Rosenberg 1992). Recent ATEM studies of clay minerals support such a conclusion. For instance, in their ATEM studies of clays from the Salton Sea Geothermal Field (SSGF), Yau et al. (1987) reported the occurrence of discrete illite and I/S with the former being constrained to lower depths (higher temperatures). The discrete illite crystals are subhedral to pseudohexagonal plates, have interlayer K contents of 0.7 to 0.8 per half unit cell and show little variation with depth. Yau et al. (1987) argued that the "relatively uniform size and shape of all SSGF illites at all depths, coupled with a lack of compositional zoning within individual illites, imply that early formed crystals underwent no further reaction with increasing depth". The lack of compositional variation in illites at the ATEM scale has also been documented by other workers. In the Broadlands-Ohaaki Geothermal System, well-formed compositionally-homogeneous illite crystals were observed using ATEM methods (Lonker et al. 1990). Limited compositional variation has also been reported from illites in sandstone formations (Warren and Curtis 1989). The presumption of attainment of equilibrium, during the crystallization and growth of these crystals, is warranted under such circumstances.

Clearly, these environments are characterized by elevated temperatures and relatively free-flowing hydrologic regimes and thus contrast with environments typical of shales, mudstones and weathering where steep chemical gradients are likely to persist. Apparently, clay minerals formed in the latter environments often show significant compositional variation. This cannot mean that such phases are not thermodynamic phases (Lippmann 1977, 1982; May et al. 1986; Essene and Peacor 1995) as such a conclusion would imply that the definition of the thermodynamic phase is based on the environment of formation. Rather, it suggests that under these lower low temperature environments, homogenization of the chemistry of early clay phases may be precluded by kinetic restrictions. This may well be the case considering that the diversity and variability in composition of slightly to moderately buried clay minerals become simpler at depths of burial exceeding two kilometers (Chamley 1989).

DISCUSSION

The primary difficulty confronting low temperature experimental geochemists is the sluggish rates of aluminosilicate reactions under these conditions. Aja and Rosenberg (1992) observed that the attainment of equilibrium in solubility experiments may be presumed if: 1) the same steady state can be approached from at least two directions; 2) the slopes of univariant boundaries representing mineral-solution equilibria are consistent with thermodynamic arguments; and 3) results of solution equilibration are independent of duration of experiments. Similar criteria have been employed by other investigators of mineral-solution equilibria (Hemley et al. 1980). By contrast, Essene and Peacor (1995) maintain that direct experimental reversals of equilibria must be obtained by documenting growth and/or dissolution of solid reactant(s) and product(s). This test for equilibrium is theoretically correct but can be accomplished only under ideal conditions. In the real world adherence to such an ideal, all or nothing, standard is impractical. Less rigorous criteria may not provide absolute proof of equilibrium, but can make a strong and convincing case that equilibrium has been attained. Constraints imposed by environmental conditions must be factored into decisions as to what constitutes acceptable "proof" of equilibrium. The evidence supporting the attainment of equilibrium in our solution equilibration experiments (Sass et al. 1987; Aja et al. 1991a, 1991b) meets or exceeds practical standards for near surface conditions.

Based on the solubility studies of Sass et al. (1987) and Aja et al. (1991a, 1991b), Rosenberg et al. (1990) proposed a multi-phase model of I/S in which the solubility controlling phases include four discrete thermodynamic entities of different chemical compositions. The compositions of these phases were shown to be comparable to compositions of natural hydrothermal illites. Nonetheless, only two of these illitic phases controlled solubility in the presence of quartz; ISII [0.69 ± 0.08 K/$O_{10}(OH)_2$] at T $\leq$ 100 °C and endmember illite [0.85 ± 0.05 K/$O_{10}(OH)_2$] at T $\geq$100 °C (Figures 3 and 4). Similarly, Yates and Rosenberg (1993, 1995) determined from their muscovite-kaolinite equilibrations that solubility was controlled by endmember illite [or 0.88 ± 0.04 K/$O_{10}(OH)_2$] at T $=$ 100–250 °C. Since the starting materials included either illite (Sass et al. 1987; Aja et al. 1991a, 1991b) or muscovite (Yates and Rosenberg 1993, 1995), the presumption of a reaction reversal indicating equilibrium is warranted. The results of these hydrothermal experimental studies appear to have general application. For instance, Srodon et al. (1992) investigated the chemistry of several natural clay samples (Silurian Welsh Borderland bentonites, Carboniferous Silesia bentonite, Tertiary Silverton Caldera sericites, Kaube sericite and Zempleni illite). According to them, a sta-

ble charge of $0.89/O_{10}(OH)_2$ exists on the illite interlayer. That is, the composition of endmember illite determined from experimental and empirical observations is essentially the same suggesting an approach toward an equilibrium composition.

The presumption, by Essene and Peacor (1995), that clay mineral transformation reactions (smectite → I/S → illite → muscovite) are irreversible is also questionable. Not only do our experimental measurements suggest otherwise, field observations appear also to indicate that this is not the case. For instance, McDowell and Elders (1983) demonstrated that detrital muscovite is altered to very fine-grained mixed-layer illite/smectite through a phengitic muscovite phase indicating reversibility of illitization reactions. Other examples of muscovite illitization are summarized by Srodon and Eberl (1984). Clearly, field and laboratory evidence show that retrograde (illitization of muscovite) and prograde (illitization of smectite) reactions proceed through intermediate steps suggesting that these transformation reactions conform to Ostwald's Step rule (Aja 1989). This does not necessarily imply intrinsic instability but may be a reflection of the role of particle thickening during illitization (Nadeau et al. 1985; Putnis 1992; Primmer 1994). In that case, the repeatability of clay mineral assemblages in space and time and as a function of temperature partially justifies clay mineral geothermometery. Although current estimates of temperature are somewhat variable, the reliability of this geothermometer is likely to improve as factors controlling illitization reactions, other than temperature, become better constrained (Aja 1995c).

We conclude by noting that whereas valuable structural and compositional data may be obtained from ATEM studies, solubility experiments provide the only means available for the determination of the chemical composition of thermodynamic phases in natural illitic materials. The arbitrary size limitations imposed by Essene and Peacor (1995) have no particular significance. In our view, any mineral that behaves as a phase in solution equilibration experiments is a thermodynamic phase (Rosenberg et al. 1990) regardless of whether it is stable or metastable. We further emphasize the need to distinguish between metastable and unstable phases (disequilibrium solids) in the context of this controversy.

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REFERENCES

Ahn JH, Peacor DR. 1986. Transmission and analytical electron microscopy of the smectite-to-illite transmission. Clays & Clay Miner 34:165–179.

Ahn JH, Buseck PR. 1990. Layer-stacking sequences and structural disorder in mixed-layer illite/smectite: image simulations and HRTEM imaging. Am Miner 70:267–275.

Aja SU. 1989. A hydrothermal study of illite stability relationships between 25 and 250°C. [PhD thesis]. Pullman, Washington:Washington State University. 191 p.

Aja SU. 1991. Illite equilibria in solutions: III. A re-interpretation of the data of Sass et al. (1987). Geochim Cosmochim Acta 55:3431–3453.

Aja SU. 1995a. Estimates of mineral dissolution rates: a semi-empirical approach. Prog. & Abstr. V.M. Goldschmidt Conf. p 24.

Aja SU. 1995b. Thermodynamic properties of some 2:1 layer clay minerals from solution-equilibration data. Eur J Miner 7:325–333.

Aja SU. 1995c. Controls on illitization: A thermodynamic approach. In:OTI MN. and POSTMA G, editors, Geology of Deltas. Rotterdam:Balkema Publishers. p 209–215.

Aja SU, Rosenberg PE. 1992. The thermodynamic status of compositionally-variable clay minerals: A discussion. Clays & Clay Miner 40:292–299.

Aja SU, Rosenberg PE, Kittrick JA. 1991a. Illite equilibria in solutions: II. Phase relationships in the system K_2O-Al_2O_3-SiO_2-H_2O. Geochim Cosmochim Acta 55:1353–1364.

Aja SU, Rosenberg PE, Kittrick JA. 1991b. Illite equilibria in solutions: II. Phase relationships in the system K_2O-Al_2O_3-MgO-SiO_2-H_2O. Geochim Cosmochim Acta 55:1365–1374.

Amouric M, Olives J. 1991. Illitization of smectite as seen by high-resolution transmission electron microscopy. Eur J Miner 3:831–835.

Anderson GM, Crerar DA. 1993. Thermodynamics in Geochemistry: The equilibrium model. New York:Oxford University Press. 588 p.

Broxton DE, Bish DL, Warren RG. 1987. Distribution and chemistry of diagenetic minerals at Yucca Mountain, Nye County, Nevada. Clays & Clay Miner 35: 89–110.

Chamley, H. (1989) Clay sedimentology. Berlin:Springer-Verlag. 623 p.

Essene EJ, Peacor DR. 1995. Clay mineral thermometry: A critical perspective. Clays & Clay Miner. 43:540–553.

Garrels RM. 1984. Montmorillonite/illite stability diagrams. Clays & Clay Miner 32:161–166.

Guthrie GD Jr., Veblen DR. 1989. High-resolution transmission electron microscopy of mixed-layer illite/smectite: computer simulations. Clays & Clay Miner. 37:1–11.

Guthrie GD Jr., Veblen DR. 1990. Interpreting one-dimensional high-resolution transmission electron micrographs of sheet silicates by computer simulation. Am Miner 75:276–288.

Hemingway BS, Robie RA. 1984. Thermodynamic properties of zeolites: low-temperature heat capacities and thermodynamic functions for phillipsite and clinoptilolite. Estimates of the thermochemical properties of zeolitic water at low temperature. Am Miner 69:692–700.

Hemley JJ. 1959. Some mineralogical equilibria in the system K_2O-Al_2O_3-SiO_2-H_2O. Am J Sci 257:241–270.

Hemley JJ, Montoya JW, Marineko JW, Luce RW. 1980. Equilibria in the system Al_2O_3-SiO_2-H_2O and some general implications for alteration/mineralization processes. Econ Geol 25:210–228.

Jiang WT, Peacor DR, Essene EJ. 1990. Clay minerals in the MacAdams Sandstone, California: Implications for substi-

tution of H_3O^+ and H_2O and metastability of illite. Clays & Clay Min 41:35–45.

Kittrick JA. 1983. Accuracy of several immiscible displacement liquids. Soil Sci Soc Am J 47:1045–1047.

Kittrick JA, Peryea FJ. 1988. Experimental Validation of the monophase structure model for montmorillonite solubility. Soil Sci Soc Am J 52:1199–1201.

Kittrick JA, Peryea FJ. 1989. The monophase model for Mg-saturated montmorillonite. Soil Sci Soc Am J 53:292–295.

Klimentidis RE, Mackinnon IDR. 1986. High-resolution electron microscopy of ordered mixed-layer clays. Clays & Clay Miner 34:155–164.

Lippmann F. 1977. The solubility product of complex minerals, mixed-crystals and three layer clay minerals. N Jb Miner Abh 130:243–263.

Lippmann F. 1982. The thermodynamic status of clay minerals. Proc 7th Intl Clay Conf 1981, 475–485 p.

Lonker SW, Fitz Gerald JD, Hedenquist JW, Walshe JW. 1990. Mineral-fluid interactions in the Broadlands-Ohaaki Geothermal System, New Zealand. Am J Sci 290:995–1068.

Macinnis I.N, Ganor J, Lasaga AC. 1995. Solubility and reaction kinetics of analcime and clinoptilolite at low temperatures. Prog and Abstr VM Goldschmidt Conf. p 66.

May HM, Kinniburgh PA, Helmke PA, Jackson ML. 1986. Aqueous dissolution, solubilities and thermodynamic stabilities of common aluminosilicate clay minerals: kaolinites and smectites. Geochim Cosmochim Acta 50:1667–1677.

McDowell SD, Elders W. 1980. Authigenic layer silicate minerals in borehole Elmore #1, Salton Sea Geothermal Field, California. Contrib Mineral Petrol 74:293–310.

McDowell SD, Elders W. 1983. Allogenic layer silicate minerals in borehole Elmore #1, Salton Sea Geothermal Field, California. Am Miner 68:1146–1159.

Montoya JW, Hemley JJ. 1975. Activity relations and stabilities in alkali feldspar and mica alteration reactions. Econ Geol 70:577–594.

Murphy WM, Prikryl JD, Pabalan RT. 1995. Reaction kinetics and reversibility of analcime dissolution at pH 9 and 25°C. EOS Trans. 76 (17), Spring Meet. Suppl. S102.

Nadeau PH, Wilson MJ, McHardy WJ, Tait J.M. 1985. The conversion of smectite to illite during diagenesis: evidence from some illitic clays from bentonites and sandstones. Mineral Mag 49:393–400.

Parks GA. 1990. Surface energy and adsorption at mineral/water interfaces: an introduction. In:Hochella MF, Jr., White AF, editors. Mineral-Water Interface Geochemistry, Reviews in Mineralogy 23:133–176.

Primmer TJ. 1994. Some comments on the chemistry and stability of interstratified illite-smectite and the role of Ostwald-type processes. Clay Miner 29:63–68.

Primmer TJ, Warren EA, Sharma BK, Atkins MP. 1993. Experimental studies of diagenesis and weathering. In: Manning DAC, Hall PL, Hughes CR, editors. Geochemistry of clay-pore fluid interaction. The Mineralogical Society Series 4. London: Chapman and Hall. p 161–180.

Putnis A. 1992. Introduction to mineral sciences. Cambridge: Cambridge University Press. 375 p.

Rosenberg PE, Kittrick JA, Aja SU. 1990. Mixed-layer illite/smectite: a multi-phase model. Am Miner 75:1182–1185.

Sass BM, Rosenberg PE, Kittrick JA. 1987. The stability of illite/smectite during diagenesis: an experimental study. Geochim Cosmochim Acta 51:2103–2115.

Srodon J, Eberl DD. 1984. Illite In:Bailey SW, editor. Micas, Reviews in Mineralogy. 13:495–544.

Srodon J, Elsass F, McHardy WJ, Morgan DJ. 1992. Chemistry of illite-smectite inferred from TEM measurements of fundamental particles. Clay Mineral 27:137–158.

Sverjensky DM, Hemley JJ, D'angelo WM. 1991. Thermodynamic assessment of hydrothermal alkali feldspar-mica-aluminosilicate equilibria. Geochim Cosmochim Acta 55:989–1004.

Vali H, Hesse R, Köhler EE. 1991. Combined freeze-etch replicas and HRTEM images as tools to study fundamental particles and multiphase nature of 2:1 layer silicates. Am Miner 76:1973–1984.

Vali H, Hesse R, Martin RF. 1994. A TEM-based definition of 2:1 layer silicates and their interstratified constituents. Am Miner 79:644–653.

Veblen DR, Guthrie GD Jr, Livi KJT, Reynolds RC Jr. 1990. High-resolution transmission electron microscopy and electron diffraction of mixed-layer illite/smectite: experimental results. Clays & Clay Miner 38:1–43.

Warren EA, Curtis CD. 1989. The chemical composition of authigenic illite within two sandstone reservoirs as analyzed by ATEM. Clay Miner 24:137–156.

Wilkin RT, Barnes HL. 1995. Solubilities of the zeolites analcime and Na-clinoptilolite at low temperatures. Prog & Abstr VM Goldschmidt Conference. 97 p.

Yates DM. 1993. Experimental investigation of the formation and stability of endmember illite from 100 to 250°C and $P_{v,H2O}$. [PhD thesis]. Pullman, Washington:Washington State University. 224 p.

Yates DM, Rosenberg PE. 1993. Hydrothermal transformation of muscovite to endmember illite at 250°C and $P_{v,H2O}$. Geol Soc Am Abst with Prog 25. p 437.

Yates DM, Rosenberg PE. 199. Formation of end-member illite: revised multi-phase model. Prog and Abstr VM. Goldschmidt Conference. p 99.

Yau YC, Peacor DR, Beane RE, Essene EJ, McDowell SD. 1987. Microstructure, formation mechanisms, and depth-zoning of phyllosilicates in geothermally altered shales, Salton Sea, California. Clays & Clay Miner 36:1–10.