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MUSCOVITE DISSOLUTION AT 25°C: IMPLICATIONS FOR ILLITE/SMECTITE-KAOLINITE STABILITY RELATIONS

Key Words—Dissolution, Free energy of formation, Illite/smectite, Kaolinite, Muscovite, Stability.

Mattigod and Kittrick (1979) conducted solubility experiments in aqueous solutions at 25°C and 1 atm using muscovite-gibbsite mixtures. Their experiments yielded solute activities (a_{K^+}/a_{H^+} and $a_{H_4SiO_4}$) that were inconsistent with the dissolution reaction based on the chemical composition of the muscovite starting materials, $K_{0.9}(Al_2)(Si_{3.1}Al_{0.9})O_{10}(OH)_2$. Precipitation of a new, nonmuscovite phase was considered to be unlikely because the solutions were not supersaturated with respect to other phases in the system K_2O-Al_2O_3-SiO_2-H_2O and none were detected. Furthermore, assuming that muscovite and gibbsite participated in the equilibrium, precipitation of a new phase would have required isothermal and isobaric invariance rather than the observed univariance. Therefore, a new dissolution reaction was derived in which the muscovite composition was adjusted to satisfy the solute activity data, the presumption being that muscovite of a new composition, $K_{0.81}(Al_2)(Si_{3.19}Al_{0.81})O_{10}(OH)_2$, had crystallized and was the solubility-controlling phase. Although a change in muscovite composition was inferred, it could not be verified directly by X-ray powder diffraction, infrared spectroscopy, or electron microscopy.

In a later study (Rosenberg *et al.*, 1984), statistical analysis was used to confirm the conclusion of Mattigod and Kittrick (1979) that solution compositions were not controlled by the bulk composition of the starting materials. The composition of the solubility-controlling phase resulting from the apparent incongruent dissolution of muscovite, however, could not be detected by analytical electron microscopy. Compositional subgroups within muscovite crystals, probably at crystal edges, were invoked to explain these results.

The apparent crystallization of a mica-like phase having a composition of 0.81 K per $O_{10}(OH)_2$ at 25°C is of great interest inasmuch as all estimates of the composition of natural, end-member illite (I) range between 0.8 K and 0.9 K per $O_{10}(OH)_2$ (Weaver, 1965; Środoń and Eberl, 1984; Eberl and Środoń, 1988; Inoue *et al.*, 1988). Evidence from experimental studies leads to similar conclusions. Hemley *et al.* (1980) observed that muscovite is somewhat K-deficient in the relatively acid environment represented by muscovite-kaolinite equilibrium. Solution equilibration studies at this phase boundary have suggested compositions of 0.9 K (Sass *et al.*, 1987) and 0.85 K (Aja, 1989) per half cell. Furthermore, muscovite-pyrophyllite solid solutions have been synthesized at elevated temperatures (Velde and Weir, 1979; Rosenberg, 1987), which suggest that illite may be a term for the end-member of this series, with a composition of about 0.8 K per $O_{10}(OH)_2$.

Synthesis of illite from muscovite amounts to a reversal of the well-documented, prograde formation of illite from smectite (Środoń and Eberl, 1984), suggesting that illite has a thermodynamic stability field in nature. Reaction of muscovite with solution to form illite has been reported in experimental studies (Yates and Rosenberg, 1987) and in nature (McDowell and Elders, 1980) at elevated temperatures, but not at 25°C. The present investigation attempts to test the inferences of Mattigod and Kittrick (1979) by examining an array of ΔG°_f values available for mica-like phases in the system K_2O-Al_2O_3-SiO_2-H_2O.

FREE ENERGIES OF FORMATION

The reaction of muscovite-gibbsite mixtures with an aqueous phase results in a univariant equilibrium, which may be expressed on a pH_4SiO_4 vs. pH-pK^+ diagram as a straight line. In the study of Mattigod and Kittrick (1979), the slope of this line was 3.93 rather than the anticipated 3.44, indicating that the stoichiometry of the solubility-controlling muscovite was not that of the starting materials. Assuming that muscovite can be represented by the general formula, K_xAl_2-(Al_xSi_{4-x})-$O_{10}(OH)_2$, Mattigod and Kittrick (1979) calculated the composition of the solubility-controlling phase, $K_{0.81}Al_2(Al_{0.81}Si_{3.19})O_{10}(OH)_2$, from the observed slope of the univariant line and the coefficients of the proposed dissolution reaction. The free energy (ΔG°_r) of the dissolution reaction, which was computed from the equilibrium constant, was, in turn, used to calculate the standard free energy of formation of the solubility-controlling muscovite, −5501.1 kJ/mole (Mattigod and Kittrick, 1979).

Because the free energy of formation determined by Mattigod and Kittrick (1979) seemed to be excessively positive in the light of current values for muscovite (e.g., −5596.72 kJ/mole, Berman, 1988), an evaluation of free energies of formation of synthetic, mica-like (smectite, illite, muscovite) phases in the system K_2O-Al_2O_3-SiO_2-H_2O was undertaken (this study).

For purposes of comparison, free energies of for-

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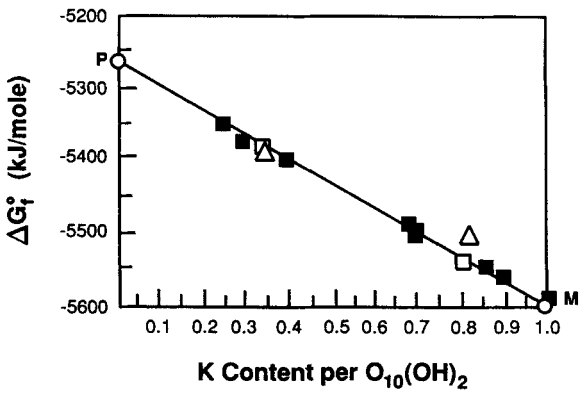


Figure 1. Variation in the ΔG°_f (kJ/mole) of mica-like phases with K content per $O_{10}(OH)_2$. Open circles, values for end-members, muscovite (M) and pyrophyllite (P) (Table 1); solid squares, calculated from experimental data of Sass *et al.* (1987), Aja (1989), and Peryea and Kittrick (1986); open squares, calculated using the method of Tardy and Garrels (1974); open triangles, calculated from the experimental data of Mattigod and Kittrick (1979), see text for details. Size of symbols approximates estimated errors.

mation were calculated for several solubility-controlling, mica-like phases each coexisting with kaolinite in experimental studies with Goose Lake illite (Sass *et al.*, 1987). Equilibrium constants (Sass *et al.*, 1987) were used to obtain the standard free energy change for the reaction:

$$K_x(Al_2)(Si_{4-x}Al_x)O_{10}(OH)_2 + xH^+ + [(1 + x)/2]H_2O = [(2 + x)/2]Al_2Si_2O_5(OH)_4 + xK^+ + (2 - 2x)SiO_{2,aq}. \quad (1)$$

Using known ΔG°_f values and thermochemical data given in Table 1, the free energies of formation of the mica-like phases were calculated by difference. The composition variable, x, was evaluated by estimating the slopes of univariant lines on log a_{K^+/H^+} vs. log $a_{H_4SiO_4}$ diagrams. ΔG°_f values for mica-like phases having K-contents of 0.24 and 0.39 K ± 0.02 per $O_{10}(OH)_2$ were calculated directly from the experimental data. The error in estimating K-content results in a precision in ΔG°_f of approximately 6.1 kJ/mole. If data were not available at ambient temperatures [0.70 K, and 0.90 K ± 0.02 per $O_{10}(OH)_2$] curves were fitted to the data using a least squares regression method with a second order polynomial function in absolute temperature units [i.e., $\Delta G^\circ_f = A + BT + C(T^2)$] and extrapolated to give ΔG°_f values at 25°C.

Also available were ΔG°_f values calculated by S. U. Aja, Department of Geological Sciences, McGill University, Montreal, Canada PQ H3A 2A7 (1989 and personal communication) for synthetic mica-like phases [0.29 K, 0.70 K, and 0.85 K per $O_{10}(OH)_2$] following procedures similar to those described above and for hypothetical 0.33 K and 0.80 K per $O_{10}(OH)_2$ using the approximation method of Tardy and Garrels (1974) and the free energy of $Al^{3+}_{(aq)}$ given by Robie *et al.* (1979). Furthermore, an extrapolation of the ΔG°_f value for K-saturated montmorillonite to 1.0 K per $O_{10}(OH)_2$ was attempted by Peryea and Kittrick (1986). All free energy values were recalculated using the same thermochemical data base (Table 1).

Table 1. Thermochemical data used in calculations of ΔG°_f.

Species	ΔG°_f (kJ/mole)	Source
$Al^{3+}_{(aq)}$	−498.8	Hemingway *et al.* (1982)
$K^+_{(aq)}$	−282.48	Pabalan and Pitzer (1987)
$SiO_{2(aq)}$	−833.26	Berman (1988)
$H_2O_{(liq)}$	−237.13	Berman (1988)
$Al(OH)_3$, gibbsite	−1154.89	Hemingway *et al.* (1982)
AlO(OH), diaspore	−920.81	Berman (1988)
$Al_2Si_2O_5(OH)_4$, kaolinite	−3799.77	Berman (1988)
$KAl_3Si_3O_{10}(OH)_2$, muscovite	−5596.72	Berman (1988)
$KAlSi_3O_8$, microcline	−3745.42	Berman (1988)
$Al_2Si_4O_{10}(OH)_2$, pyrophyllite	−5266.87	Berman (1988)

These free energies of formation appear to vary with the K content of the mica-like phases (Figure 1). For purposes of comparison, a straight line has been drawn between the free energies of formation of muscovite and pyrophyllite (Table 1; Figure 1, open circles).

DISCUSSION

All ΔG°_f values for the mica-like phases, except that of Mattigod and Kittrick (1979), lie on or close to a line connecting the values for the end-members, muscovite and pyrophyllite, indicating that the K content is the principal variable and that it varies linearly with ΔG°_f. Thus, it may not be possible to use solution equilibration data to make structural distinctions in this system.

Sass *et al.* (1987) suggested that illite-smectite equilibrium is metastable with respect to kaolinite-microcline equilibrium at <100°C and that decreases in the Gibbs free energies of illite and smectite of about 6 kJ/mole, due to ordering of I/S (Perry and Hower, 1970), stabilize the assemblages illite-smectite-kaolinite and illite-smectite-microcline at >100°C. Inasmuch as error in estimating the K content may account for variations in ΔG°_f of about 6 kJ/mole, this interpretation is open to question.

The recalculated value of the free energy of formation of muscovite [$K_{0.81}/O_{10}(OH)_2$], −5498.6 kJ/mole, assuming muscovite-gibbsite equilibrium (Mattigod and Kittrick, 1979), is discordant with the linear relationship between ΔG°_f and K content, lying about 35 kJ/mole above the line in Figure 1 (open triangle). In similar experiments with muscovite and kaolinite at

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100°C, Yates and Rosenberg (1987) reported a univariant equilibrium involving kaolinite and smectite. If the data of Mattigod and Kittrick (1979) refer to kaolinite-smectite equilibrium [Eq. (1)] rather than muscovite [0.81 K per $O_{10}(OH)_2$]-gibbsite equilibrium, the slope (3.93) of the experimentally determined line on a pH-pK^+ vs. pH_4SiO_4 diagram implies a composition of 0.34 K per $O_{10}(OH)_2$; the calculated free energy of formation of a phase of this composition (−5381.6 kJ/mole) lies on the line in Figure 1 (open triangle). Although a mica-like phase with a composition of 0.34 K per $O_{10}(OH)_2$ falls into the compositional range of smectite as defined by Bailey *et al.* (1984), this composition may actually represent thin, lath-like illite (IS) with R1 ordering (Inoue *et al.*, 1987). Mixed-layer I/S and kaolinite were not observed in the products of the experiments, but they may occur in thin zones at grain edges where they would be difficult to detect by analytical electron microscopy.

SUMMARY AND CONCLUSIONS

No evidence for the stability of end-member illite (I) at 25°C has been found. In accord with other experimental investigations (e.g., Sass *et al.*, 1987), a reinterpretation of the data of Mattigod and Kittrick (1979) suggests that kaolinite and a mica-like phase having the composition 0.34 K per $O_{10}(OH)_2$ are the solubility-controlling phases in the system K_2O-Al_2O_3-SiO_2-H_2O under these conditions.

To a first approximation, structural variations in the mica-like phases (i.e., pyrophyllite, smectite, illite, muscovite) contribute little to the differences in their free energies of formation. Within the experimental error, $\Delta G°_f$ varies only with the composition of these phases and in the same linear manner for all.

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