Mixed-layer illite/smectite: A multiphase model

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Abstract

Comparison of the inferred chemical compositions of solubility-controllng, mica-like phases with those of apparent phases in natural, hydrothermal materials suggests the existence of four illitic layer (ordering) types [S (R0), IS (R1), ISII (R ≥ 3) and I] that behave as discrete, thermodynamic phases. Mixed-layer I/S is apparently a mixture of one or more of these phases.

According to the fundamental particle hypothesis, the various layer (ordering) types represent different particle thicknesses (e.g., IS, 20 Å; ISII, 40 Å). The multiphase illite model proposes that these particles, including their smectitic edges, are metastable phases. As crystal growth proceeds, phases having greater stability and particle thickness appear in accordance with Ostwald's step rule and Ostwald ripening, respectively.

Introduction

In recent discussions of sericite from the Silverton caldera, Colorado (Altaner and Vergo, 1988; Eberl et al., 1988), two models have been proposed to account for mixed-layer illite/smectite (I/S). However, neither of these discussions adequately takes into account solution equilibration studies in the system $K_2O-Al_2O_3-SiO_2-H_2O$ (Kittrick, 1984; Sass et al., 1987; Aja et al., 1988; Aja, 1989) that provide data from which the compositions of illitic phases may be calculated. The problem of the nature of mixed-layer I/S cannot be fully resolved without consideration of the implications of these studies.
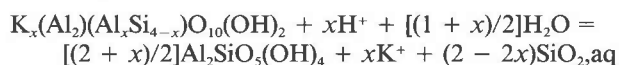
The term illite as used here refers to a nonexpandable, dioctahedral, aluminous, K-bearing micaceous phase or layer that has less charge than phengite (Bailey et al., 1984). All estimates of the composition of end-member illite (I) range between 0.8K and $0.9K/O_{10}(OH)_2$ (Weaver, 1965; Środoń and Eberl, 1984; Rosenberg, 1987; Eberl and Środoń, 1988; Inoue et al., 1988). Thus, the minimum interlayer charge for illite, as defined here, is about −0.8. Smectite refers to a structurally similar phase with expandable layers and a maximum interlayer charge of −0.4 (Bailey et al., 1984); intermediate interlayer charges denote mixed-layer illite/smectite (I/S).

Multiphase solubility

The compositions of solubility-controlling phases may be calculated from the slopes of certain univariant lines on stability diagrams (Sass et al., 1987). If it is assumed that the micalike phases (smectite, illite, muscovite) can be represented in the system $K_2O-Al_2O_3-SiO_2-H_2O$ by the general formula $K_x(Al_2)(Al_xSi_{4-x})O_{10}(OH)_2$, where x is the

number of tetrahedral Al^{3+} and interlayer K^+ ions, the reaction between a micalike phase and a stoichiometric, nonmica-like phase may be expressed as a univariant reaction in log a_K^+/a_K^+ vs. log $a_{SiO_2,aq}$ space: for example, the reaction,

$$K_x(Al_2)(Al_xSi_{4-x})O_{10}(OH)_2 + xH^+ + [(1 + x)/2]H_2O = [(2 + x)/2]Al_2SiO_5(OH)_4 + xK^+ + (2 - 2x)SiO_2,aq$$

with an equilibrium constant (K_1) expression given by

$$\log a_K^+/a_H^+ = [(2x - 2)/x]\log a_{SiO_2,aq} + (1/x)\log K_1.$$

Inasmuch as the coefficients of this reaction can be expressed in terms of a single variable, x, the slopes of univariant boundaries, which depend only on the composition of the solid phases participating in the univariant equilibrium, may be calculated. The contribution of surface free energy, which is significant in clay-sized particles, affects the intercepts but not the slopes of these univariant lines. Thus, the compositions of discrete, thermodynamic phases may be determined unambiguously by this method if the assemblage includes at least one phase that is not micalike. [Note that the coefficients of a univariant reaction between two micalike phases can be expressed only in terms of two variables. The slopes of such univariant boundaries equal 3, regardless of the composition of either solubility-controlling phase, and neither variable can be determined. The compositions of the solubility-controlling phases cannot be estimated in this case (Sass et al., 1987).]

Altaner and Vergo (1988) cite solution equilibration experiments on Goose Lake (GL) illite (Rosenberg et al., 1985) in support of their two-phase model of mixed-layer

illite/smectite (I/S). However, these and subsequent experiments with GL and other natural illite samples do not support a model limited to two phases.

The calculated composition of the phase that equilibrated with kaolinite and solution at 25 °C in experiments with GL illite [$0.25K/O_{10}(OH)_2$; Rosenberg et al., 1985] is, by definition, that of a smectite (Bailey et al., 1984). The presence of at least one additional micalike phase was inferred after consideration of the bulk composition of GL illite [$0.59K/O_{10}(OH)_2$; Kittrick, 1984]. Thus, GL illite was thought to be an assemblage of at least two phases, the smectite representing one component of random I/S. However, recent studies of natural, hydrothermal illite by Inoue et al. (1987) show that flakelike, randomly interstratified I/S is structurally and chemically distinct from lathlike, regularly interstratified I/S; they suggest that random I/S is a single-phase solid solution extending to a composition of $<0.5K/O_{10}(OH)_2$ and that K fixation limits the expandability of these solid solutions to a range between 50 and 100%. Thus, random I/S may be a smectitic phase and could have the composition referred to as smectite by Rosenberg et al. (1985).

In later solution equilibration experiments with GL and Beavers Bend illite at elevated temperatures (Sass et al., 1987), two illitic phases, $0.67K/O_{10}(OH)_2$ and $0.90K/O_{10}(OH)_2$, were observed in addition to a smectite very similar in composition to the phase observed in the earlier study (Rosenberg et al., 1985). When solution equilibration data for Marblehead illite (Aja, 1989) are also taken into account, illite phase relationships appear to involve at least four micalike phases having compositions of approximately $0.29 \pm 0.04K$-, $0.50 \pm 0.05K$-, $0.69 \pm 0.03K$-, and $0.85 \pm 0.05K/O_{10}(OH)_2$ (Table 1). These compositions have been inferred, within narrow limits, in the products of many experiments over a range in temperatures; intermediate compositions apparently do not exist. Furthermore, changes in temperature or solution composition are not accompanied by gradual changes in the K content of illitic phases. These data are best explained by the existence of multiple, stoichiometric, micalike phases.

If it is assumed that the composition $0.252K/O_{10}$-$(OH)_2$ represents K-saturated smectite (Sass et al., 1987) and that $0.85K/O_{10}(OH)_2$ represents end-member illite (I) (Aja, 1989), then the compositions $0.50K/O_{10}(OH)_2$ and $0.69K/O_{10}(OH)_2$ correspond closely to those expected for phases with IS and ISII ordering, $0.55K/O_{10}(OH)_2$ and $0.70K/O_{10}(OH)_2$, respectively. Thus, four layer types, S, IS, ISII, and I, distinguished in natural illite by X-ray diffractometry (Środoń and Eberl, 1984), have tentatively been identified as discrete phases in solution equilibration studies (Rosenberg et al., 1987).

A MULTIPHASE ILLITE MODEL

Natural, hydrothermal illite, characterized by chemical composition [$K_x/O_{10}(OH)_2$], ordering and expandability (Inoue et al., 1987, 1988), is compared with the solubility-controlling phases in Table 1. Three morphologies of

TABLE 1. Comparison of the chemical compositions of solubility-controlling phases* with apparent phases in natural, hydrothermal illite**

Solubility-controlling phases†		Apparent natural phases		
$K_x/O_{10}(OH)_2$	Ordering type‡	$K_x/O_{10}(OH)_2$	Ordering R§	Expandability %
0.29 ± 0.04	S	0.29 ± 0.07	0	55 ± 5
		0.31 ± 0.09	0	50 ± 10
0.50 ± 0.05	IS	0.34 ± 0.07	1	40 ± 5
		0.43 ± 0.10	1	30 ± 5
0.69 ± 0.03	ISII	0.73 ± 0.06	≥3	12 ± 3
		0.76 ± 0.06	≥3	5 ± 5
0.85 ± 0.05	I	0.80 ± 0.01	—	0

* Rosenberg et al. (1987); Sass et al. (1987); Aja et al. (1988); Aja (1989).
** Inoue et al. (1988).
† Ranges in K_x represent variations in the compositions calculated for different natural illite samples at several temperatures.
‡ Inferred.
§ Reichweite.

micalike phases appear to crystallize successively during the conversion of smectite to illite under hydrothermal conditions in nature (i.e., flakelike, lathlike, and hexagonal platelike crystals). The flakelike crystals ($1M_d$) are identified as random I/S, whereas the successions of ordered lathlike ($1M$) and platelike ($2M_1$) crystals with increasing K content and decreasing expandability are referred to as regularly interstratified I/S (Inoue et al., 1988). However, there is considerable overlap in the K contents of the flakelike and lathlike crystals. Apparently, the lathlike crystals, which are identified as metastable, ordered I/S solid solutions distinct from rectorite (IS), grow at the expense of the flakelike crystals. Several flakelike crystals with K contents between 0.34 and 0.48 show R1 ordering and are probably mixtures of S and IS ordering types. One exceptional flakelike crystal that has a K content of 0.61 and R2 ordering, corresponding to IIS, may be a mixture of IS and ISII. Particle thicknesses of these morphological types (Inoue et al., 1987) appear to support the fundamental particle-interparticle diffraction hypothesis (Nadeau et al., 1985).

These mineralogical studies provide evidence of the chemical composition, expandability, and structural states of illitic materials but no direct evidence of the behavior of illite as a discrete phase. On the other hand, solution equilibration studies (e.g., Sass et al., 1987) permit the calculation of the compositions of discrete, thermodynamic phases that equilibrate with solutions but offer no direct insight into the structural state of these phases. If the results of these two approaches are combined by equating the chemical compositions of the illitic phases, a consistent, multiphase illite model emerges that suggests that as many as four discrete, thermodynamic phases may exist during prograde illitization (Table 1). IIS(R2) has been neglected in this discussion because its existence is uncertain; Środoń and Eberl (1984) believe that it may be a mixture of IS- and ISII-ordered I/S. Discrepancies

between the K contents of the solubility-controlling phases and that of the hydrothermal illite may be due to the admixture of small amounts of a second ordering type in the natural materials.

According to the multiphase model, natural illite is composed of at least four discrete micalike phases, corresponding in composition to S, IS, ISII, and I. Mixed-layer I/S may be a mixture of one or more of these phases. Thus, ordered I/S (0–50% expandable) may consist of one or more discrete, ordered phases (e.g., IS, ISII), not two phases, illite and smectite, as suggested by Altaner and Vergo (1988). In this light, GL illite appears to consist of three illitic phases, a K-fixed smectite (random I/S), an ordered I/S corresponding in composition to ISII, and end-member illite (I), in addition to segregated smectite (Gaudette et al., 1966).

Natural illite consisting of a single ordering type exhibits a narrow range of compositions. For example, the alkali contents (K + Na) of the ISII-ordered San Juan sericite (0.78 ± 0.05 1SD, 21 samples; Eberl et al., 1987) and illite M11 (0.73; Środoń and Eberl, 1984) are in accord with that of the ISII-ordered illite observed by Inoue et al. (1988; Table 1) suggesting a direct correlation between ordering type and chemical composition and implying the existence of a discrete phase of this composition. The observed decrease in illitization reaction rates accompanying the formation of ISII ($R \geq 3$) in nature implies that this ordering type is relatively stable (Jennings and Thompson, 1986).

DISCUSSION

The multiphase model is in accord with neither the two-phase model of I/S (Altaner and Vergo, 1988) nor the fundamental particle-interparticle diffraction hypothesis in the form proposed by Eberl et al. (1987, 1988). Despite their differences, both of the latter are, in fact, two-phase models. Altaner and Vergo (1988) argue for the existence of interstratified illitic I/S but suggest that illite and smectite layers may be two distinct thermodynamic phases, whereas Eberl et al. (1987, 1988) explain ordered illite/smectite (0–50% expandable, R1, 2 ≥ 3) as an artifact of interparticle diffraction in populations of fundamental illite particles and disordered illite (50–100% expandable, R0) as random mixtures of illitic and smectitic layers.

The multiphase illite model does not deny the existence of fundamental particles or the importance of interparticle diffraction. In accord with the model of Nadeau et al. (1985), ordered IS (R1) may form as fundamental illite particles (20 Å thick) having smectitic outer edges. According to the fundamental particle hypothesis, the various ordering types (e.g., IS, ISII) represent different particle thicknesses (20 Å, 40 Å, respectively) and smectitic interlayers are artifacts of interparticle diffraction effects. The multiphase illite model merely proposes that these particles, including their smectitic edges, behave as metastable, thermodynamic phases. For example, ordering-type ISII ($R \geq 3$) represents particles

consisting of four illitic layers of 10 Å with smectitic edges that are shared with other similar particles, whereas particles of end-member illite (I) are eight 10-Å layers thick. As crystal growth proceeds, phases having greater stability and particle thickness (20 Å, 40 Å, 80 Å) appear. Particle thickening may be accounted for by Ostwald ripening (Eberl and Środoń, 1988), whereas the appearance of successive phases with increasing stability may be viewed as an example of Ostwald's step rule.

The process of particle thickening [20 Å, particle (phase) composition, $0.5K/O_{10}(OH)_2$; 40 Å, $0.75K/O_{10}(OH)_2$; 80 Å, $0.875K/O_{10}(OH)_2$] could, conceivably, culminate with the formation of end-member muscovite, changes in the chemistry and relative stability of successive phases becoming imperceptible as muscovite composition is approached asymptotically. However, muscovite may be unstable with respect to illite at temperatures below 280 °C (Yates and Rosenberg, 1987; McDowell and Elders, 1980) and, thus, the relationship between illite (I) and muscovite is problematic.

The multiphase and fundamental-particle models are in accord if discrete particles behave as discrete thermodynamic phases. However, it is not possible to rule out the Markovian model (Altaner and Bethke, 1988) based on solution equilibration studies alone, inasmuch as MacEwan crystallites of different ordering types (Altaner and Bethke, 1988) may behave as thermodynamic phases.

It is important to emphasize the contribution of solution equilibration studies to the multiphase illite model. Whereas structural and compositional data may be obtained from solid-state studies, solution equilibration studies provide the only means available for determining the chemical composition of discrete, thermodynamic phases in natural illite.

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