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NOTES

COMPOSITION OF THE CONTROLLING PHASE IN MUSCOVITE EQUILIBRIUM SOLUBILITY

Key Words—Analytical electron microscopy, Chemical composition, Dissolutions, Mica, Muscovite.

Mattigod and Kittrick (1979) conducted equilibrium solubility experiments of muscovite in aqueous solution at 25°C and 1 atm over a 2-yr period using mica-gibbsite mixtures. These experiments yielded solute activity ratios that were inconsistent with the dissolution reaction

$$K_{0.9}Al_{2.9}Si_{3.1}O_{10}(OH)_2 + 9.6H^+ + 0.4H_2O = 2.9Al^{3+} + 3.1Si(OH)_4^0 + 0.9K^+, \quad (1)$$

based on the chemical composition of the muscovite starting materials. Solute activity relationships, based on linear regression analyses of equilibrium solubility data, were expressed by the equation,

$$[pH - pK^+] = 3.93pSi(OH)_4^0 - 5.60[pH - 1/3pAl^{3+}] + 5.93. \quad (2)$$

The equilibrium ratio of 3.93 for $pSi(OH_4^0/[pH - pK^+]$ was significantly different from the ratio of 3.40 predicted by the equation for the dissolution of muscovite of this particular composition in the presence of gibbsite. A new dissolution equation was derived in which the muscovite composition was adjusted to satisfy the solute activity data, the presumption being that muscovite of a new composition had formed during the lengthy equilibration period and that this new muscovite controlled the equilibrium. Although a change in muscovite composition from $K_{0.9}Al_{2.9}Si_{3.1}O_{10}(OH)_2$ to $K_{0.8}Al_{2.8}Si_{3.2}O_{10}(OH)_2$ was inferred, it could not be verified directly by X-ray powder diffraction, infrared spectroscopy, or electron microscopy.

Incongruent solubility and the substitution of Si^{4+} for Al^{3+} and K^+ are of considerable interest because they imply that muscovite can be degraded to an illite-like composition under surface conditions. The present study tests the conclusions of Mattigod and Kittrick (1979) concerning the incongruent dissolution of muscovite and the inferred change in muscovite composition by statistical studies of their muscovite analyses and solubility data and by chemical analysis of the products of their experiments.

Mattigod and Kittrick's solutions were initially undersaturated but were never far from equilibrium during the 2-yr equilibration period. Congruent solubility is much more likely under equilibrium conditions where both dissolution and precipitation take place than in strongly undersaturated solutions (e.g., Lin and Clemency, 1981) where only dissolution takes place. Thus, the dissolution experiments of Mattigod and Kittrick (1979) offer an ideal opportunity to resolve the problem of muscovite solubility (Lin and Clemency, 1981).

STATISTICAL ANALYSIS OF SOLUTION COMPOSITIONS

Mattigod and Kittrick (1979) determined solute activity relationships by linear regression analysis of monomeric silica activities, $pSi(OH)_4^0$, and the ion activity ratios $[pH - pK]$ and $[pH - 1/3pAl^{3+}]$. Eq. (2), with a correlation coefficient of .99, expresses this relationship. At any value of $[pH - 1/3pAl^{3+}]$ a linear relationship can be obtained with a slope given by the ratio $pSi(OH)_4^0/[pH - pK^+]$. Although the equilibrium value of this ratio, 3.93, appeared to be significantly different from the value, 3.40, predicted from the dissolution equation (Eq. (1)), the statistical significance of this difference was not evaluated in their paper.

The standard error of the ratio based on solute activities is 0.12, whereas the standard error of the ratio predicted by the dissolution equation with muscovite of average starting composition is 0.05. Assuming that the ratios are independent random variables and that errors are normally distributed, the Students' t-test indicates that these slopes are distinguishable at the 95% level of confidence. Thus, the equilibrium solute activity ratios are inconsistent with the dissolution reaction based on the original chemical composition of muscovite (i.e., the dissolution of muscovite appears to be incongruent) as suggested by Mattigod and Kittrick (1979).

CHEMICAL ANALYSIS OF MUSCOVITE

The solute activity data (Mattigod and Kittrick, 1979) suggest that the dissolution of muscovite is incongruent and that new and/or altered muscovite-like phases should have been produced. Chemical analyses of the experimental products were sought to provide direct

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Table 1. Chemical analyses of natural muscovites.[1]

	North Carolina[2] (wt. %)	Mica Mountain[2] (wt. %)	Mica Mountain[3] (wt. %)
SiO_2	44.99 ± 0.93	46.41 ± 0.73	45.36
TiO_2	0.11 ± 0.02	0.27 ± 0.02	0.25
Al_2O_3	36.65 ± 1.06	34.30 ± 0.80	34.99
Cr_2O_3	0.06 ± 0.01	0.03 ± 0.01	0.02
Fe_2O_3	1.27 ± 0.12	0.90 ± 0.11	—
FeO	0.86 ± 0.01	1.17 ± 0.02	2.17[4]
MnO	0.02 ± 0.01	0.03 ± 0.01	0.06
MgO	0.14 ± 0.01	0.34 ± 0.04	0.72
CaO	0.39 ± 0.12	0.41 ± 0.10	0.22
K_2O	10.42 ± 0.01	10.58 ± 0.40	10.16
Na_2O	0.64 ± 0.01	0.57 ± 0.01	0.69
H_2O^+	4.60	4.75	—
H_2O^-	0.25	0.23	—
	100.40	99.99	94.64

[1] Mitchell County, North Carolina; Mica Mountain, Avon District, Deary, Idaho.
[2] "Wet" chemical, except Mn and Cr which were made by X-ray fluorescence; mean (2 analyses) ± std. dev. (Mattigod, 1976).
[3] Electron microprobe, this study.
[4] Fe calculated as FeO.

evidence of muscovite compositions. The products of two experiments (Mattigod and Kittrick, 1979) with muscovites from Mitchell County, North Carolina, (NC-2b), and Mica Mountain, Avon District, Deary, Idaho, (MM-1), were selected for analysis.

Bulk chemical analyses of the muscovites used in the experiments were originally obtained by "wet" chemical and X-ray fluorescence techniques (Mattigod, 1976). Electron microprobe analysis of at least one of these samples was desirable to confirm the earlier results and compare methods. Mattigod's (1976) sample of Mica Mountain muscovite was analyzed on a Cambridge Geoscan electron microprobe using an output voltage of 15 kV and a relatively large beam diameter (10 μm) in order to minimize potassium loss. Despite minor differences, the agreement between the Mica Mountain analyses (Table 1) is quite good. Mattigod's (1976) analyses of the Mica Mountain muscovite and the North Carolina muscovite (Table 1), which was not available for further study, have been adopted on the strength of this agreement.

Partial analyses of single crystals were obtained using a Philips EM 400 analytical electron microscope (AEM) in the transmission mode and an energy dispersive analysis system (EDX) which permitted quantitative determination of elemental ratios. Isolated muscovite crystals were easily resolved and analyzed at magnifications of 16,000 and 22,000×. Analyzed crystals remained stable and were virtually unchanged after repeated exposure to the beam. Relative percentages of SiO_2, TiO_2, Al_2O_3, MgO, CaO, and K_2O were calculated from count-rate data using conversion factors derived from analyses of mineral standards (Champness *et al.*, 1981). Ten random point analyses were averaged to obtain the chemical composition of each sample (Table 2). Structural formulae were then calculated using conventional procedures and assuming ideal muscovite stoichiometry (Table 2). For purposes of comparison, the chemical compositions of North Carolina and Mica Mountain muscovites (Table 1) have been recalculated to 100% of the seven oxides determined for the experimental products, with Fe calculated as Fe_2O_3.

The North Carolina muscovite appears to have changed very little, if at all, during the 2-yr equilibration. Standard deviations can be accounted for by an-

Table 2. Comparison of muscovite analyses before and after equilibration.

	North Carolina		Mica Mountain	
	Before[1]	After[2]	Before[1]	After[2]
SiO_2	47.39 ± 0.93	47.10 ± 0.53	49.11 ± 0.73	47.59 ± 1.64
TiO_2	0.12 ± 0.02	0.23 ± 0.31	0.29 ± 0.02	0.42 ± 0.53
Al_2O_3	38.61 ± 1.06	38.46 ± 0.71	36.29 ± 0.80	37.70 ± 1.52
Fe_2O_3	2.35 ± 0.13	3.15 ± 0.65	2.33 ± 0.13	4.51 ± 2.19
MgO	0.15 ± 0.01	0.15 ± 0.31	0.36 ± 0.04	0.39 ± 0.43
CaO	0.41 ± 0.12	0.27 ± 0.24	0.43 ± 0.10	0.33 ± 0.29
K_2O	10.98 ± 0.01	10.63 ± 0.52	11.19 ± 0.40	9.64 ± 0.72

North Carolina

Before: $K_{0.89}Ca_{0.03}(Mg_{0.01},Ti_{0.01},Fe^{3+}_{0.11},Al_{1.89})(Si_{3.0}Al_{1.0})O_{10}(OH)_2$

After: $K_{0.86}Ca_{0.02}(Mg_{0.01},Ti_{0.01},Fe^{3+}_{0.15},Al_{1.87})(Si_{2.99}Al_{1.01})O_{10}(OH)_2$

Mica Mountain

Before: $K_{0.90}Ca_{0.03}(Mg_{0.03},Ti_{0.01},Fe^{3+}_{0.11},Al_{1.82})(Si_{3.11}Al_{0.89})O_{10}(OH)_2$

After: $K_{0.77}Ca_{0.02}(Mg_{0.04},Ti_{0.02},Fe^{3+}_{0.21},Al_{1.80})(Si_{3.00}Al_{1.00})O_{10}(OH)_2$

[1] Table 1, Mattigod (1976), recalculated to 100% with Fe as Fe_2O_3.
[2] Average of 10 analytical electron microscope analyses; errors are standard deviations (1 σ) from the mean. North Carolina, NC-2b; Mica Mountain, MM-1 (Mattigod and Kittrick, 1979).

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alytical error. All elemental analyses except Fe_2O_3 agree within 1 σ of the mean. For Mica Mountain muscovite all elemental analyses except K_2O are within 1 σ of the mean, but the limits of error are larger than for the North Carolina muscovite implying greater heterogeneity. Analytical electron microscopy showed that the Mica Mountain muscovite is highly heterogeneous on a sub-micrometer scale and, therefore, perhaps not well-suited for use in a study of muscovite dissolution. Nevertheless, despite rather large standard deviations and an apparent decrease in K-content, the compositions of North Carolina and Mica Mountain muscovites are not greatly different before and after equilibration (Table 2). The apparent decrease in K-content of the Mica Mountain muscovite may reflect an initial K excess due to grinding in 1 M KCl solutions (Mattigod, 1976).

Multivariate analysis indicated no significant difference between muscovite compositions before and after the experiments (Table 2) when all components were considered simultaneously. Separate analysis of each component revealed only one significant difference, K_2O for the Mica Mountain muscovite. If, however, the electron microprobe data for K_2O in the Mica Mountain muscovite (Table 1) is substituted for the analysis by Mattigod (1976), the difference is not significant.

DISCUSSION

Statistical analyses at the 95% level of confidence show that equilibrium solution compositions were not controlled by the bulk chemical composition of muscovite and that AEM analyses of the muscovites after equilibration are indistinguishable from the original bulk muscovite compositions. It is, therefore, highly likely that the solid phase controlling solute-activity ratios in solution has a chemical composition different from that of the bulk sample as determined by the initial analyses and the AEM analyses after equilibration. This behavior leads to the following hypotheses:

(1) A new muscovite composition (resulting from incongruent dissolution) escaped detection in the AEM analyses of 10 crystals of each muscovite.
(2) The average chemical composition of a muscovite sample that includes crystals with a range in composition, does not coincide with the chemical composition of a *subgroup* of those crystals that dominate the equilibrium solubility of the sample.

Compositional subgroups were not observed among discrete muscovite crystals, but such subgroups may exist within crystals, for example at crystal edges. Such intracrystalline subgroups probably could not be distinguished by AEM. Although no new phases were detected, it is not possible to choose between these alternatives.

CONCLUSIONS

Statistical analysis confirms the incompatibility of solute activity ratios with the dissolution reaction based on the composition of the muscovite starting materials reported by Mattigod and Kittrick (1979). AEM analyses of muscovite after equilibration, however, provide no evidence of a significant change in bulk chemical composition; on the contrary, they suggest that the average muscovite composition and the composition of muscovite controlling solute activity ratios in solution may be different. If this compositional difference is due to edge effects, AEM may be incapable of resolving the problem of muscovite dissolution (Mattigod and Kittrick, 1979; Lin and Clemency, 1981).

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