

## REPLY

### ILLITE AND SMECTITE: METASTABLE, STABLE OR UNSTABLE? FURTHER DISCUSSION AND A CORRECTION

E. J. ESSENE AND D. R. PEACOR

Department of Geological Sciences, The University of Michigan,  
Ann Arbor, Michigan 48109-1063

**Key Words**—Illite Phase Equilibria, Metastability, Schreinemakers' Rules, Stability.

Essene and Peacor (1995 = "EP") published a general review of clay mineral thermometry, the stability of clay minerals and the relevance to natural clay mineral assemblages. Some of the conclusions in that paper have been criticized by Aja and Rosenberg (1996 = "AR"). Our paper dealt with some issues about which there has been healthy (and sometimes highly charged) debate. Such dialogue normally takes the form of 2 papers frequently published in tandem, one a criticism and another a response. We are grateful for a belated opportunity to further discuss the thermodynamic and mineralogical status of compositionally and structurally variable clay minerals, in part because this subject is of critical importance to clay mineralogists. It is therefore essential that the basic theory be clearly defined and understood. This has largely to do with some elementary, but critically important, thermodynamic relations. The discussion of issues by AR is largely in error or misleading and begs for correction. Although Aja and Rosenberg (1992) is not specifically addressed here, many of the points raised represent a criticism of that assessment as well. We will respond only to some of the more important points of disagreement below.

#### THE SIGNIFICANCE OF EXPERIMENTS THAT MAY NOT ATTAIN EQUILIBRIUM

AR note that the usual test for equilibrium (experimental reversals) "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." They imply that they have done the best that can be done in systems for which more rigorous tests are impractical. We are pleased that AR recognize that their experiments do not meet rigorous criteria. Wishing them to represent stable equilibrium because (in their opinion) the evidence supports such

a contention is not sufficient, when such conclusions are at the roots of a subject as important as the understanding of the driving forces behind maturation of clay minerals in prograde environments and at variance with a plethora of data as described, in part, by EP. Petrologists long ago learned the dangers of premature application of experimental results for which equilibrium was not rigorously proven (Fyfe 1960). Whether or not illite or smectite is metastable is not a matter of probability. They either formed in states of equilibrium, or they did not. We only plead that experimentalists do not claim or even imply that equilibrium is attained in a system when it is not rigorously demonstrated. Claiming it to be so when rigorous tests cannot or are not made, *even if one has done the best that can be done*, does not make it so.

AR imply that EP believe that experiments that involve metastable reactants and/or products are without value. On the contrary, EP noted that kinetic experiments of the kind carried out by Huang et al. (1993) are both valuable and necessary. The kinetic factors controlling rates of reaction and occurrences of metastable phases can be completely understood only with respect to such experiments. There is much value in relating the occurrence of metastable clay minerals to geological variables, including temperature, through the concept of reaction progress. The relations must, however, be properly interpreted, as we believe has been done with clarity by Huang et al. (1993). By recognizing that clays such as illite and smectite are metastable, the framework for understanding kinetic factors affecting mineral occurrences can be established.

#### THE STATUS OF COMPOSITIONALLY VARIABLE CLAYS AS MINERALS OR PHASES

AR state that EP concluded that such clays are not distinct minerals or phases solely because of their

chemical variability. This is a misleading summary of our views, which are that:

clays often comprise heterogeneous assemblages of submicroscopic layers consisting of different structure types such as illite, smectite and chlorite, with variable composition in a given structure. The dimensions of mixed layers, the semi-coherent to coherent nature of the structures across the layering, and compositional heterogeneity occur at a scale well below that of an individual thermodynamic phase. These relations imply that most clays are not distinct minerals or phases, and that assemblages of clays in shales and mudstones are incompatible with the phase rule. Such relations are better evaluated in terms of the formation of metastable materials with each small unit having unique chemical properties, rather than as a small number of stable homogeneous phases. Consequently, treatment of most clay minerals in terms of equilibrium stability with either a thermodynamic or experimental approach is subject to error. (EP abstract)

It is the *structural* heterogeneity and complexity of many clay minerals at the ultrastructural level that is the major-concern for their consideration as phases in the Gibbsian sense. The observed structural complexities and their implications are largely ignored by AR. That is surprising in that the literature is now replete with transmission electron microscopy (TEM) studies that document such structural and compositional heterogeneity. Furthermore, there is a growing array of data showing that such heterogeneity decreases with increasing grade, as equilibrium is approached (Peacor 1992a). Although Rosenberg and coworkers have not studied natural materials systematically, they should be aware of the structural complexities of natural clays as described in many papers in general, and in those natural systems analogous to their experiments, in particular.

#### TESTS FOR EQUILIBRIUM IN NATURAL MATERIALS

AR describe TEM studies in which chemical homogeneity of illite was demonstrated by analytical electron microscopy (AEM), i.e., at the highest levels of analytical resolution now possible. They then state that “the presumption of attainment of equilibrium, during the crystallization and growth of these crystals, is warranted under such circumstances.” The circumstances include no data other than the claimed chemical homogeneity. We maintain that this kind of conclusion is at the core of the problem. Although chemical homogeneity (if present) is *necessary* to a state of stable equilibrium, it is not even close to providing *sufficient* evidence. Our original review was meant to caution against such claims of stable chemical equilibrium.

AR go on to say that the above studies imply that chemical homogeneity vs. heterogeneity is related to environment of formation, with chemical homogeneity enabled by higher temperatures and fluid/rock ratios, and heterogeneity occurring in rocks such as mudstones and shales. They then note that “This cannot mean that such phases are not thermodynamic phases . . . as such a conclusion would imply that the definition of the thermodynamic phase is based on the environment of formation.” A material that is a thermodynamic phase is so-judged only on the basis of its physico-chemical characteristics. No one would fail to characterize muscovite as such in most mica schists, in part because equilibrium was approached. If illite has features that preclude its being a phase in some very low-temperature systems, where kinetic factors are paramount, so be it. The definition is not connected to environment of formation, but to properties of the materials, which are a *function* of that environment.

Peacor (1992a) emphasized that clay minerals that form at low temperatures generally have maximum structural and chemical heterogeneity and defect densities and minimum sizes (as measured, in part, by illite crystallinity). These features are directly related to kinetic factors that depend upon the environment of formation. There is a well-recognized trend of decreasing complexity and increasing homogeneity with increasing grade, up to the greenschist facies where stable equilibrium is approached or attained. It is exactly because the state of earth materials is a direct consequence of the environment of formation that we are able to unravel the apparent complexities of natural systems. It is precisely because minerals such as illite reflect metastable states that we are able to discern such sequences and to rationalize their causes in factors such as reaction kinetics as partially understood through the Ostwald Step Rule.

#### DISTINCTION BETWEEN METASTABLE AND UNSTABLE ASSEMBLAGES

AR argue that EP did not distinguish between metastable and unstable assemblages, although AR conclude that the distinction can only be made in well-understood systems. The difference is really moot, equivalent to problems envisioned if “ice IX” in a work of science fiction (Vonnegut 1963) or polywater (Franks 1981) were a stable phase in the system H<sub>2</sub>O at standard temperature and pressure (STP). One can never rule out the possibility of a yet more stable phase and/or assemblage based only on its nonoccurrence. In addition, all compound phases or phase assemblages that can be specified have yet less stable chemical equivalents. For instance, all minerals (crystalline phases) ± H<sub>2</sub>O are more stable at low temperatures than chemically equivalent noncrystalline material, whether it is an amorphous solid, gel, glass or plasma of gaseous atoms. Thus, any crystalline assem-

blage judged to be less stable than all other alternative crystalline assemblages  $\pm \text{H}_2\text{O}$  is still more stable than wholly noncrystalline alternatives at low temperatures, and therefore any mineral or mineral assemblage is metastable instead of unstable. The important question for this discussion is whether or not illite and smectite are stable or metastable. There are at least 3 possibilities.

1) *Are illite and/or smectite only stable with water at a silica activity  $> 1$  and therefore always metastable in equilibrium with quartz, although stable with amorphous silica?* Amorphous silica itself should not be regarded as a single phase with unique thermodynamic properties, as it must depend on variable short-range order and  $\text{H}_2\text{O}$  content. This possibility is analogous to relationships for the assemblages pyrophyllite-microcline and kaolinite-microcline, which may always be metastable relative to muscovite-quartz- $\text{H}_2\text{O}$ . El Shazly (1995) assumed that reported low-temperature occurrences of kaolinite-microcline indicate that it is a stable rather than metastable assemblage. He forced large changes in the thermodynamic properties of kaolinite to generate phase equilibria consistent with this unsupported inference. An alternative and more reasonable view is that kaolinite can be equilibrated with microcline only in low-temperature aqueous solutions supersaturated with silica (Bowers et al. 1984; Björkum and Gjelsvik 1988). Whether microcline-kaolinite is more or less stable than illite or smectite at  $a_{\text{SiO}_2} > 1$  is still unclear. If El Shazly's supposition were correct, there would be even less room for illite or smectite stability, even at  $a_{\text{SiO}_2} > 1$ .

2) *Is illite  $\pm \text{H}_2\text{O}$  less stable than muscovite-pyrophyllite and/or muscovite-kaolinite-quartz, as maintained by Lippmann (1977, 1982) and Jiang et al. (1990, 1994)?* AR interpret this relationship as requiring illite to be unstable. AR's classification of one relationship as metastable and another as unstable (if indeed pyrophyllite-muscovite is always more stable than illite) has no thermodynamic basis. If a more stable assemblage involving quartz-kaolinite or pyrophyllite-muscovite fails to nucleate or grow, metastable reactions producing kaolinite + microcline, smectite or illite may proceed. Comparison of the stability field for kaolinite-muscovite (Bowers et al. 1984; Sverjensky et al. 1991) with the experimental data for kaolinite-illite by Sass et al. (1987), Aja (1991), Aja et al. (1991) and AR suggests that the experimental illite is metastable in the stability field with water and quartz.

3) *Are illite and smectite  $\pm \text{H}_2\text{O}$  more stable than gel, amorphous solid or glass?* Volcanic glass of basaltic to andesitic composition rapidly hydrates to form amorphous "palagonite", which then is transformed to

smectite (Eggleton 1987; Zhou et al. 1992; Schiffman and Southard 1996). These relations indicate that the noncrystalline materials  $\pm \text{H}_2\text{O}$  are less stable than smectite and other products (Masuda et al. 1996). Smectite is therefore clearly more stable than the noncrystalline materials. However, the widespread formation and persistence of illite or smectite in sediments cannot be used to address their stability relative to muscovite-kaolinite.

#### TEM AND AEM STUDIES OF CLAY MINERALS

TEM has become one of many tools for studying the complexities of clay minerals. Not only must natural materials be intensively studied, but reactants and products of laboratory experiments should be rigorously characterized. This is critical when reactants and products include materials such as illite and smectite that are known to be heterogeneous. Although AR have claimed to have so-tested their materials, they have yet to publish the TEM/AEM data that support such claims. Science is based on providing appropriate data that are subject to scrutiny and testing. Conclusions cannot be reached without the necessary data, and claiming that appropriate data exist is not sufficient. If characterization of clay minerals is to be carried out in part through TEM observations, those observations should be properly described in publications. Peacor and coworkers have emphasized that it is precisely because clay minerals can be heterogeneous, especially with respect to mixed-layering, that they should be characterized using the full power of TEM (Peacor 1992a, 1992b, and references therein). Moreover, AEM analytical methods must take a multitude of problems into consideration, and be so-described. The companion paper of Rosenberg and Hooper (1996) contains AEM analyses for several flat samples of "sericite" from Silverton, Colorado, with a 1300-nm (1.3- $\mu\text{m}$ ) raster, at the analytical resolution of modern scanning electron microscopes (SEMs) and electron microprobes (EMPs). Contrary to the statements in AR, the "sericites" analyzed by Rosenberg and Hooper (1996) are not their experimental run products. No textural evidence is provided that a neoformed clay mineral has grown on nuclei on the experimental runs, nor that the clay mineral has shifted its Si content during the experiments. Low-resolution TEM images of crystal separates on holey-carbon films, lacking details of high-resolution analysis, constitute insufficient characterization. Published AEM and scanning TEM (STEM) data for the run products in the experiments are lacking.

Yates and Rosenberg (1993) concluded that the variation of Gibbs free energy with illite composition is linear between  $K_{0.69}$  and  $K_{0.88}$ . This conclusion is exceedingly unlikely; it implies that illites are acting as physical mixtures of pyrophyllite and muscovite rather than as chemically and structurally distinct com-

pounds. Compounds such as IS and ISII are not physical mixtures but distinct materials with different structures and compositions that are not linear mixtures of I and S (Jiang et al. 1990).

#### APPLICABILITY OF SCHREINEMAKERS' RULES TO EXPERIMENTS ON CLAY MINERALS

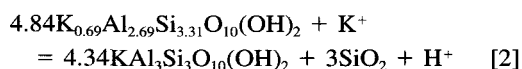
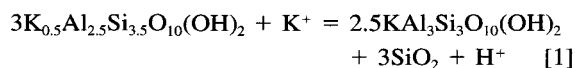
AR misinterpret our Schreinemakers' analysis of solubility experiments on illite and present another diagram that is violation of Schreinemakers' rules. Contrary to the statement of AR, EP did not confuse the run products. The kaolinite-muscovite phase boundary was established based on the 2 experimental points given by Aja et al. (1991) for the assemblage kaolinite-muscovite, the kaolinite-illite phase boundary was based on the experimental data for the assemblage kaolinite-illite (Figures 1a and 1b), etc. EP noted that a phase diagram (Figure 1a) purported by Aja et al. (1991) to represent equilibrium relations cannot be correct as presented because it violates Schreinemakers' principles (Zen 1966). Both Figures 4 and 5 of Aja et al. (1991) have such infringements and their Figures 1 and 6 do not show inflections at invariant points. The alternative diagram presented by EP (Figure 1b) was not assumed to be correct as stated by AR but is simply the diagram required by the experimental data presented by Aja et al. (1991) *if equilibrium were attained*. It requires muscovite to be stable only at low temperature and illite at high temperature, providing *prima facie* evidence that some or all of the solubility experiments of Aja et al. (1991) cannot represent stable or even metastable equilibrium relations. This point of view was also made clear in the caption to Figure 1b of EP and by E. J. Essene's personal communication to Professor Rosenberg at the 1995 Goldschmidt conference. AR miss the point completely in criticizing EP for presenting a geologically absurd diagram; *it is the topology required by AR's own experiments*—if they represent equilibrium relationships!

Let us review some essentials of Schreinemakers' rules, which are based on the concept that an equilibrium phase or phase assemblage cannot have its stability field extended by consideration of another yet more stable assemblage (Zen 1966). A first corollary is the so-called "180° rule", which requires a given assemblage around an invariant point to be constrained to <180° in intensive variable space. This rule applies at the invariant point whether or not a phase boundary has curvature away from the invariant point, contrary to AR. They also object to the straight lines of Figure 2 of EP (the lines were drawn as straight because the experimental data do not justify a curvilinear fit), although AR use mostly straight lines in their preferred diagram (their Figure 4). A second corollary is that metastable extensions of phase boundaries constraining the stability fields of a given assemblage must not

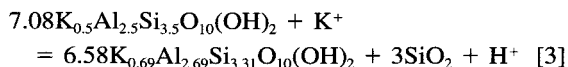
extend into the stable region involving that assemblage. A third corollary is that apparently stable extensions of equilibrium systems that violate the first and second corollaries must be metastable segments. Thus, at equilibrium, the metastable extensions extrapolated from Aja et al. (1991) are stable continuations, as shown in Figure 1b. A fourth corollary is the pencil theorem, which is related to the number of univariant bundles around an invariant point (Zen 1966). *Schreinemakers' rule and the 4 corollaries were violated by Aja et al. (1991) and AR*. They are also disobeyed if an equivalent diagram is constructed for the stability fields of illite ( $K_{0.84}$ ), muscovite and kaolinite from the experiments of Sass et al. (1987) and the phase diagrams of Aja (1991). A thermodynamically consistent equivalent of AR's Figure 3 cannot be generated, as the metastable extensions at the 2 invariant points involving muscovite and illite are inconsistent (one requires muscovite as the low-temperature phase and one has illite as the low-temperature phase). We have no reason to modify our conclusion that "interpretations of available experiments on the solubility of illite . . . are in violation of Schreinemakers' rules and indicate lack of equilibrium" (EP abstract).

#### IONIC EQUILIBRIA INVOLVING MUSCOVITE, ILLITE AND PYROPHYLLITE

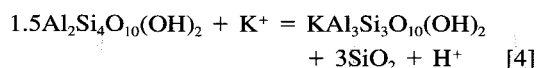
Ionic equilibria in the system  $K_2O-Al_2O_3-SiO_2-H_2O$  relating illite to muscovite include:



Different combinations of these 2 reactions can be used to generate those involving other illite compositions and those with 1 illite formula unit reacting to form another illite. For example:



(Sass et al. 1987). These aluminum-conservative reactions involving simple illite and muscovite compositions on the pyrophyllite-muscovite join are also conservative in  $H_2O$  and therefore are controlled more by the activity product than  $T$  (Sverjensky et al. 1991). Equations [1] through [3] have the same coefficients for  $K^+$ ,  $SiO_2$  and  $H^+$  as:



relating pyrophyllite to muscovite (Montoya and Hemley 1975) because all of these sheet silicates are assumed to be compositionally collinear.

Aja et al. (1991) did not explicitly write Equations [1] through [3] relating the illites that they postulated

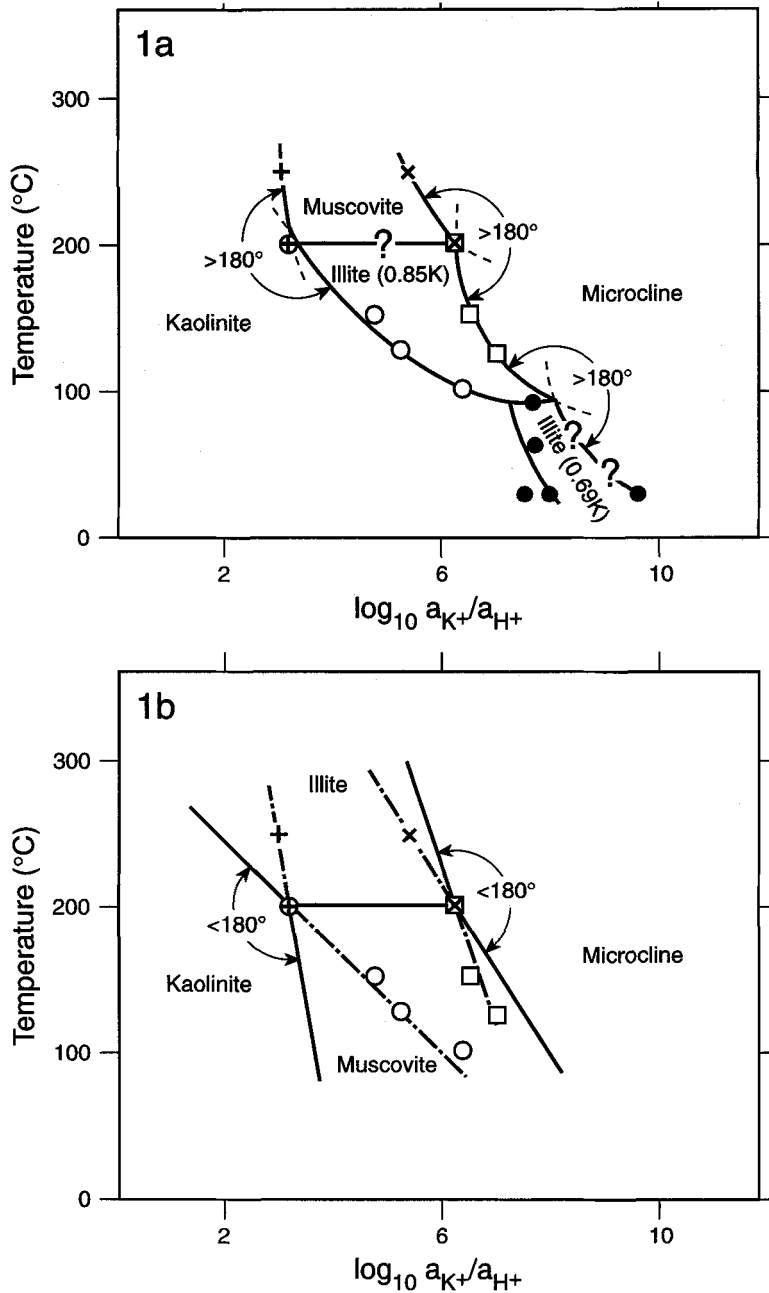


Figure 1a. Diagram of  $T$  vs.  $\log(aK^+/aH^+)$  of illite, muscovite, kaolinite and microcline in equilibrium with quartz from Aja et al. (1991), where + represents their experimental determinations of kaolinite-muscovite, o kaolinite-illite, x muscovite-microcline, [] illite-microcline. The sets of univariant curves that violate Schreinemaker's 180° rule are marked with arrows labeled ">180°". The inconsistencies suggest that equilibrium was not attained in some or all of the experiments.

Figure 1b. Diagram of  $T$  vs.  $\log(aK^+/aH^+)$  of illite, muscovite, kaolinite and microcline in equilibrium with quartz from EP. Symbols as for Figure 1a. The phase boundaries between reactions around the invariant points now satisfy the 180° rule.

to be stable. They assumed that their illite compositions were well-represented by the system pyrophyllite-muscovite, even though their starting illite contains significant Mg (0.4 atoms per 11 oxygens). In addition, their starting microcline is  $Ab_{17}$ , also lying

well outside the assumed chemical system  $K_2O-Al_2O_3-SiO_2-H_2O$ . If the phase equilibria are nonetheless well-represented by  $K_2O-Al_2O_3-SiO_2-H_2O$  and the illites lie on the pyrophyllite-muscovite join, reactions with the same ratios of coefficients for  $H^+$ ,  $K^+$  and  $SiO_2$  apply

to the relative stabilities of illite ( $K_{0.69}$ ), illite ( $K_{0.81}$ ) and end-member muscovite ( $K_{1.00}$ ). The coefficients require near-parallelism of the reaction represented by Equation [4] with ones similar to the reactions represented by Equations [1] through [3] relating illite ( $K_{0.69}$ ), illite ( $K_{0.85}$ ) and muscovite ( $K_{1.00}$ ). If a given illite or several illites of different compositions have stability fields related by such reactions, they should be interposed between that for pyrophyllite vs. muscovite even where it is metastable relative to kaolinite. However, the phase boundaries of AR for the illite and muscovite reactions are not subparallel with that for pyrophyllite  $\rightarrow$  muscovite in  $T$  vs. pK-pH diagrams (Bowers et al. 1984). If the illite compositions in AR's experiments are compositionally collinear with pyrophyllite and muscovite, reactions involving illite ( $K_{0.69}$ )  $\rightarrow$  illite ( $K_{0.85}$ )  $\rightarrow$  muscovite ( $K_{1.00}$ ) cannot be located as near-horizontal lines in  $T$  vs. pK-pH diagrams as shown by AR (Figure 1). If their experiments attained equilibrium, the illites must have higher water contents, significant additional components (Mg or Na) or variable compositions along the univariant curves; or they must have undergone progress of other ionic reactions; or the flat slopes could simply indicate lack of equilibrium. AR argue that their illite ( $K_{0.50}$ ) is IS and illite ( $K_{0.69}$ ) is ISII although no chemical, XRD or STEM data are provided to support this inference. Discrepancies between the inferred and experimental phase boundaries are a strong indication of nonequilibrium or that the "illites" have unexpected compositions.

#### THE STABILITY OF PYROPHYLLITE VS. KAOLINITE

AR question the assertion of EP that kaolinite is less stable than pyrophyllite in some of the solubility experiments. Citing Sverjensky et al. (1991), AR state that the stability field of pyrophyllite is located at 300 °C, well above the temperatures of their experiments at 25 to 250 °C. Sverjensky et al. (1991) located the reaction kaolinite-quartz-pyrophyllite-water at 1 kbar, whereas Aja et al. (1991) conducted experiments at only 1–50 bars. The equilibrium pyrophyllite- $H_2O$  vs. kaolinite + quartz is located at only about 230–250 °C on the critical curve for  $H_2O$ . Moreover, AR cite experiments by Yates on muscovite-kaolinite at  $T \geq 300$  °C, well within the stability field of pyrophyllite- $H_2O$ .

#### EXCESS SURFACE ENERGY OF FINE-GRAINED SOLIDS: IMPLICATIONS FOR PHASE EQUILIBRIA

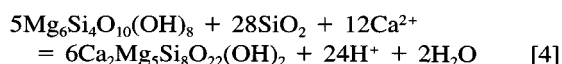
AR argue that the size of particulate materials is no bar to the phase concept. This view is in direct contradiction to the many studies that establish the inverse relation between grain size and the increasing importance of surface effects in the destabilization of

phases. The driving force for Ostwald ripening, which involves coarsening at the expense of smaller crystallites of the same composition, is based in part on this difference. Any ultra fine-grained material has a less-negative free energy and a higher entropy than the chemically equivalent coarse-grained material, such that the fine-grained material does not have the same chemical properties in bulk as those of the coarse phase. To state that a test of a phase is simply its behavior in unreversed solubility experiments is to ignore numerous publications. With such logic, petrologists would still be debating the stability fields of anatase, sillimanite-X and protodolomite. As pointed out by EP, the apparent approach to steady-state conditions in solubility experiments can be explained by dissolution of the fine-grained portion of the starting materials. The apparent reversibility in mobile cations like  $H^+$  and  $K^+$  may also be related to the exchangeability of these atoms on the surfaces or in the structures rather than indicating growth of illite with a new Si content. AR's claim that muscovite is less stable than "ideal illite" ( $K_{0.88}$ ) needs documentation by STEM and AEM observations. Many metamorphic muscovites are reported to have only 85–90% of the interlayer site filled with K, yet no one presumes that they are coarse illites. The degradation of muscovite forming illite in nature (or the replacement of illite by smectite) need not indicate that muscovite (or illite) is intrinsically less stable, as assumed by AR. Solutions out of equilibrium with the original phase may lead to its dissolution followed by precipitation of metastable materials; witness the dissolution of most aluminous silicates by HF followed by the precipitation of amorphous  $AlF_3$ . Proof of AR's hypothesis that muscovite is metastable relative to illite at  $T < 300$  °C requires documented STEM and AEM techniques to identify growth vs. dissolution of the reactants and products and directly document structural (including polytypic) and chemical changes (if any).

#### CORRECTION TO THE REVIEW PAPER OF ESSENE AND PEACOR (1995)

One equation relating to chlorite thermometry in EP was inadvertently repeated. Equation [4] should read:

actinolite-quartz-fluid:



Equation [1] of EP will shift the chlorite toward lower Al content with increasing temperature in a fluid of constant composition. The other chlorite reactions in EP, including Equation [4] above, will cause chlorite to become more aluminous at a fixed fluid chemistry with increasing temperature. The Al content of the chlorite will vary, however, with the coexisting assemblage, and also with pH and other ion activities in the

case of the ionic equilibria. The Al-in-chlorite system as currently applied can have only limited value as a quantitative geothermometer.

## REFERENCES

- Aja SU. 1991. Illite equilibria in solutions: III. A reinterpretation of the data of Sass et al. (1987). *Geochim Cosmochim Acta* 55:3431–3435.
- 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. 1996. The thermodynamic status of compositionally variable clay minerals: Discussion of “Clay mineral thermometry—A critical perspective”. *Clays Clay Miner* 44:560–568.
- Aja SU, Rosenberg PE, Kittrick JA. 1991. Illite equilibria in solutions: I. Phase relationships in the system  $K_2O-Al_2O_3-SiO_2-H_2O$  between 25° and 250 °C. *Geochim Cosmochim Acta* 55:1353–1364.
- Bjørkum PA, Gjelsvik N. 1988. An isochemical model for formation of authigenic kaolinite, K-feldspar and illite in sediments. *J Sed Petrol* 58:506–511.
- Bowers TS, Jackson KJ, Helgeson HC. 1984. Equilibrium activity diagrams. Berlin and NY: Springer-Verlag. 397 p.
- Eggleton RA. 1987. Noncrystalline Fe-Si-Al-oxyhydroxides. *Clays Clay Miner* 35:29–37.
- El Shazly ALDK. 1995. On the thermodynamic data of kaolinite. *Am Mineral* 90:1048–1053.
- Essene EJ, Peacor DR. 1995. Clay mineral thermometry—A critical perspective. *Clays Clay Miner* 43:540–553.
- Franks F. 1981. *Polywater*. Cambridge, MA: MIT Pr. 288 p.
- Fyfe WS. 1960. Hydrothermal synthesis and determination of equilibrium between minerals in the subliquidus region. *J Geol* 68:553–566.
- Huang W-L, Longo JM, Pevear DR. 1993. An experimentally derived kinetic model for smectite-to-illite conversion and its use as a geothermometer. *Clays Clay Miner* 41:162–177.
- Jiang W-T, Peacor DR, Essene EJ. 1990. Transmission electron microscopic study of coexisting pyrophyllite and muscovite: Direct evidence for the metastability of illite. *Clays Clay Miner* 38:225–240.
- Jiang W-T, Peacor DR, Essene EJ. 1994. Analytical and transmission electron microscopic study of clay minerals in sandstone of Kettleman North Dome, California: Implications for the metastability of illite. *Clays Clay Miner* 42:35–45.
- Lippmann F. 1977. The solubility products 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. In: van Olphen H, Veniale F, editors. *Proc Int Clay Conf*; Bologna, Pavia: 1981. NY: Elsevier. p 475–485.
- Masuda H, O’Neil JR, Jiang W-T, Peacor DR. 1996. Relation between interlayer composition of authigenic smectite, mineral assemblages, I/S reaction rate and fluid composition in silicic ash of the Nankai Trough. *Clays Clay Miner* 44:443–459.
- Montoya JW, Hemley JJ. 1975. Activity relations and stabilities in alkali feldspar and mica alteration reactions. *Econ Geol* 70:577–583.
- Peacor DR. 1992a. Diagenesis and low-grade metamorphism of shales and slates. In: Buseck PR, editor. *Minerals and reactions at the atomic scale*. *Rev Mineral* 27:335–380.
- Peacor DR. 1992b. Analytical electron microscopy: X-ray analysis. In: Buseck PR, editor. *Minerals and reactions at the atomic scale*. *Rev Mineral* 27:113–140.
- Rosenberg PE, Hooper RL. 1996. Determination of the chemical composition of natural illites by analytical electron microscopy. *Clays Clay Miner* 44:569–572.
- Sass BM, Rosenberg PE, Kittrick JA. 1987. The stability of illite/smectite during diagenesis: An experimental study. *Geochim Cosmochim Acta* 51:2103–2115.
- Schiffman P, Southard RJ. 1996. Cation exchange capacity of layer silicates and palagonitized glass in mafic volcanic rocks: A comparative study of bulk extraction and *in situ* techniques. *Clays Clay Miner* 44:624–635.
- Sverjensky DM, Hemley JJ, D’Angelo WM. 1991. Thermodynamic assessment of hydrothermal alkali feldspar-mica-aluminosilicate equilibria. *Geochim Cosmochim Acta* 55:989–1004.
- Vonnegut K. 1963. *Cat’s cradle*. NY: Delacorte. 191 p.
- Yates DM, Rosenberg PE. 1993. Hydrothermal transformation of muscovite to endmember illite at 250 °C and  $P_V, H_2O$  [abstract]. *Geol Soc Am Abst Prog* 25:437.
- Zen E-An. 1966. Construction of P-T diagrams for multi-component systems after the method of Schreinermakers—A geometrical approach. Washington DC: US Geol Surv Bull 1225. 37 p.
- Zhou Z, Fyfe WS, Tazaki K, van der Gaast SJ. 1992. The structural characteristics of palagonite from DSDP Site 335. *Can Mineral* 30:75–81.

(Received 3 October 1996; accepted 16 December 1996; Ms. 2818)