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NOTES

IMPLICATIONS OF ILLITE/SMECTITE STABILITY DIAGRAMS: A DISCUSSION

Key Words—Chemical activity, Illite, Mixed layer, Phase equilibria, Smectite, Stability.

INTRODUCTION

Although all interstratified illite/smectites contain some Mg and/or Fe, changes in the site occupancies of these cations are not required in the conversion of interlayers from smectite to illite (Garrels, 1984). Thus, to a first approximation, illite/smectite phase relationships can be represented in the simplified system K_2O-Al_2O_3-SiO_2-H_2O. On this premise, Garrels (1984) recently constructed chemical activity diagrams of the system K_2O-Al_2O_3-SiO_2-H_2O to compare phase relationships expected if illite/smectite (I/S) behaves as a solid solution (single phase) or as a mixture of two phases.

Analyses of natural aqueous solutions in contact with clays (Aagaard and Helgeson, 1983) were found to lie close to the phase boundary representing I/S (two phase) equilibrium, assuming arbitrary but reasonable illite and smectite compositions, whereas these analyses cross the field of I/S solid solution (one phase). It is difficult, however, to determine whether these aqueous solutions are actually in equilibrium with illite, because no compositions are available for natural solutions known to coexist with illite (Aagaard and Helgeson, 1983). In the absence of conclusive data, Garrels (1984) reasoned that the available data are more nearly consistent with the interpretation that I/S is a two-phase assemblage rather than a single-phase solid solution. Inasmuch as the evidence available to Garrels was not definitive, he suggested criteria for distinguishing between these two hypotheses and proposed long-term experiments to resolve the problem.

If I/S behaves as two phases, equilibration with kaolinite should result in isothermal, isobaric invariance, thus fixing solution composition at the kaolinite-illite-smectite triple point (Garrels, 1984, Figure 4). On the other hand, if I/S behaves as a solid solution, equilibration with kaolinite would not result in isothermal, isobaric invariance. A range of solution compositions (a_{K^+}/a_{H^+}, a_{SiO_2}) could, therefore, coexist at equilibrium with kaolinite and I/S solid solution (Garrels, 1984, Figure 3). Garrels' analysis is particularly timely because the critical data necessary to test these hypotheses concerning the nature of illite have recently become available.

EXPERIMENTAL DATA AND THEIR IMPLICATIONS

Kittrick (1984) equilibrated Goose Lake illite with kaolinite in long-term solubility experiments. Equilibrium was indicated by constant solution compositions attained from undersaturation and supersaturation in experiments of long duration. Solubility measurements were made at intervals terminating with solution samples taken after more than 300 and more than 500 days. The final analyses for each experiment are shown in Figure 1 (circles). Sass (1984) equilibrated Goose Lake illite with 0.2 M and 2.0 M KCl/HCl solutions in the presence of kaolinite and quartz. Equilibrium was approached from two directions by starting with solutions having high and low a_{K^+}/a_{H^+} ratios. Each data point (triangles) in Figure 1 thus represents a reversal pair.

Data for both sets of experiments appear to lie close to a single straight line on a log a_{K^+}/a_{H^+} vs. log a_{SiO_2} diagram (Figure 1). Linear regression analysis was used to determine the correlation coefficient (−.95) and the equation of the line; its slope, −6.09, is directly related to the composition of the phase controlling the solubility. Calculations following the method of Mattigod and Kittrick (1979) indicate that the composition of the solubility controlling phase is approximately $K_{0.25}Al_{2.00}(Si_{3.75}Al_{0.25})O_{10}(OH)_2$. The close accordance of solution compositions obtained in experiments with 0.2 M and 2 M solutions (Sass, 1984) suggests that K^+ activity is solubility controlled. Thus, K^+ behaves as a common ion and an integral part of the structure of this phase.

The mineralogical term applied to a phase of this composition is a matter of definition. The boundary between illite and smectite is customarily placed at −0.4 charge units per half cell (Hower and Mowatt, 1966). A recent report of The Clay Minerals Society Nomenclature Committee (Bailey *et al.*, 1984) and S. W. Bailey (University of Wisconsin, Madison, Wisconsin, personal communication, 1985), however, suggest that the boundary should be defined by expandability, illite being a nonexpanding clay mineral. The minimum interlayer charge for illite by the latter definition is about −0.6, whereas the maximum interlayer charge for smectite is less than −0.4. Goose Lake illite has the formula $K_{0.59}(Al_{1.58}Fe_{0.24}Mg_{0.15})(Si_{3.64}Al_{0.35})O_{10}(OH)_2$ (Kittrick, 1984) and is 25–30% expandable (Routson, 1970, p. 79). Thus, Goose Lake illite is actually an illite/smectite, while the solubility-controlling phase is a smectite.

DISCUSSION

If illite is considered to be a single-phase solid solution, the kaolinite-illite boundary (Garrels, 1984,

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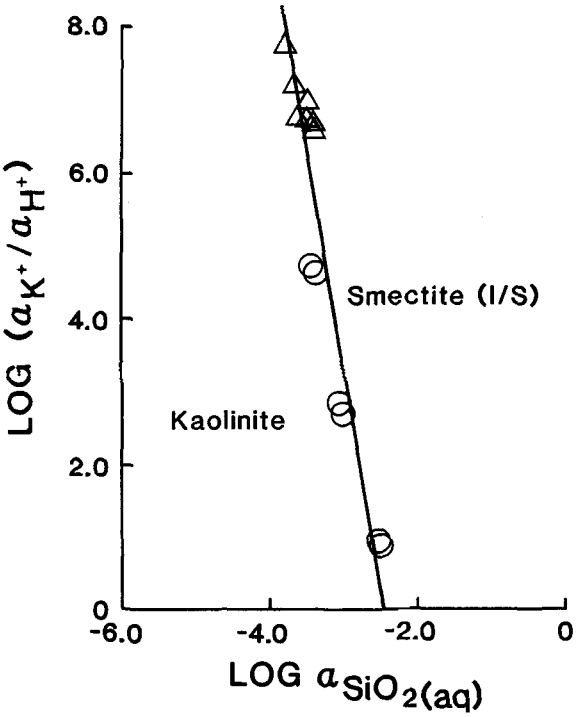


Figure 1. Compositions of solutions equilibrated with Goose Lake illite + kaolinite; triangles, Sass (1984); circles, Kittrick (1984). Smectite (I/S), smectite component of I/S.

Figure 3) should be a curve corresponding to progressively lower dissolved-silica activities with increasing K-content of illite. Garrels (1984) proposed that this range of silica values indicates that illite is a solid solution, whereas fixed values of silica and a_{K^+}/a_{H^+} at the triple point (Garrels, 1984, Figure 4) indicates that illite is a two-phase assemblage.

The data points in Figure 1 define a univariant solubility line representing a single "illite" composition which appears to control solubility over a large range of a_{K^+}/a_{H^+} values. Inasmuch as the solubility-controlling phase has a composition in the range associated with smectites and the bulk chemical composition of Goose Lake illite cannot be represented by this composition alone, this phase may represent the smectite component of I/S. Thus, assuming congruent solubility, Goose Lake illite appears to behave as a two-phase assemblage.

Although equilibrium with respect to the illite component of I/S has not been attained, kaolinite-smectite equilibrium may be used to deduce illite phase relationships qualitatively. The presence of an illite-smectite boundary and a triple point can be inferred on this basis, even though direct experimental evidence is lacking. Consequently, the portion of the solubility line (Figure 1) at values of a_{K^+}/a_{H^+} greater than the triple point represent metastable kaolinite-smectite equilibrium.

Because similar experimental results have been obtained for illites from other localities (Kittrick, 1984; Sass, 1984), inferences for Goose Lake illite may be generally applicable to I/S random. Thus, recent evidence strongly suggests that I/S random behaves as a two-phase assemblage (Kittrick, 1984; Sass and Rosenberg, 1984; Nadeau *et al.*, 1984) as inferred by Garrels (1984).

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