

COMPARISON OF STRUCTURAL MODELS OF MIXED-LAYER ILLITE/SMECTITE AND REACTION MECHANISMS OF SMECTITE ILLITIZATION

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Abstract—This paper compares mechanisms of the reaction of smectite to illite, in light of structural models for interstratified illite/smectite (I/S). The crystal structure of I/S has been described previously by a nonpolar and polar 2:1 layer model. In a nonpolar model, individual 2:1 layers are chemically homogeneous, whereas a polar model assumes a 2:1 layer can have a smectite charge on one side and an illite charge on the other side. Several kinds of data support the polar model; however, more determinations of the negative charge of expandable sites in I/S are needed to confirm such a model.

Assuming a polar 2:1 layer model for I/S, we compare the mineralogical and geochemical consequences of several reaction mechanisms for smectite illitization: 1) solid-state transformation (SST), 2) dissolution and crystallization (DC) and 3) Ostwald ripening (OR). Features of an SST model are the replacement of smectite interlayers by illite interlayers, resulting in gradual changes in interlayer ordering, polytype, chemical and isotopic composition and crystal size and shape. Several SST models are possible depending on the nature of the reaction site (framework cations, polyhedra or interlayers). In contrast, DC models allow for abrupt changes in the structure, composition and texture of I/S as illitization proceeds. Several DC models are possible depending on the nature of the rate-controlling step, for example, diffusional transport or surface reactions during crystal growth. The OR model represents the coarsening of a single mineral where the smallest crystals dissolve and nucleate onto existing larger crystals, allowing for evolution in the overgrowth but not in the template crystal.

An SST mechanism, involving either reacting polyhedra or reacting interlayers, seems to best model illitization in rock-dominated systems such as bentonite. A DC mechanism seems to best model illitization in fluid-dominated systems such as sandstone and hydrothermal environments. Both DC and SST mechanisms can occur in shale. Differences in reaction mechanism may be related to permeability. An OR model poorly describes illitization because of the progressive mineralogical and chemical changes involved. For many geologic environments, it is important to consider alternate origins for I/S such as kaolinite illitization and detrital. Further work is needed to clarify the DC crystal growth process in terms of a structural model of I/S and to determine which specific SST or DC model best characterizes illitization in geologic systems.

Key Words—Illite, Illite/Smectite, Mixed-Layer, Reaction Mechanism, Smectite.

INTRODUCTION

Smectite Illitization

Documenting the degree of reaction of smectite to illite, termed “smectite illitization”, is frequently used as an independent geothermometer to allow reconstructions of the thermal and tectonic history of sedimentary basins (Weaver and Beck 1971; Hoffman and Hower 1979; Schoonmaker et al. 1986) and active and fossil hydrothermal systems (Inoue and Utada 1983; Jennings and Thompson 1986). The chemical consequences of this reaction may influence the development of geopressures (Freed and Peacor 1989), growth faults (Bruce 1984), oil migrations (Burst 1969), mineral cements and porosity (Lahann 1980). Radiometric ages of illite can date regional overthrusting (Hoffman et al. 1976) and migrations of hydrothermal fluids, oil and natural gas (Aronson and Burtner 1983; Lee et al. 1985; Hay et al. 1988).

Smectite illitization is considered to proceed through mixed-layer illite/smectite (I/S) intermediates in which the percentage of illite interlayers typically

increases with increasing temperature (Hower et al. 1976), geologic time (Pytte and Reynolds 1989), K concentration (Huang et al. 1993) and water/rock ratio (Whitney 1990). As I/S becomes illitic, the interlayer arrangements change from random (R0) to short-range (R1) ordered, and then to long-range (R3) ordered, as inferred from computer-generated X-ray diffraction (XRD) patterns (Bethke et al. 1986) and as directly observed using high-resolution transmission electron microscopy (HRTEM; Veblen et al. 1990; Środoń et al. 1990). Polytypes generally evolve from turbostratic stacking in smectitic I/S to IM_d or IM in illitic I/S to $2M_1$ in pure illite (Inoue et al. 1987; Reynolds 1993). The octahedral vacancy can occur in either the M1 (*trans*) or M2 (*cis*) octahedral site (Drits et al. 1993; Reynolds 1993). Chemical changes in I/S include an increase in K and Al, and a decrease in Si, Fe, Mg, Na, Ca and H₂O (Środoń et al. 1992).

I/S as MacEwan Crystallites and Fundamental Particles

The crystal structure of mixed-layer I/S can be described using either the Markovian model or the fun-

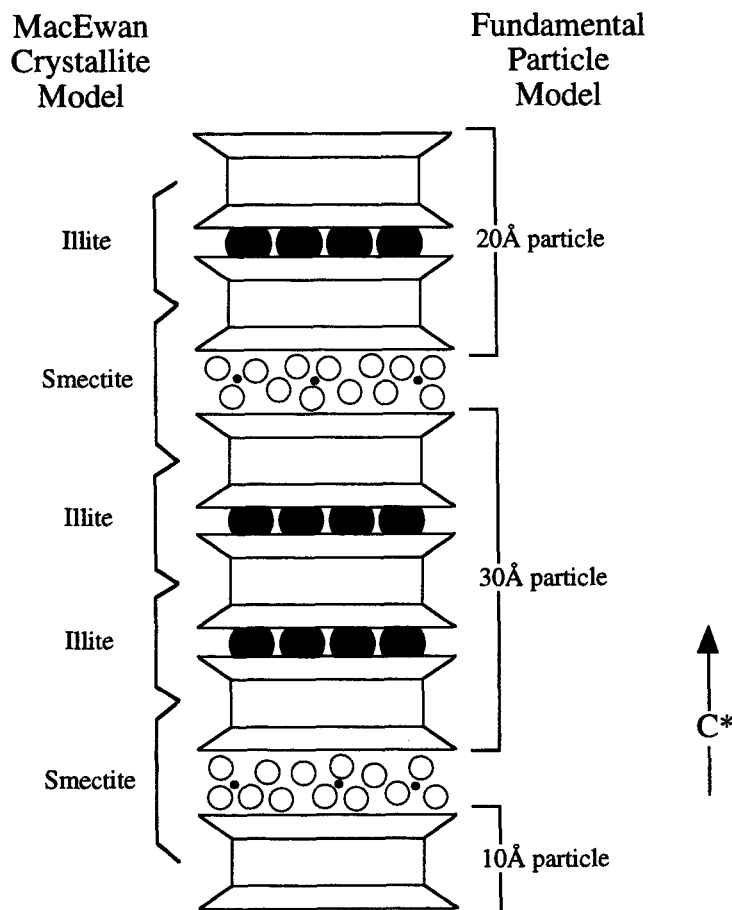


Figure 1. Mixed-layer I/S represented as a MacEwan crystallite and as an aggregate of fundamental particles. Anvils represent 2:1 layers and regions between 2:1 layers represent the interlayer. The c^* -axis is vertical. Large dark circles are fixed K, open circles are water molecules and small dark circles are exchangeable cations.

fundamental particle model (Figure 1). The Markovian model, derived from XRD studies of dispersed samples, views I/S as relatively large (typically 5 to fifteen 2:1 layers thick) MacEwan crystallites comprising both illite and smectite interlayers (Reynolds 1980). In this model, the proportion and sequence of interlayers (that is, c -unit cell boundaries at the middle of each octahedral sheet) control the I/S ratio and interlayer ordering observed in XRD analysis. The fundamental particle model, derived from TEM analysis of dilute dispersed samples, views I/S as an aggregate of much thinner crystallites (typically 1 to five 2:1 layers thick), termed "fundamental particles" (Nadeau et al. 1984). In this model, smectitic behavior (expandability) occurs at interfaces between fundamental particles, although the interfaces may not necessarily have a smectitic charge (Nadeau and Bain 1986). The proportion and thickness of fundamental particles influences the I/S ratio and interlayer ordering observed in XRD analysis. Ransom and Helgeson (1989) have emphasized that expandability observed by XRD should not

necessarily be equated to a smectite composition unless there are supporting chemical data.

HRTEM lattice fringe observations of *in situ* I/S commonly reveal crystallite thicknesses more similar to MacEwan crystallites than to fundamental particles (Veblen et al. 1990; Ahn and Buseck 1990; Środoń et al. 1990), which supports the Markovian model of I/S. However, Reynolds (1992, 1993) has used distributions of fundamental particle thickness to calculate XRD patterns (hkl peaks) of I/S. His results indicate that the interfaces between fundamental particles have turbostratic disorder and that 3-dimensional order occurs within them. Analysis of fundamental particle thickness also yields a more accurate measure of the total amount of smectite structural sites than does XRD analysis because of the presence of smectite sites (located at the top and bottom of MacEwan crystallites), which are not observable by XRD (Altaner et al. 1988; Eberl and Środoń 1988). Altaner and Bethke (1988) attributed the observation of fundamental particles to osmotic swelling during sample preparation

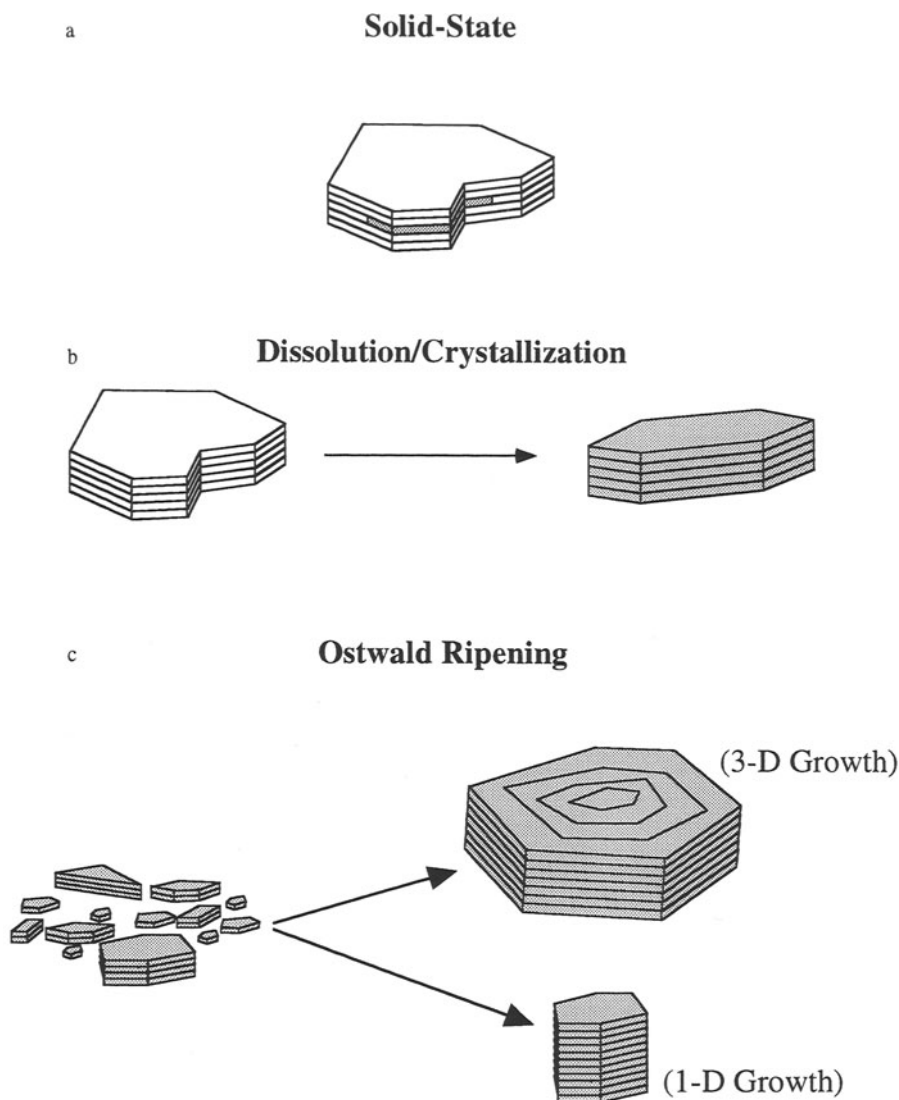


Figure 2. Different mechanisms for the hypothetical reaction of mineral A to mineral B (stippled pattern). a) Solid-state transformation, b) dissolution and crystallization and c) Ostwald ripening, which involves recrystallization of only mineral B.

which resulted in the disarticulation of I/S crystallites at expandable interfaces. Smectitic I/S commonly occurs as very large (tens of 2:1 layers), defect-rich crystals termed “megacrystals” (Ahn and Peacor 1986a) and “quasi-crystals” (Środoń et al. 1990).

Reaction Mechanisms for Smectite Illitization

Reaction mechanisms for smectite illitization can be classified into 2 broad categories: 1) SST and 2) DC. SST mechanisms, which typically also involve fluids that can act as catalysts and transport media (Veblen 1992), involve gradual replacement of the parent mineral (smectite) by the daughter mineral (illite) in close topotactic contact (Figure 2a). Such a model is sometimes referred to as a “layer-by-layer transformation”. Other general features of an SST mechanism are sim-

ilar polytypes for the parent and daughter crystals as well as daughter crystals with a similar size and shape as the parent (Baronnet 1992). Pollard (1971) presented an SST model for smectite illitization in which Al and Si diffuse through the hydrous interlayer and the tetrahedral sheet distorts while Al replaces Si. Based on TEM observations of shale and bentonite, Bell (1986) describes an SST process in which smectite layers are replaced laterally by illite layers. Using mathematical simulations of the illitization process, Bethke and Altaner (1986) show that a layer-by-layer transformation model can account for the transition from R0- to R1-ordered I/S in bentonite and shale, but they calculated XRD patterns of I/S with partial ordering at <50% illite, which is not usually observed in nature. Other investigators have proposed that

smectite illitization can follow an SST mechanism; however, they do not present a specific model (Shutov et al. 1969; Hower 1981; Hunziker et al. 1986; Inoue et al. 1990; Lindgreen et al. 1991). K-fixation (dehydration of K in smectite interlayers without modification to the silicate framework) is an SST mechanism that can occur during wetting and drying of smectite at earth's surface temperatures. Eberl et al. (1986) showed that K-fixation can produce R0 I/S with up to 50% illite layers from smectite with a high layer charge.

DC mechanisms involve complete dissolution of the parent mineral followed by nucleation and growth of the daughter mineral as a separate or epitaxial grain (Figure 2b). During dissolution, the structural memory of the parent is lost. Indications of a DC mechanism are changes in polytype and loss of morphological characteristics of the parent. Several DC models for smectite illitization have developed from mineralogical and TEM studies of I/S (Nadeau et al. 1984, 1985; Yau et al. 1987; Inoue et al. 1987; Eberl and Środoń 1988; Drits et al. 1996). Pollastro (1985) concluded that smectitic I/S dissolves and reprecipitates as both illitic I/S and discrete illite, resulting in a decreasing abundance of I/S as illitization proceeds. Awwiller (1993) concluded that the abundance of I/S increases during illitization. According to the model of Inoue et al. (1987), anhedral smectite crystallites (10-Å thick) become unstable, dissolve and recrystallize forming thin (20-Å thick) euhedral illite laths, some of which in turn dissolve and grow into larger (≥ 40 -Å thick) euhedral illite laths and hexagons. Whitney and Velde (1993) propose a DC model with several stages including smectite dissolution, nucleation of small illite crystals onto smectite templates and coalescence and growth of illite crystals. Eberl and Środoń (1988) and Inoue et al. (1988) conclude that illite recrystallization is controlled by an OR mechanism whereby the smallest crystallites dissolve and reprecipitate onto larger crystallites in order to minimize the interfacial free energy (Figure 2c). To describe illitization in Gulf Coast shale, Ahn and Peacor (1986a) present a mechanism intermediate to the SST and DC models in which smectite dissolves and illite crystallizes from an aqueous fluid in the same space as the parent smectite.

Considerable controversy exists as to which reaction mechanism applies to illitization in natural systems. Some investigators favor a DC mechanism for describing illitization (Nadeau et al. 1985), others favor an OR mechanism (Eberl et al. 1990) and others favor an SST mechanism (Hunziker et al. 1986; Lindgreen et al. 1991; Clauer et al. 1995). Several studies emphasize that different mechanisms apply in different geologic environments, an SST-like mechanism describing illitization in bentonite or shale (Ahn and Peacor 1986a; Inoue et al. 1990) and a DC or OR model describing illitization in hydrothermal settings (Yau et al. 1987;

Inoue et al. 1988). Another common interpretation is that the reaction mechanism for illitization changes from SST while I/S exhibits R0 ordering to DC while I/S exhibits $R \geq 1$ ordering (Drits 1987; Whitney and Northrop 1988). For hydrothermal I/S from Japan, Inoue et al. (1987) describe a K-fixation process, followed by DC, and then followed by OR. Several HRTEM studies conclude that both SST and DC mechanisms can occur in a single sample (Yau et al. 1987; Amouric and Olives 1991; Murakami et al. 1993).

This paper examines relations between reaction mechanisms of smectite illitization and structural models of I/S. In addition, we outline mineralogical and geochemical consequences of SST and DC reaction mechanisms and attempt to identify the mechanism that best describes illitization in different geologic environments.

DISCUSSION

Crystal Chemical Structure of I/S

It is important to understand the crystal structure of I/S because any reaction mechanism for smectite illitization should be consistent with a structural model of I/S. Mixed-layer I/S minerals are considered to be polysomatic intergrowths (Allen 1992), which are crystals composed of smaller, chemically distinct layer modules (Thompson 1978). Based on chemical analyses of a large number of I/S samples, Środoń et al. (1992) determined the average interlayer cation content for the end-member components in I/S to be 0.4 per $O_{10}(OH)_2$ for smectite and 0.9 per $O_{10}(OH)_2$ for illite; however, there is some uncertainty regarding the physical boundaries of the 2 chemically distinct units (Nadeau et al. 1985; Nadeau and Bain 1986; Eberl and Środoń 1988; Altaner et al. 1988; Wilson 1990; Güven 1991; Primmer 1994). (Although Ransom and Helgeson 1993 conclude that I/S does not exhibit a 2-component solid solution series, their study focuses on the detailed chemical variability of the end members, smectite and illitic I/S, rather than on the broad compositional differences among I/S intermediates.)

The chemically distinct units in I/S could be interstratified 2:1 layers of illite and smectite or interstratified interlayers (that is, c-unit cell boundaries at the middle of each octahedral sheet) of illite and smectite. The interstratified 2:1 layer model assumes that an individual 2:1 layer in I/S is always chemically homogeneous, consisting of either smectite or illite, whereas the interstratified interlayer model assumes that an individual 2:1 layer in I/S can be chemically heterogeneous, containing a low smectite charge on one side and a higher illite charge on the other.

Chemically homogeneous 2:1 layers are termed "nonpolar" and chemically heterogeneous 2:1 layers, "polar" (Güven 1991). In a polar 2:1 layer model, low-charge tetrahedral sheets surround hydrous, expandable

interlayers and high-charge tetrahedral sheets surround anhydrous, nonexpandable interlayers (Figures 3a, 3d, 3g). Because cations in the octahedral sheet lie midway between 2 interlayer regions, we assume that the octahedral sheet charge contributes equally to each interlayer region. In this model, fundamental particles have a smectite composition on the top and bottom tetrahedral sheets and an illite composition on internal tetrahedral sheets. In a nonpolar 2:1 layer model, 3 interlayer sites are expected: low-charge interlayers produced by adjacent smectite 2:1 layers, high-charge interlayers produced by adjacent illite 2:1 layers and intermediate-charge (vermiculite) interlayers produced by a smectite 2:1 layer adjacent to an illite 2:1 layer (Figures 3b, 3e, 3h). The above discussion assumes that the interlayer cation charge is balanced locally by negative charge in the tetrahedral and octahedral sheets immediately adjacent to the interlayer region. We consider the assumption of local charge balance to be more likely than other possibilities, for example, interlayer cation charge balanced by the negative charge on a 2:1 layer from only 1 side of the interlayer.

In light of fundamental particle thicknesses, Nadeau et al. (1984) proposed a structural model in which 10-Å thick particles have a smectitic composition and ≥ 20 -Å thick particles are considered to be illite. Chemical analyses (Inoue et al. 1987) indicate that 10-Å thick particles have a smectitic charge (-0.3 per $O_{10}(OH)_2$), ≥ 50 -Å thick particles have an illitic charge (-0.85 per $O_{10}(OH)_2$) and 20–40-Å thick particles have compositions between end-member smectite and illite. Figures 3c, 3f and 3i depict this conceptual model (termed the “multi-phase model” of I/S, Rosenberg et al. 1990; Aja et al. 1991; Vali et al. 1991) assuming nonpolar 2:1 layers. The multi-phase model of I/S predicts a broad range in charge for expandable interlayer sites, including a vermiculite charge produced by occurrence of ≥ 20 -Å thick particles adjacent to each other.

Numerous workers support the polar 2:1 layer model for I/S and rectorite, R1-ordered mica/smectite with 50% mica layers (Brown and Weir 1965; Ahn and Peacor 1986b; Altaner et al. 1988; Veblen et al. 1990; Ahn and Buseck 1990; Güven 1991; Jakobsen et al. 1995). Nonpolar 2:1 layer models have difficulty explaining why certain interlayer sites are expandable and others are not. For example, the multi-phase model predicts that an expandable interlayer between a 20-Å and a 40-Å thick particle has a higher charge than a nonexpandable interlayer within a 20-Å thick particle (Figure 3i). Chemical analyses of I/S correlate well with measurements of expandability, assuming only a 2-component system of low- and high-charge sites (-0.4 and -0.9 respectively, Środoń et al. 1992). Based on inversion/recovery nuclear magnetic resonance (NMR) analysis of 1 hydrothermal I/S sample, Altaner et al. (1988) found that low-charge (-0.3) tetrahedral sheets were associated with expandable sites

and high-charge (-0.8) tetrahedral sheets were associated with nonexpandable sites. Assuming the octahedral sheet charge (-0.1) is distributed equally between expandable and nonexpandable sites results in total interlayer charges identical to those identified by Środoń et al. (1992). Barron et al. (1985) and Jakobsen et al. (1995) found similar results for rectorite, although the mica sites in rectorite have a greater charge than illite sites in I/S. XRD analysis of alkylammonium-treated I/S samples indicates that expandable interlayers in R0- and R1-ordered I/S have a smectite composition (Lagaly 1979; Cetin and Huff 1995a). The polar 2:1 layer model can account for the chemical variations of fundamental particles as averages of the illite and smectite interlayer sites present in each particle, for example, 20-Å thick particle:

$$= \frac{I + S}{2} = \frac{0.9 + 0.4}{2} = 0.65,$$

40-Å thick particle

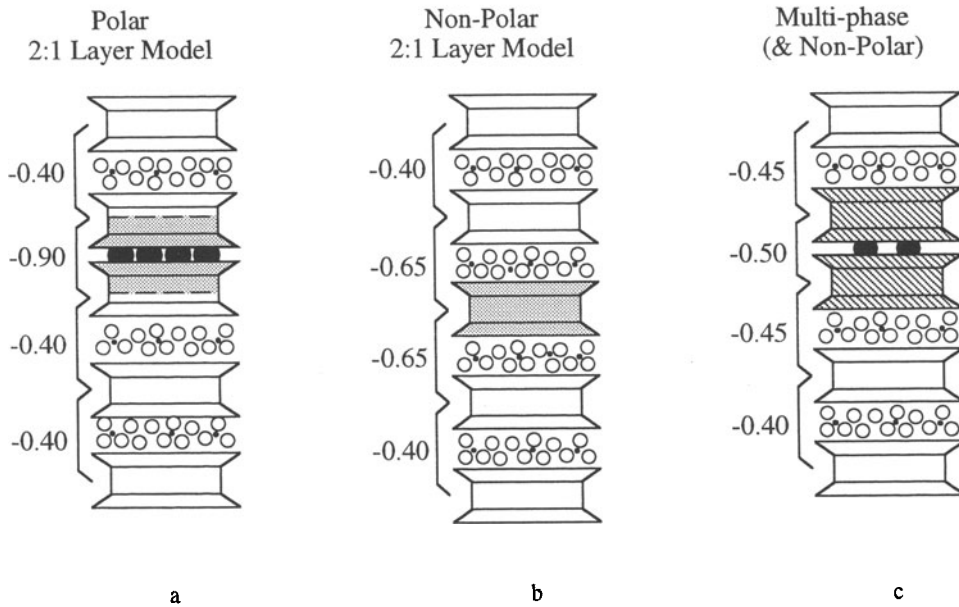
$$= \frac{3 \times I + S}{4} = \frac{3 \times 0.9 + 0.4}{4} = 0.78 \quad [1]$$

Nevertheless, on the basis of TEM and XRD analysis of alkylammonium-treated I/S samples, several investigators (Vali and Hess 1990; Vali et al. 1991; Cetin and Huff 1995a, 1995b) conclude that expandable interlayers in illitic I/S are not in fact, smectite but vermiculite in charge. Based on chemical and TEM data, Nadeau and Bain (1986) made similar conclusions. Further work is needed to document the charge of expandable and nonexpandable sites in I/S.

Reaction Mechanisms for Smectite Illitization

Numerous investigators have proposed that smectite illitization follows either an SST, a DC or an OR mechanism; however, the models are commonly incomplete or poorly related to structural models of I/S. An SST mechanism can produce I/S with either polar or nonpolar 2:1 layers; however, SST is incompatible with the multi-phase model of I/S with nonpolar 2:1 layers (depicted in Figures 3c, 3f and 3j) because entire crystallites must be chemically transformed. If layer-by-layer transformation describes an SST mechanism that produces I/S with nonpolar 2:1 layers, then interlayer-by-interlayer transformation seems appropriate to describe an SST mechanism that produces I/S with polar 2:1 layers. In an interlayer-by-interlayer transformation model, the region surrounding a smectite interlayer reacts to an illite interlayer with the reactant and product species moving through the hydrous interlayer (Figure 4). Therefore, along a single reaction front, 2 planes of anions (the plane of basal oxygens and the mixed plane of hydroxyls and apical oxygens) and 2 planes of cations (in the tetrahedral and octahedral sheets) on both sides of the interlayer can undergo chemical substitution and isotopic ex-

Smectitic I/S



Rectorite

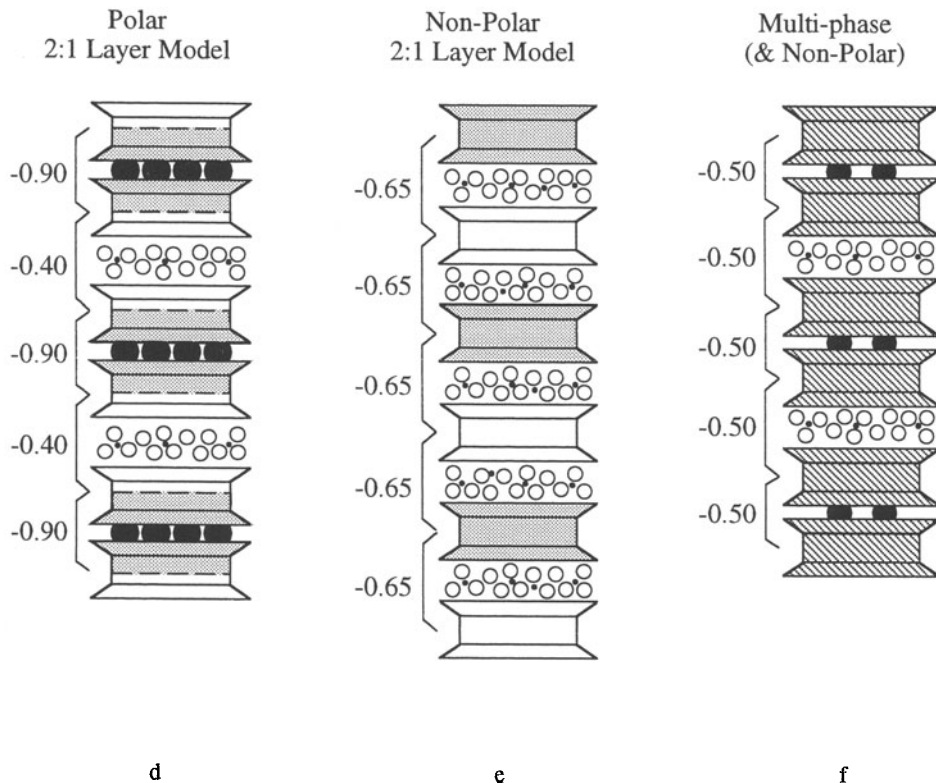
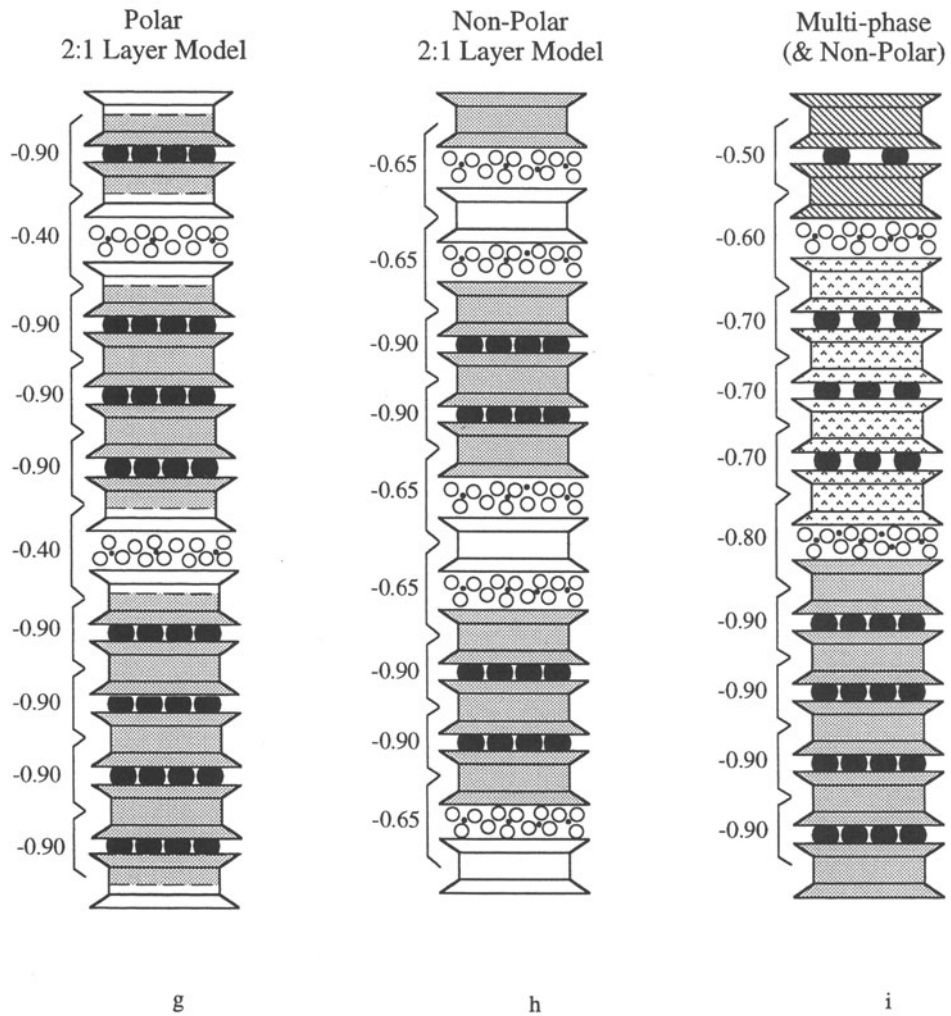


Figure 3. Crystal structure of smectitic I/S, rectorite and illitic I/S depicted by 3 different models: polar 2:1 layers, nonpolar 2:1 layers and multi-phase model of Rosenberg et al. (1990) assuming nonpolar 2:1 layers. Anvils represent 2:1 layers with different negative charges. Average negative charge of the structure surrounding the interlayer is shown.

Illitic I/S



LEGEND

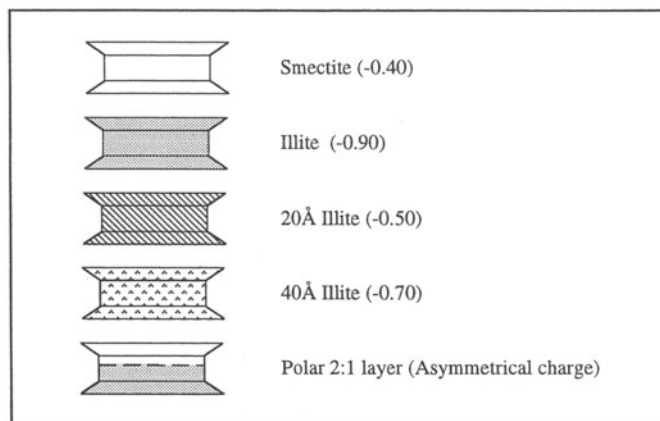


Figure 3. *Continued.*

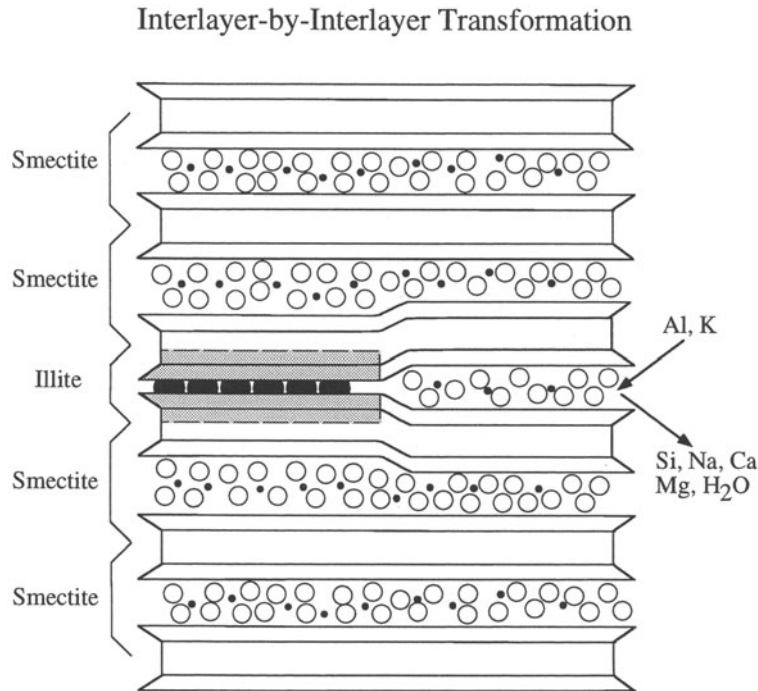


Figure 4. Depiction of the interlayer-by-interlayer transformation mechanism. Chemical exchange of reactant and product species occurs through the hydrous interlayer region.

change. The chemical substitutions to produce illite could range from those that produce no effect on framework oxygens (framework cation exchange, Figure 5a), moderate effect on framework oxygens (dissolution and crystallization of reacting polyhedra, Figure 5b), and extensive effect on framework oxygens (dissolution and crystallization of reacting interlayers, Figure 5c).

The reacting interlayer model is somewhat intermediate between an SST and a DC mechanism because significant structural modifications (such as conversion of a *cis*-vacant to a *trans*-vacant structure) could occur during transformation of smectite to illite, which is a typical feature of a DC mechanism. Alternatively, parent and daughter minerals are in close topotactic contact and the lateral dimensions of illite should have a similar size and shape to those of the smectite precursor, which are typical features of an SST mechanism. Because of stronger similarities to SST, we prefer to consider the reacting interlayer model as an SST mechanism.

All of the above SST mechanisms need to consider the issue of the supply of Al, which typically has a low solubility in moderate pH solutions. The Al for illitization must be transported from the source (for example, from the dissolution of smectite, Boles and Franks 1979; K-feldspar, Hower et al. 1976; or kaolinite, Awwiller 1993) to the reacting smectite interlayer. The presence of a chelating agent, such as a carboxylic acid,

can enhance Al solubility in the bulk solution (Crossey et al. 1986), but the movement of Al with a chelating agent could be inhibited in the more confined region of the interlayer. Finally, K-fixation represents an SST process of interlayer cation exchange and dehydration with no accompanying changes to the 2:1 layer.

DC mechanisms generally involve dissolution of smectitic crystals and transport of the chemical species, followed by nucleation and growth of illitic crystals. Nucleation probably occurs on preexisting particles (heterogeneous nucleation) rather than as a new crystal (homogeneous nucleation), because of energy barriers associated with homogeneous nucleation. DC mechanisms can vary in detail depending on the nature of the slowest or rate-controlling step, which most commonly is diffusional transport of the chemical species to the growing crystal, slow surface reaction during crystal growth or both (Berner 1980). Surface reaction controls most commonly involve nucleation on crystal defects such as spiral dislocations. It should be noted that previous studies that propose a DC mechanism have referred to growth of illitic crystals and not I/S crystals. However, if the crystal chemistry of illitic clays is better represented as I/S with polar 2:1 layers (that is, with illitic interiors and smectitic tops and bottoms), then a DC model should account for the growth of compositionally zoned crystallites. The growth of a small fundamental particle with polar 2:1 layers to a larger fundamental particle with polar 2:1

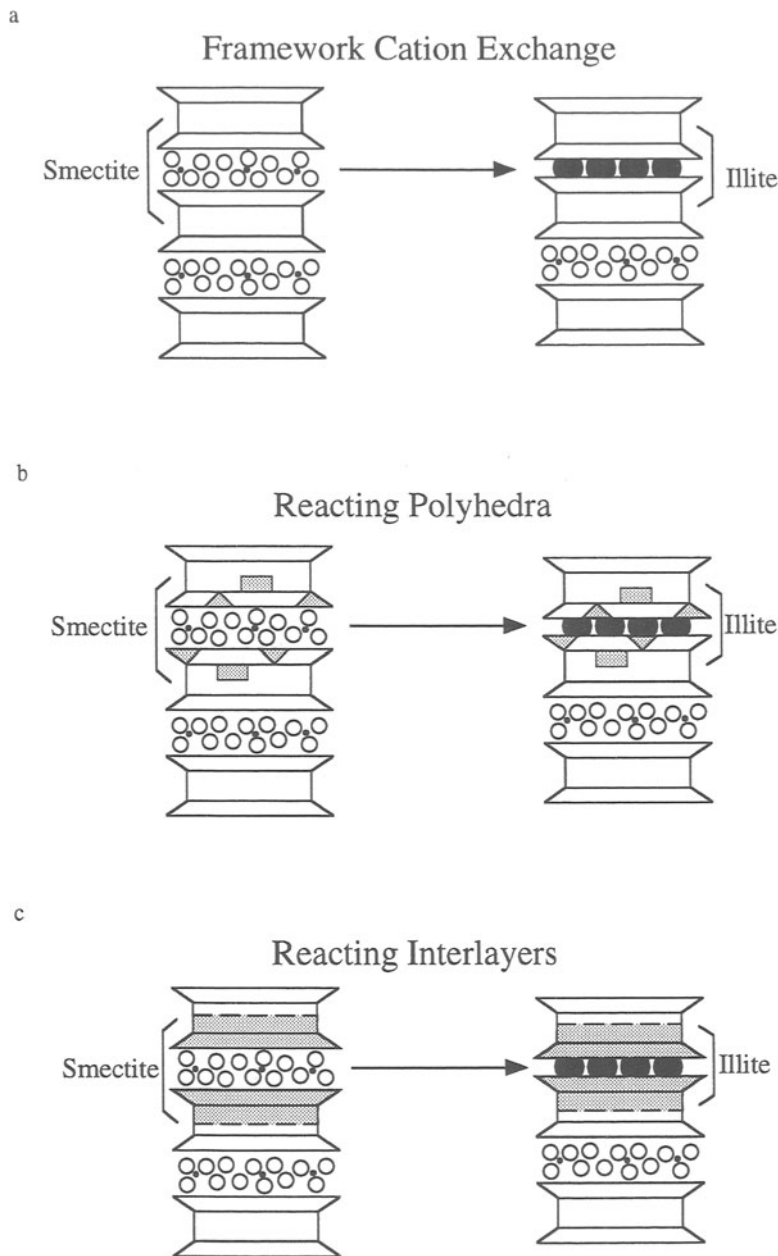


Figure 5. Different SST mechanisms for smectite illitization: a) framework cation exchange, b) reacting polyhedra and c) reacting interlayers. Stippled area represents the portion of I/S crystallite that undergoes dissolution and reprecipitation during illitization.

layers seems complex. Figure 6 depicts 2 possible pathways. In Figure 6a, the tops and bottoms of template crystals are chemically reacted to an illite composition before nucleation of a chemically heterogeneous overgrowth. Alternatively, if the smaller template crystal remains inert, smectite sites should be trapped within the growing crystal (Figure 6b). The exact relationship between structural and crystal growth models for I/S is unclear.

Measurement of steady-state profiles of the thickness (Eberl et al. 1990) and lateral dimensions (Inoue et al. 1988; Inoue and Kitigawa 1994) of fundamental particles has led to the idea that OR describes the illitization reaction. OR refers to a recrystallization process that occurs after initial nucleation of different-sized crystals. The smallest crystals, having a high solubility, dissolve and nucleate onto larger preexisting crystals, resulting in crystal growth (Figure 2c). Large crystals

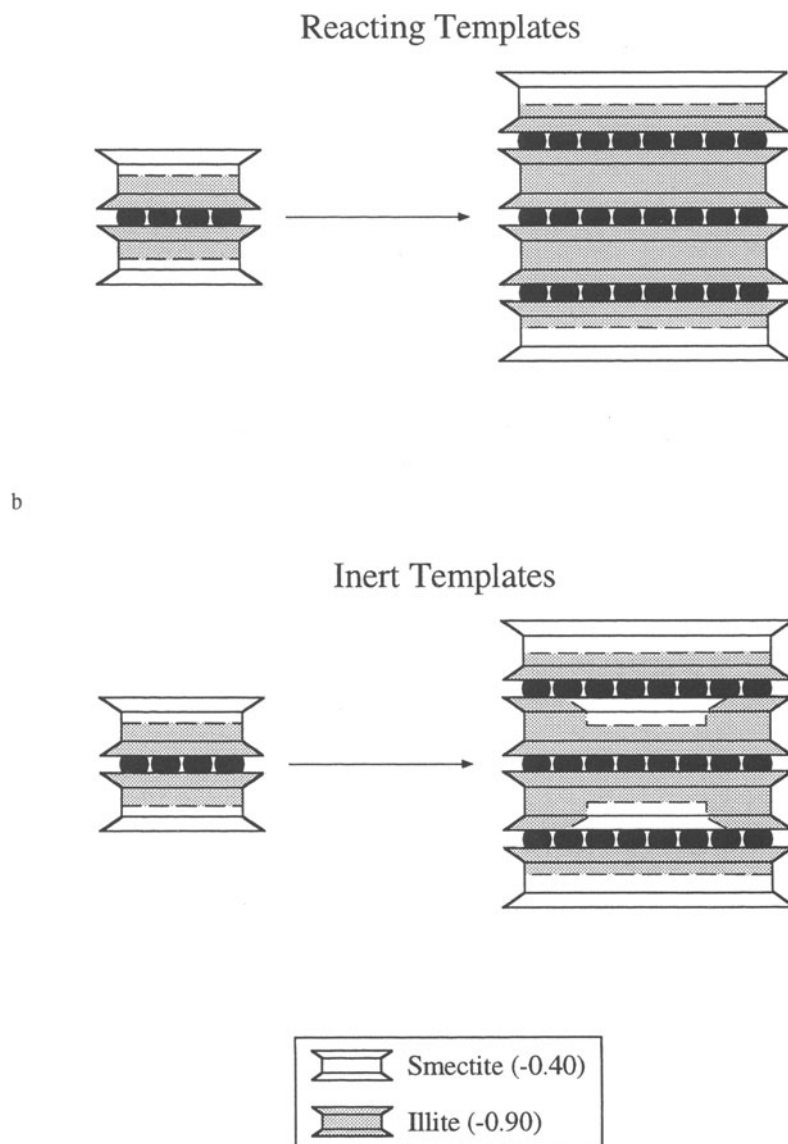


Figure 6. Crystal growth models of fundamental particles with polar 2:1 layers. a) Reacting template crystals and b) unreactive template crystal, which results in smectite sites trapped within the growing crystal.

produced by OR will consist of an authigenic core with a set of progressively younger epitaxial overgrowths.

Although measurements of the dimensions of fundamental particles provide compelling indirect support for an OR model, we do not think that OR applies to smectite illitization because of the large chemical and mineralogical changes associated with the reaction. Primmer (1994) recently made a similar conclusion. OR refers to the crystal coarsening of a single mineral, for example, pure calcite or dioctahedral mica (Baronnet 1982). Although OR can apply to chemically open systems, such as constant supply of Ca or CO₂ for calcite growth, OR is not normally used to describe

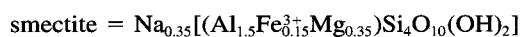
mineral transformation reactions. Smectite illitization involves significant chemical and mineralogical changes as well as crystal growth (Inoue et al. 1987), indicating that illitization is driven not only by minimization of interfacial free energy but also by minimization of chemical free energy.

Mineralogical Consequences of Reaction Mechanisms for Illitization

SST, DC and OR mechanisms define distinctive trends in the structure, composition and texture of I/S as illitization proceeds (Table 1). In Table 1 and this discussion, the SST mechanism assumes an interlayer-

by-interlayer transformation (Figures 2a and 4). The DC mechanism assumes that smectite or smectitic I/S dissolves and illitic I/S crystallizes and grows according to the reacting template model (Figures 2b and 6a). The OR mechanism assumes initial crystallization of illite grains, followed by dissolution of the smallest grains and reprecipitation onto existing larger illite grains (Figure 2c). All 3 mechanisms predict that the average thickness of fundamental particles should increase as illitization proceeds. Therefore, thickening of fundamental particles along the c^* -axis should not necessarily be interpreted as supporting any particular reaction mechanism.

The SST mechanism predicts that during illitization I/S undergoes gradual mineralogical and chemical changes that are proportional to the percentage of illite interlayers produced (Table 1). If there is only small progress in the degree of illitization (for example, from 65% to 66% illite interlayers in I/S), an SST mechanism cannot account for large mineralogical changes (such as from R0 to R1 ordering, from a $1M$ polytype to a $2M_1$ polytype, or from a *cis*-vacant structure to a *trans*-vacant structure). In contrast, a progressive transition from turbostratic stacking in smectite interlayers to $1M$ or $1M_0$ stacking in illite interlayers seems possible by SST. Other than thickening of fundamental particles, SST predicts no major change in the size and shape of I/S plates. Assuming that Ar does not diffuse from illite interlayers in the solid state, the SST mechanism predicts that all radiogenic Ar should be retained in I/S because the reaction site involves only smectite interlayers. Oxygen isotope analysis should be particularly useful in determining whether the SST mechanism involves framework cation exchange, reacting polyhedra or reacting interlayers (Figure 5). Assuming that oxygen isotopic exchange occurs only if dissolution and crystallization occurs, the framework cation exchange model predicts no isotopic exchange during illitization, and both the reacting polyhedra and reacting interlayer models predict progressive isotopic exchange during illitization. A reacting interlayer model predicts complete isotopic exchange for pure illite, whereas a reacting polyhedra model predicts only partial isotopic exchange for pure illite, depending on the percentage of polyhedra undergoing chemical reaction. Assuming the following hypothetical smectite composition and the illite composition from Środoń et al. (1992):



a reacting polyhedra model predicts 44% oxygen exchange for pure illite:

$$\begin{aligned} & [(0.35 \text{ oct. cations} \times 6 \text{ oxygens per oct. site} \\ & + 0.8 \text{ tetr. cations} \times 4 \text{ oxygens per tetr. site}) \\ & \div (12 \text{ total oxygens})] \times 100 \end{aligned} \quad [2]$$

K-fixation predicts mineralogical trends similar to a framework cation exchange SST mechanism, except that the framework cation composition should remain constant.

The DC mechanism predicts that I/S can undergo abrupt changes in chemical and isotopic composition, texture, interlayer ordering and polytype during illitization. A DC model allows for, but does not require, the lateral growth of plates and development of euhedral grain boundaries during illitization. As I/S crystals dissolve, Ar is lost, resetting the mineral's K/Ar clock. Neoformed crystals will undergo complete oxygen exchange compared with the precursor mineral.

According to the OR model, the chemical composition of growing illite crystals (overgrowth and illite template) remains constant; however, abrupt textural and structural changes can occur in the overgrowth. As the smallest illite grains recrystallize, there is partial loss of Ar and partial oxygen isotope exchange in the growing crystal.

Mechanisms of Illitization in Geologic Environments

Evaluation of reaction mechanism for smectite illitization in geologic environments is subject to considerable uncertainty despite accurate analyses of the mineralogy, chemistry and texture of I/S. For example, studies of smectite illitization in burial diagenetic or hydrothermal systems may implicitly assume that illitic I/S forms from a smectitic precursor; however, illite and I/S can form readily from a kaolinite precursor (Chermak and Rimstidt 1990; Huang 1992). Kaolinite illitization commonly occurs in sandstone (Rossel 1982) and may also occur in shale and bentonite, both of which usually contain kaolinite (Pevear et al. 1980; Awwiller 1993). During hydrothermal alteration of volcanic rocks (where reaction temperatures can be high and reaction times can be relatively short), illitic I/S may form directly from volcanic glass rather than through a series of I/S intermediates. Moreover, even if a smectitic precursor can be determined, observed mineralogical changes in I/S (such as plate morphology, isotopic composition and K/Ar age) could be caused by changes in the characteristics of the initial smectitic phase rather than by the illitization process. For example, changes in the detrital source area or in the conditions of smectite formation (such as water composition, precursor mineral, precursor volcanic glass composition or temperature) could affect the characteristics of the initial smectite. Therefore, it is important to consider factors other than smectite illitization to explain a set of mineralogical observations.

An SST mechanism seems to best describe illitization in most bentonites, a conclusion that was also made by Inoue et al. (1990). For example, the size (lateral dimensions) of I/S plates from a variety of bentonite samples shows little change over a wide range

Table 1. Predicted trends in mineralogical and geochemical data as illitization proceeds according to different mechanisms of illitization.

Mechanism†	Chemistry	Texture	Crystal structure	K/Ar
SST	<ul style="list-style-type: none"> ● Gradual chemical changes proportional to extent of illitization 	<ul style="list-style-type: none"> ● No major change in size and shape of plates ● Smectite interlayers may grade laterally into illite interlayers 	<ul style="list-style-type: none"> ● Gradual structural changes (interlayer ordering and polytype) 	<ul style="list-style-type: none"> ● Ar retained in illite interlayers
DC	<ul style="list-style-type: none"> ● Permits abrupt changes in chemistry 	<ul style="list-style-type: none"> ● Permits formation of euhedral crystals ● Smectite crystals can be physically separate from illite crystals 	<ul style="list-style-type: none"> ● Permits abrupt structural changes between parent and daughter crystals 	<ul style="list-style-type: none"> ● Complete Ar loss from any dissolving illite crystals
OR	<ul style="list-style-type: none"> ● ~Constant chemical composition for overgrowth and template 	<ul style="list-style-type: none"> ● Permits formation of euhedral crystals ● Crystal coarsening 	<ul style="list-style-type: none"> ● Permits abrupt structural changes between template and overgrowth 	<ul style="list-style-type: none"> ● Partial Ar loss (illite template crystals retain Ar)

† SST = solid-state transformation; DC = dissolution and crystallization; OR = Ostwald ripening.

‡ FCE = framework cation exchange model, RP = reacting polyhedra model, RI = reacting interlayer model.

of I:S ratios (Figure 7a). (Figures 7 and 8 plot the abundance of smectite in I/S determined by XRD, which underestimates the total amount of smectite structural sites in I/S; Środoń et al. 1992. The use of other more accurate measures of smectite content, such as fundamental particle thickness or fixed cation content, should not change the overall nature of the observed trends.) In contrast, Sucha et al. (1993) observed progressive growth of I/S plates in bentonite from the Neogene East Slovak basin (data not shown), which supports a DC mechanism. Although it is unclear why crystal growth apparently has occurred in bentonite from the East Slovak basin and not other basins, the relatively high geothermal gradient (~50 °C/km) of the East Slovak basin may enhance development of a DC mechanism. Bentonite I/S typically consists of anhedral flakes (see Figures 2a, 2b, 2f, 2h of Nadeau et al. 1985 and Figure 4 of Inoue et al. 1990), although laths are sometimes present (see Figure 2d of Nadeau et al. 1985). Additional support for an SST mechanism for illitization in bentonite is the gradual transition from R0 to R1 ordering (Figure 8a) and from turbostratic stacking in smectitic I/S to either *1M* or *1M₀* in illitic I/S (Reynolds 1993). McCarty and Reynolds (1995) found that octahedral occupancy (*cis* vs. *trans*) showed no correlation with degree of illitization. An SST mechanism is also supported by K/Ar ages of I/S from bentonite, which indicates that Ar is retained during burial metamorphism. Elliott et al. (1991) found that I/S in K-bentonites from the Denver basin becomes more illitic and radiogenically older with depth (Figure 9). This observation indicates that early formed illite interlayers are not subject to later Ar loss from dissolution and recrystallization. In addition, a thick, mineralogically zoned K-bentonite from Montana contains illitic R1-ordered I/S that is radiogenically older than smectitic R0 I/S (Altaner et

al. 1984), supporting the idea of Ar retention during development of R1 ordering.

Determination of the degree of oxygen isotope exchange may allow discrimination among the different SST models (framework cation exchange, reacting polyhedra and reacting interlayers). I/S in bentonites from Montana exhibits large changes in oxygen isotopic composition (+20 per mill for pure smectite to +12 per mill for illitic I/S, Eslinger and Yeh 1986), clearly indicating the SST mechanism does not involve only framework cation exchange. Such a large isotopic variation in I/S seems to support the SST model of reacting interlayers, which predicts greater isotopic exchange than the SST model of reacting polyhedra. Because illitization likely occurs over a range of temperatures and in contact with fluids of variable isotopic composition, it is difficult to completely prove either SST model based on data from natural systems.

A DC model best describes illitization in most hydrothermal and sandstone environments because of abrupt textural and structural changes in I/S as illitization proceeds. Euhedral crystals (Nadeau et al. 1985; Yau et al. 1987) that exhibit considerable crystal growth (Figure 7b) are commonly observed in these environments. I/S from a hydrothermal setting from Japan (Inoue et al. 1987, 1988) shows an abrupt change from R0 to R1 ordering (Figure 8b) as well as several other mineralogical modifications. During early stages of illitization, anhedral smectite flakes dissolve and crystallize as thin euhedral illite laths with a *1M* polytype and R1 ordering. The position of the octahedral vacancy changes from *cis*-sites to *trans*-sites (Drits et al. 1996). Thin laths subsequently grow into larger euhedral illite laths, which later dissolve and crystallize as small hexagonal plates with a *2M₁* polytype and *R* ≥ 3 ordering. The small plates subsequently grow into larger plates. Inoue and Kitagawa

Table 1. Extended.

Oxygen isotopes
<ul style="list-style-type: none"> • No isotope exchange—FCE model‡ gradual + partial exchange—RP model gradual + complete exchange—RI model
<ul style="list-style-type: none"> • Complete isotope exchange
<ul style="list-style-type: none"> • Partial isotope exchange (template crystals retain isotopic composition)

(1994) present compelling TEM evidence that crystal growth in hydrothermal I/S involves a spiral growth mechanism. As discussed above, we do not think that OR describes most crystal growth observed during illitization because of the large changes in mineralogy and chemistry; however, OR may appropriately describe the crystal growth observed for highly illitic I/S, where little chemical variation occurs (Inoue and Kitigawa 1994).

Illitization in shale appears to follow multiple mechanisms because euhedral laths and plates as well as anhedral flakes are observed (Pollastro 1985; Ahn and Peacor 1986a; Glasmann et al. 1989; Lanson and Champion 1991; Freed and Peacor 1992). I/S in shale typically exhibits a gradual transition from R0 to R1 ordering (Figure 8a), consistent with an SST mechanism. Interpretation of mineralogical data from shale clay size-fractions is complicated by the likelihood of detrital mica. Although Eberl (1993) concluded that a DC mechanism describes the formation of R1-ordered I/S from the Texas Gulf Coast, all I/S ages are older than the depositional age (Aronson and Hower 1976), which indicates the presence of a detrital component. Determination of mechanism of smectite illitization in shale is complex because of other possible origins for I/S, such as illitization of kaolinite (a reaction that can produce either euhedral or anhedral illite, Huang et al. 1993) or illitization of euhedral smectite laths and plates (Lindgreen and Hansen 1991).

We conclude that fluid/rock ratio and permeability influence which reaction mechanism of smectite illitization occurs in different geologic environments. Other investigators have reached a similar conclusion (Yau et al. 1987; Inoue et al. 1990). Because of its high clay content, bentonite typically has a low permeability, that is, a low fluid/rock ratio, which may inhibit large-scale dissolution and recrystallization. The higher permeability of hydrothermal and sandstone environments should favor a mechanism for illitization with a greater degree of dissolution and recrystallization.

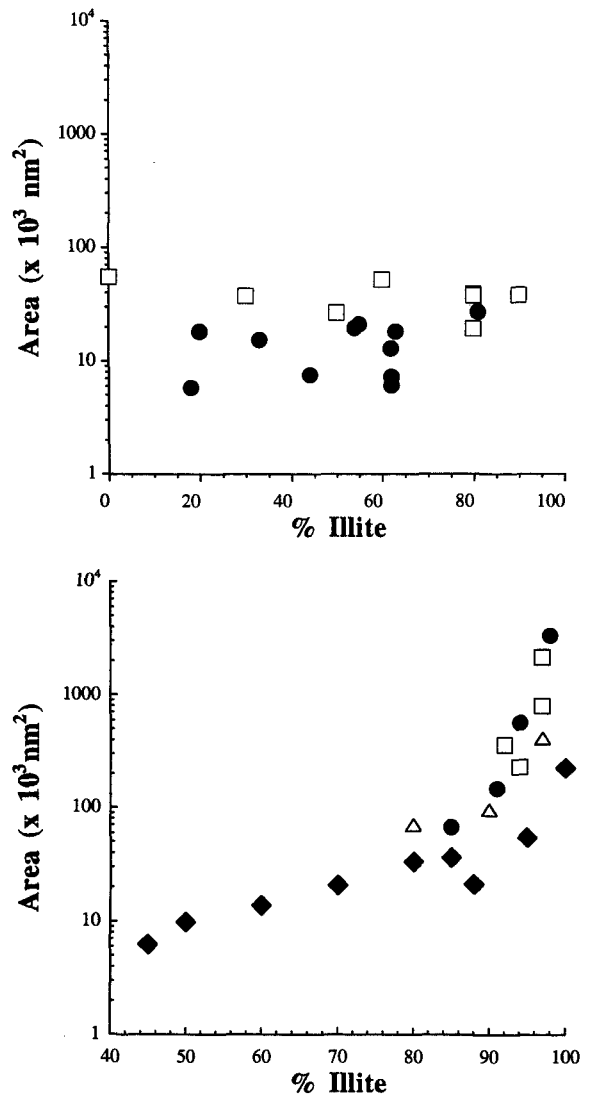


Figure 7. TEM-measured particle areas (*a-b* dimensions) vs. % illite interlayers in I/S (XRD-measured). a) (top) Bentonite data: closed circles are from Środoń et al. (1992) and open squares are from Nadeau (1985). b) (bottom) Hydrothermal and sandstone data: closed diamonds are from Inoue et al. (1988), closed circles are from Środoń et al. (1992), open triangles are from Nadeau (1985) and open squares are from Nadeau (1987).

illitization with a greater degree of dissolution and recrystallization.

CONCLUSIONS

1) Reaction mechanisms of smectite illitization need to be consistent with crystal structural models of I/S. We favor a structural model of I/S with polar 2:1 layers, although more data are needed on the layer charge of expandable sites in I/S.

2) Different reaction mechanisms of smectite illitization result in distinctive mineralogical consequences

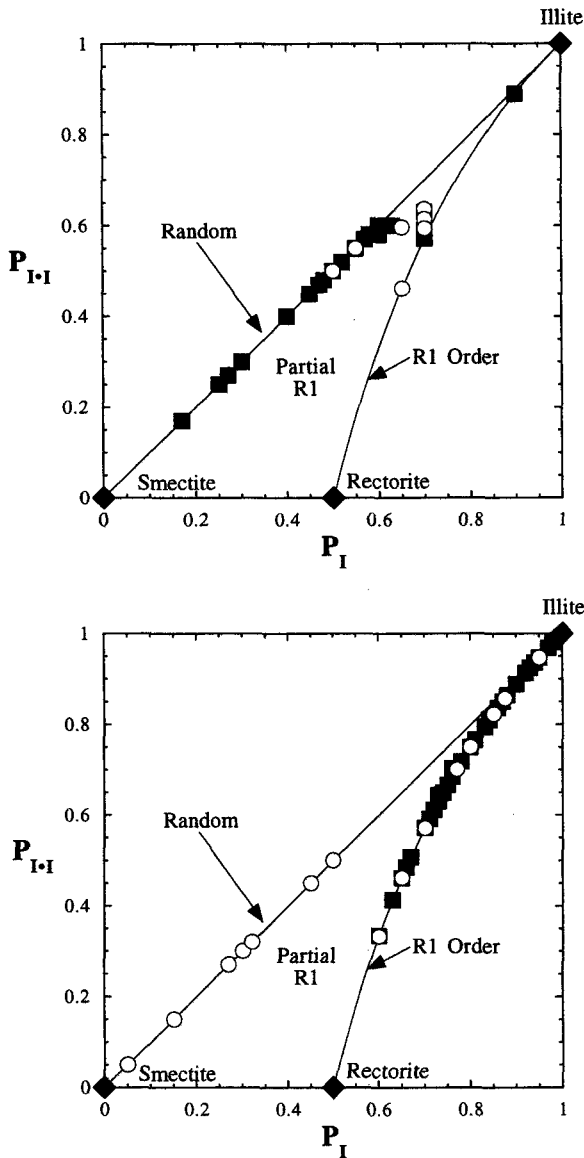


Figure 8. Junction probability diagram of I/S. P_{I-I} , which describes interlayer ordering, is the probability of an illite interlayer following an illite interlayer. P_I is the fraction of illite interlayers. a) (top) Shale and bentonite data: closed squares are shale data from Bethke et al. (1986) and open circles are bentonite data from Inoue et al. (1990). b) (bottom) Hydrothermal data: closed squares are from Bethke et al. (1986) and open circles are from Inoue et al. (1987).

for I/S. For example, an SST model of smectite illitization must involve gradual changes in the structure, chemical composition and texture of I/S, whereas DC models can permit abrupt mineralogical changes.

3) An SST model, perhaps involving local dissolution of a smectite interlayer and recrystallization to an illite interlayer, seems to describe illitization in most bentonite environments. A DC model describes illitization in hydrothermal and sandstone environments;

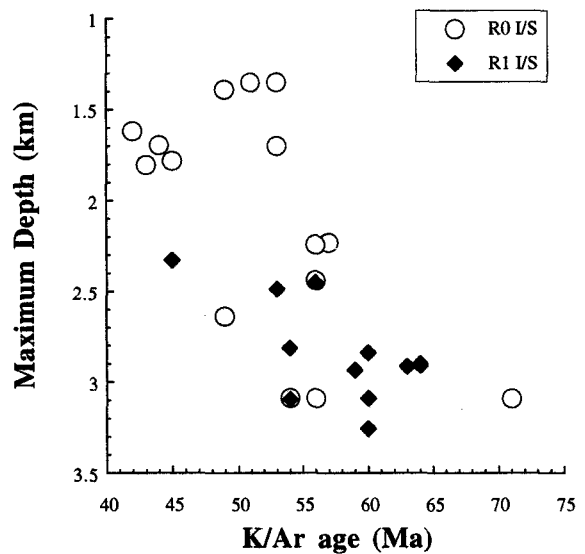


Figure 9. K/Ar age of I/S from K-bentonites of the Denver Basin vs. estimated burial depth (from Elliott et al. 1991). Estimated burial depths are current burial depth corrected for any uplift.

however, the relationship between the DC model and a structural model of I/S needs clarification. Illitization in shale may involve both the SST and DC models. The lower permeability of bentonite and shale may inhibit large-scale dissolution and recrystallization in those environments.

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