

ROLE OF WATER IN THE SMECTITE-TO-ILLITE REACTION

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Abstract—A series of hydrothermal experiments was performed to determine the effect of fluid abundance on the reaction of smectite to illite. Experiments were conducted on K-saturated montmorillonite (<0.1- μm fraction) in a closed system at 250° to 400°C using run times of 1, 7, 14, 30, and 60 days at 100 MPa (1 kbar) pressure. In fluid-deficient systems (pore spaces not saturated), the rate and extent of illitization was significantly inhibited. A rock : water ratio of 20:1 (mass : mass) produced an R0 illite/smectite (I/S) having 82% smectite layers after 60 days at 250°C, whereas a rock : water ratio of 1:1 produced an I/S having 57% smectite layers under the same conditions. The effect became less pronounced at higher temperatures, with the 20:1 and the 1:1 experimental products differing by only 11% expandability at 400°C after 60 days. In addition, the low-fluid experiments produced fewer crystalline byproducts (quartz, cristobalite, chlorite) than did the fluid-rich runs, and the I/S was more difficult to disperse and orient in the fluid-deficient samples, suggesting enhanced cementation at grain contacts or the production of particle morphologies that did not lend themselves to orientation. The difference in reactivity of the smectite and I/S as a function of water content appears to be attributable to the reduced capacity for low volumes of water to mediate the dissolution, solute transport, and precipitation reactions that make up the series of reactions collectively termed illitization. Of these variables, solute transport is likely to be affected most by reduction of fluid.

Key Words—Hydrothermal, Illite, Interstratification, Smectite, Water.

INTRODUCTION

The reaction of smectite to illite via an intermediate mixed-layer series (illitization) has been used as an empirical geothermometer or thermal maturity indicator in a wide range of geologic environments (e.g., Hoffman and Hower, 1979). Recent studies have demonstrated that the illitization reaction is more complex than previously thought and that several chemical and physical variables may affect the rate of reaction (Inoue *et al.*, 1988; Whitney and Northrop, 1988; Huang, 1987; Howard, 1987). Although a sixth-order kinetic expression effectively models the overall reaction, the reaction undoubtedly represents a series of poorly understood processes which together constitute the total reaction (Pytte and Reynolds, 1989).

The purpose of the present study was to assess the effect of rock : water ratio on the rate of illitization and thereby to investigate further the details of the overall illitization reaction. Rock : water ratios used in these experiments ranged from 1:1 to 20:1. These ratios, calculated on a mass : mass basis, represent fluid contents for saturated sediments having porosity values of about 70% to 10%, respectively, and correspond to compacting sediments within the burial and pressure regime in which illitization normally proceeds in sedimentary basins (Rieke and Chilingarian, 1974).

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

The hydrothermal experiments were conducted using standard cold-seal reaction vessels in horizontal

resistance furnaces equipped with proportional temperature controllers. Temperatures were maintained within $\pm 1^\circ\text{C}$ of the desired temperature. All runs were made at 100 MPa (1 kbar) pressure.

The starting material for all experiments was the <0.1- μm fraction of Wyoming bentonite (sample SWy-1 from the Source Clays Repository of The Clay Minerals Society). This material was determined to be pure smectite and was saturated with potassium prior to hydrothermal treatment by repeated washing with 1 N KCl, followed by washing in distilled water until the supernatant was chloride free. Prior to loading, the clay was dried at 150°C, and adsorbed water was determined thermogravimetrically to be <1% by weight. The chemical analysis and structural formula for the K-saturated starting smectite (without the special drying step) are in Table 1.

Each sample was prepared by placing the smectite into a gold capsule (5-mm o.d., 4-mm i.d., 30-mm length) containing a known mass of distilled water. Solid and water were combined in ratios of 60 mg/60 mg, 60 mg/12 mg, 80 mg/8 mg, and 100 mg/5 mg to produce the desired rock : water ratios of 1:1, 5:1, 10:1, and 20:1, respectively. The gold capsules were welded shut and weighed before and after hydrothermal treatment to detect leakage during the run. Samples that leaked were discarded. The gold capsules were also flattened after welding to eliminate free space within the experimental volume. Although no detailed analysis was made of precision and reproducibility, several duplicate runs suggest that the experimental techniques

Table 1. Chemical analysis (by X-ray fluorescence spectrometry) and structural formula for K-saturated smectite starting material (<0.1- μm fraction of SWy-1).

SiO ₂	60.1
Al ₂ O ₃	21.3
Fe ₂ O ₃ ¹	4.41
MgO	2.75
CaO	0.05
Na ₂ O	0.15
K ₂ O	3.66
TiO ₂	0.08
LOI ²	7.53
Total	100.03

¹ Total iron as Fe₂O₃.

² Without special drying precautions. Includes both structural and adsorbed water.

Structural formula:



permit a reproducibility estimated to be about $\pm 10\%$ expandability at short run times and about $\pm 5\%$ expandability at longer run times.

After hydrothermal treatment, each capsule was cut open, and the sample was removed and dispersed in a small volume of water. It was then placed on a glass slide to produce an oriented mount for X-ray powder diffraction (XRD) analysis. Each sample was examined by XRD after air-drying and again after saturation with ethylene glycol (60°C overnight in an ethylene glycol atmosphere). The proportions of illite and smectite layer types in the resulting interstratified illite/smectite (I/S) were determined by comparison with calculated XRD patterns using the computer program NEWMOD (available from R. C. Reynolds, Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755), which uses the algorithm described by Reynolds (1980). Expandabilities reported are MacEwan crystallite expandabilities, with no corrections for short stacks or disarticulated particles (Eberl and Środoń, 1988).

RESULTS

The expandabilities (proportion of smectite layers) of I/S produced during experiments using different temperature, time, and rock : water ratios are listed in Table 2. Important reaction trends include the following:

1. The development of illite layers in I/S proceeded rapidly at first and leveled off with increasing run time (Figure 1). This reaction trend is consistent with the trends outlined by Whitney and Northrop (1988).
2. For each rock : water ratio, the extent of illitization for each run time increased almost linearly with increasing temperature (Figure 2).
3. The rock : water ratio had a greater effect at lower temperatures than at higher temperatures. The differ-

Table 2. Percentage of smectite layers in interstratified illite/smectite run products for different temperatures and rock : water (R:W) ratios.

T (°C)	1 day	3 days	7 days	14 days	30 days	60 days
R:W = 1:1						
250	88	79	77	71	66	57
300	76	64	52	51	48	38
350	54	43	39	35	32	29
400	39	38	32	27	22	18
R:W = 5:1						
250	85	85	78	69	62	58
300	68	62	49	44	41	41
350	50	43	33	29	28	27
400	33	33	30	29	24	18
R:W = 10:1						
250	85	83	78	78	72	62
300	81	65	52	44	41	41
350	54	55	45	36	34	33
400	39	36	30	30	26	23
R:W = 20:1						
250	95	93	92	89	83	82
300	84	82	72	70	65	65
350	71	64	54	52	48	42
400	49	49	35	33	30	29

ence in final expandability between the 1:1 experiments and the 20:1 experiments was much larger at 250°C (Figure 3a) than at 400°C (Figure 3b). For samples having rock : water ratios of 1:1, 5:1, and 10:1, measured expandabilities for the 300°C to 400°C runs were nearly indistinguishable within the precision of the experimental and analytical techniques, whereas the experiments using a 20:1 ratio produced measurably and systematically greater expandabilities (Figure 4).

In summary, the illitization reaction was significantly inhibited if the water content was reduced to a 20:1 rock : water ratio; this effect was more pronounced at lower temperature than at higher temperature. This relationship is summarized in Figure 5.

Because the samples having a rock : water ratio of 20:1 still exhibited substantial reaction, samples were prepared that contained no added water. Thus, the total water content of these samples was less than 1% by weight. After 3 days at 400°C and 100 MPa (1 kbar), increased low-angle scattering on the XRD pattern indicated that a reaction had occurred and that it was significantly different from similar samples heated for 3 days at 400°C at 1 atmosphere pressure (open air).

In addition to the difference in the rate and extent of illitization, two other characteristics of the run products were found to differ, depending on rock : water ratio. First, the fluid-deficient samples produced opal-CT as the only crystalline byproduct (Figure 6), even though the I/S was significantly illitized. The fluid-rich samples at the same temperature produced significant quantities of chlorite, cristobalite, and/or quartz as

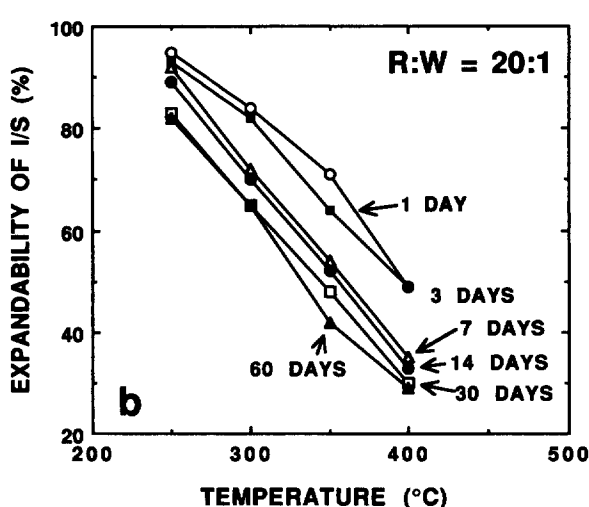
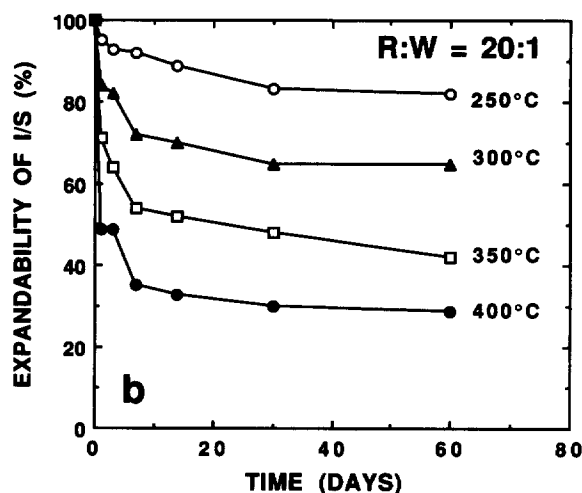
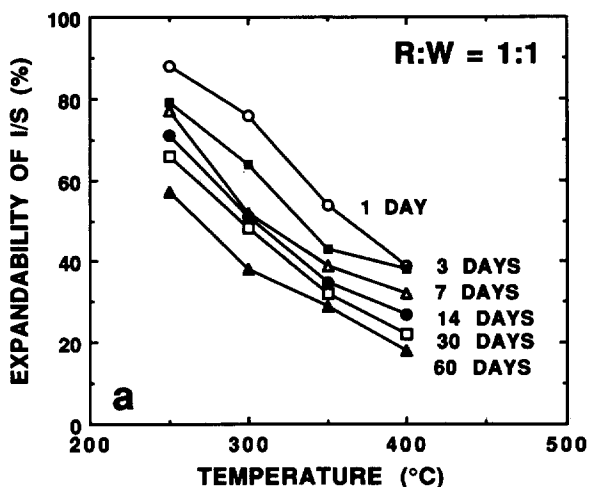
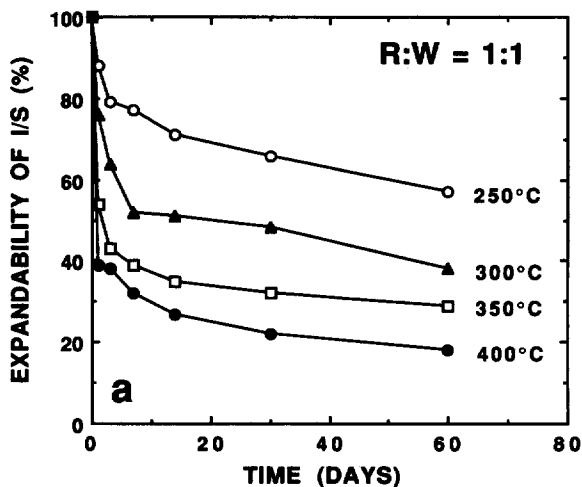


Figure 1. Reaction trends for illitization at rock : water ratios of 1:1 (A) and 20:1 (B).

Figure 2. Proportion of smectite layers in interstratified illite/smectite as a function of temperature for each run time for rock : water ratios of 1:1 (A) and 20:1 (B).

crystalline byproducts of the illitization reaction (Figure 6). Second, the absolute intensities of the basal I/S reflections on the XRD patterns were smaller for the fluid-deficient samples than for the fluid-rich samples. The presence of a strong hk band at $19.9^\circ 2\theta$ in the fluid-deficient samples suggests that the fluid-deficient material did not disperse and orient on the glass slides as well as the fluid-rich samples. Even ultrasonic disaggregation techniques did not produce well-oriented XRD mounts from runs having a rock : water ratio of 20:1.

DISCUSSION AND CONCLUSIONS

The nature of the illitization reaction

Our knowledge of the details of the illitization reaction remains incomplete, but a more comprehensive

picture of the reaction is emerging. Based on a literature review of chemical, isotopic, and textural data, the major steps in the reaction from smectite to illite are as follows (Figure 7). First, the original smectite becomes unstable in the regime of increased temperature, and smectite layers begin to react. Evidence exists that some layers are transformed into high-charge smectite layers during this stage, producing random (Reichweite = 0, or R0) I/S (Howard and Roy, 1985; Inoue *et al.*, 1988; Whitney and Northrop, 1988). This random I/S exhibits incomplete chemical and isotopic resetting. Random I/S may also be produced at this stage by mechanical rearrangement of layers, facilitated by wetting and drying in an open system, which fixes K between the high-charge smectite layers (Eberl *et al.*, 1986). Second, illite layers begin to crystallize from the byproducts of the smectite dissolution. This neoformed

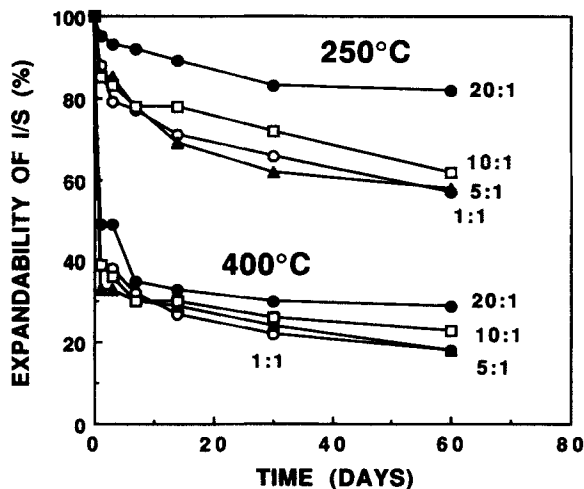


Figure 3. Illitization reaction trends for different rock : water ratios at 250°C (upper curves) and 400°C (lower curves).

illite is chemically, morphologically, and isotopically distinct from the original smectite and from the random I/S (Pollastro, 1985; Inoue *et al.*, 1987; Whitney and Northrop, 1988; Nadeau and Bain, 1986; Lee *et al.*, 1985). At about 50% expandability, the original smectite layers have largely disappeared, and the thin illite layers constitute R1 I/S by virtue of their uniform thickness; they may exhibit interparticle diffraction effects when prepared for XRD analysis (Nadeau *et al.*, 1984a, 1984b, 1984c). These thin illite particles begin to undergo the process of Ostwald ripening, whereby the very thin illite layers are gradually replaced by thicker lath-like and then more plate-like particles (Eberl and Šrodoň, 1988; Inoue *et al.*, 1988). The particles grow and coalesce with increasing temperature and time (Eberl and Šrodoň, 1988). The final stages of the Ostwald ripening of illite involves an evolution from $1M_d$ to $1M$ to the $2M$ polytype (Inoue *et al.*, 1988). Quartz and, locally, kaolinite and/or chlorite, may precipitate as a by-product of this reaction, depending upon the original composition of the smectite and the flux of materials into and out of the system. The details of the reaction may vary somewhat from one geologic situation to another, but this sequence is a general summary of the overall reaction.

The nature of water in the experimental system

To understand the role of fluid abundance in these reactions, it is instructive to examine the physical state of the water in the experimental capsules. At 25°C and one atmosphere pressure, molecular water in smectite-water systems is closely associated with the exchangeable interlayer cations and the clay surface (Sposito, 1984). At very low water content, the first monolayer of adsorbed water is bound strongly to surface oxygen

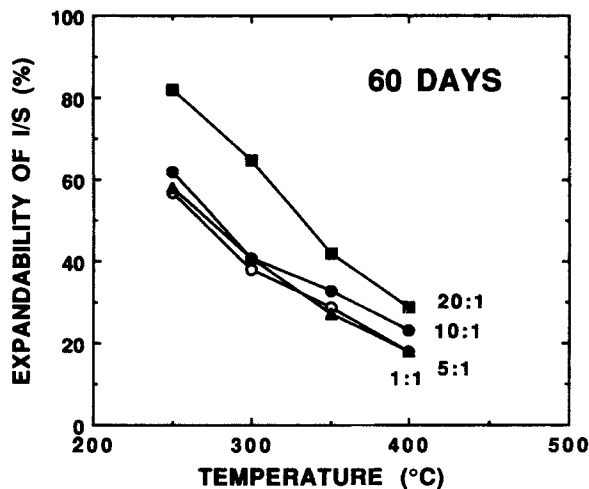


Figure 4. Final expandabilities (after 60 days) for each rock : water ratio as a function of temperature.

atoms and entrained immediately above the ditrigonal cavities in the 2:1 layer (Sposito and Prost, 1982). In fact, the structural differences between the interlayer water and bulk liquid water persist, regardless of how much water is in the system (Sposito, 1984). Interlayer water exhibits strong Brønsted acidity, and the acidity of solvated interlayer cations increases as the total water content decreases (Sposito, 1984, p. 72). Thus, even at a very low water content, the surface or interlayer reactivity of the smectite is significant.

The clay-water mixtures in the present experiments were subjected to mechanical compaction within the gold capsules. Experimentally, mechanical compaction of saturated smectite having a particle size of $<0.1\text{-}\mu\text{m}$ equivalent spherical diameter, under a pressure of 100 MPa (1 kbar), results in a maximum porosity of about 30% and, perhaps, much less, depending upon the rearrangement and deformation of clay particles in the capsule (Rieke and Chilingarian, 1974, p. 8). The result of this mechanical compaction is that the samples having a rock : water ratio of 1:1 were the only samples that contained sufficient water to saturate the pores in the compressed aggregate. In other words, pressure was hydrostatic in the 1:1 experiments. For all other rock : water ratios, the samples experienced some degree of fluid undersaturation. The degree of pore saturation depends on the specific interlayer cation (Sposito and Prost, 1982). Using the data of Prost (1975) and assuming that K has hydration properties intermediate between Cs and Na, the 20:1 samples would have had about 10% of their interlamellar surfaces hydrated, the 10:1 samples would have had about 25% of their interlamellar surfaces hydrated, the 5:1 samples would have had about 50% of their surfaces hydrated, and the 1:1 samples would have been completely hydrated. Again, only the samples having a rock :

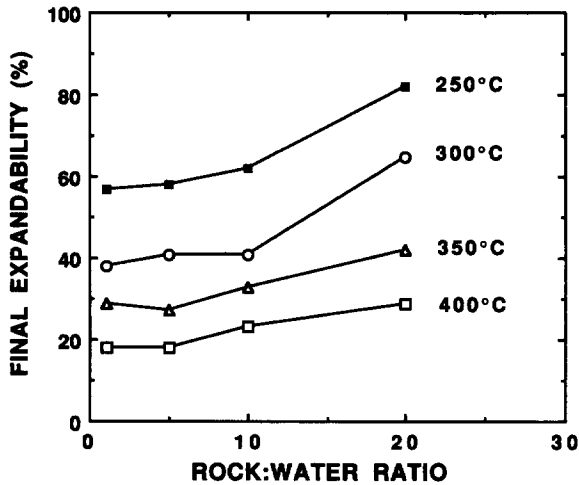


Figure 5. Final expandability (percentage of smectite layers in illite/smectite after 60 days) as a function of rock : water ratio for each temperature.

water ratio of 1:1 would have contained free molecular pore water at 25°C.

The nature of water in the smectite-water system does not change significantly at higher temperatures. In a series of high-temperature, high-pressure DTA experiments, Koster van Groos and Guggenheim (1984, 1986, 1987) demonstrated that molecular water remains bound to the clay (adsorbed on interlayer surfaces or bound to interlayer cations) at temperatures as high as 485°C at 100 MPa (1 kbar) in a system having a rock : water ratio of 10:1. In their 1986 experiments, they used the K-saturated, <0.1- μm fraction of smectite sample SWy-1, which is precisely the same material used in the present experiments. Their data show a similar range of dehydration temperatures for other rock : water ratios at high pressure, even above the critical point of water. Thus, the water in the 5:1, 10:1, and 20:1 experiments was closely bound to the clay surfaces and interlayer cations and did not exist primarily as free molecular water in open pore spaces. An examination of the liquid-vapor curve of water at high temperatures and pressures (Koster van Groos and Guggenheim, 1984) shows that water in excess of the adsorption capacity of the clay surfaces and interlayer cations should be present as liquid in the temperature range of the present experiments and at a pressure of 100 MPa (1 kbar). Therefore, it is the solvent behavior of this adsorbed water, interlayer water, and pore water that must be examined to understand the observed change in illitization reaction rates for experiments having different water contents.

Effect of reduced water content on the processes of illitization

All stages of the illitization reaction were retarded by low water content. Even though the early reaction

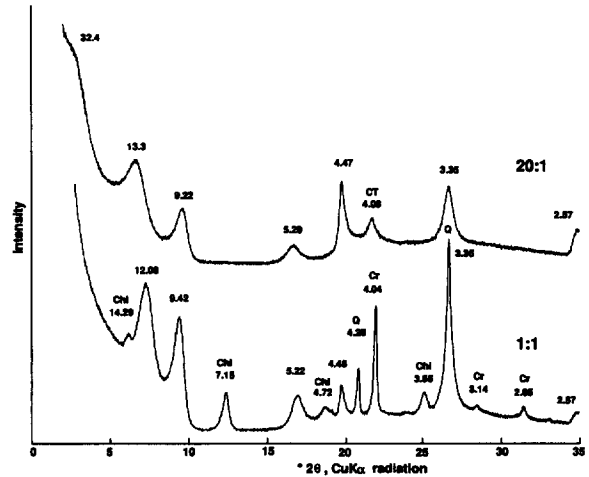


Figure 6. X-ray powder diffraction patterns of the run products of samples treated hydrothermally at 400°C for 60 days with rock : water ratios of 1:1 (lower pattern) and 20:1 (upper pattern). Labeled peaks are for chlorite (Chl), cristobalite (Cr), quartz (Q), and opal-CT (CT). d-values are labeled in Å, using CuK α radiation. Peaks not specifically identified are interstratified illite/smectite peaks.

of smectite to randomly interstratified I/S is thought to involve less profound structural rearrangement than the later stage in which ordered I/S is produced, the reaction was nevertheless slowed by low water content. The later, ordered stage of illitization, which is widely believed to involve dissolution and precipitation, was likewise effectively slowed by reduction of water content. Therefore, both stages of the illitization reaction must be fluid mediated: the reduction of fluid slowed one or more processes involved in the reaction.

Like other fluid-mediated reactions, illitization probably involves three fundamental processes: dissolution, solute mass transfer, and precipitation or crystallization (which may include the processes of nucleation, crystal growth, Ostwald ripening, and crystal coalescence) (Eberl and Środoń, 1988; Baronnet, 1982). In a fluid-dominated system, dissolution of the primary smectite is unlikely to be the rate-limiting step in the illitization reaction, although the dissolution of smectite is currently a poorly understood process (May *et al.*, 1986). The very fine grain size of the starting smectites (<0.1- μm equivalent spherical diameter) and the sheet-like morphology of the grains significantly increase the rate of dissolution of the minerals relative to large, compact particles of the same composition (Mullin, 1972). This accelerated dissolution is enhanced further by extensive cationic substitution within the smectite (May *et al.*, 1986). As the total amount of water in the clay-water system decreased, however, dissolution may have had a somewhat different character. At a rock : water ratio of 20:1, the water which existed chiefly as adsorbed or interlamellar water was

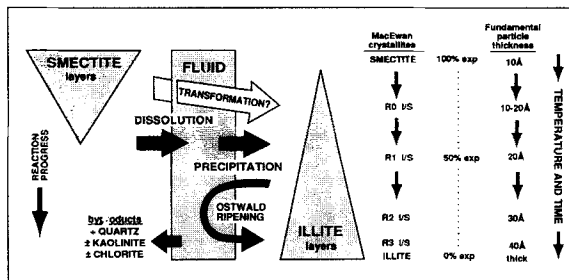


Figure 7. Schematic summary of the illitization reaction. Decreasing smectite and increasing illite layers as a function of temperature and time are represented as both MacEwan crystallites ordering type or fundamental particle thickness at the right side of the figure. Fluid-mediated transformation and dissolution/precipitation reactions are represented at the left.

the sole medium of dissolution. How effective is adsorbed water as a solvent? According to Sposito (1984), the interlayer water in smectite is structurally different from bulk liquid water, regardless of the overall amount of water in a clay-water mixture. Therefore, the enhanced complex formation and Brønsted acidity which marks adsorbed water in fluid-dominated systems (Mortland and Raman, 1968) also characterizes the adsorbed water in a fluid-deficient system. Therefore, the surface reaction portion of dissolution of primary smectite layers should not decrease with decreasing water content; in fact, it might increase slightly.

Conversely, another of the processes of illitization that may be sensitive to fluid content is the process of nucleation and/or crystallization. The nucleation of illite on existing smectite layers must be considerable, because the lateral dimensions of the sheet structures for the two phases are almost identical. Such epitaxial growth reflects a free energy barrier for nucleation near zero (Mullin, 1972). In a fluid-deficient smectite-water system, as the primary smectite dissolves and the more stable illite begins to form, the site for nucleation of the illite layers must be on the surface or in the interlamellar space of the smectite. Because no free pore water was present, except in the 1:1 samples, no alternate nucleation site existed. Thus, the high-resolution transmission electron microscope observations of Ahn and Peacor (1986) that illite begins to form within smectite masses rather than at the boundaries suggest the nucleation of illite at or near the site of smectite dissolution within the primary smectite mass. This mode of illite layer formation should be the norm in smectitic shales, which are deficient in fluid either because of compression or displacement by other fluids (oil, natural gas, or air). Crystal growth mechanisms for illite may change as a function of fluid abundance, but the exact crystal growth mechanisms are not well understood and are still under study (Sunagawa *et al.*, 1975; Eberl and Środoń, 1988).

Although the epitaxial precipitation of illite was facilitated by surface reaction on smectite, the nucleation and crystal growth of other secondary phases, such as quartz and cristobalite, may have been retarded by such a structured environment. These minerals precipitated in the present experiments only if free bulk pore water was in the system. In the low-water systems, the components of these minerals probably formed noncrystalline products that may have precipitated preferentially at grain contacts.

Perhaps the process most sensitive to low fluid content during illitization is the transport of dissolved solute from dissolution sites to crystallization sites. The experimental system employed here corresponds to crystal growth processes within very small capillary spaces, because there was probably no convective flow within the porous clay mass in the capsules (Simon, 1978). Furthermore, because bulk liquid water was absent from most of the experimental runs, transport of dissolved components must have occurred chiefly by surface diffusion and by interlamellar diffusion. In general, the diffusion coefficient for solute transport in a porous medium may be described by the following expression:

$$D = D_1 \theta_1 f_1 \frac{\partial C_1}{\partial C} + D_s \theta_s f_s \frac{\partial C_s}{\partial C}, \quad (1)$$

(Wild, 1981), where D is the total diffusion coefficient for the porous medium, which consists of both bulk liquid (l) and surface solute (s) components. D_1 and D_s are diffusion coefficients for the bulk solute and surface solute, θ_1 and θ_s are the volumetric fractions of total fluid, f_1 and f_s are tortuosity factors, and $\partial C_1/\partial C$ and $\partial C_s/\partial C$ are the fraction of a solute existing in bulk pore fluid and the fraction associated with the solid surfaces. Although the total diffusion is the sum of the diffusion through the bulk pore fluid plus surface diffusion, the surface diffusion portion of the sum has often been ignored in saturated media, because surface diffusion is so much slower than diffusion in bulk fluid (Wild, 1981). In the present experiments, however, only the 1:1 runs contained pores saturated with bulk liquid water. All other experiments contained lesser amounts of water, requiring solute transport to proceed mainly via surface diffusion. Therefore, the domination of transport by surface diffusion in the low-water experiments explains why the reaction was slowed. Also, as the amount of water decreases, the tortuosity of the solute path increases, thus decreasing the rate of diffusion. Simultaneously, the importance of surface diffusion relative to bulk-fluid diffusion should increase in importance until, at rock: water ratios of 10:1 and 20:1, only surface diffusion is possible. Under these conditions, the bulk water portion of the sum becomes zero, and both θ_s and $\partial C_s/\partial C$ become unity, thereby

reducing the diffusion expression to:

$$D = D_s f_s \quad (2)$$

Thus, under conditions of very low water content, the overall rate of diffusion of solutes depends only on the diffusion coefficient of the solute through the surface layer and the tortuosity of that surface layer. In addition, the diffusion of solutes through the interlamellar space of smectite must be significantly slower than diffusion through bulk liquid water or on colloid surfaces because of the highly structured nature of the water in the interlamellar space, especially at low water contents (Sposito and Prost, 1982). Thus, although dissolution and precipitation processes may be affected by water content, solute transport is probably the rate-limiting step during illitization in low-water systems.

Application to natural systems

The results of these experiments suggest that illitization may be affected by reduction of water content to values below that required to saturate pore spaces. A hypothetical natural setting in which this effect might be observed is the intrusion of a smectitic host rock by an igneous dike. If the host rock is dry, little illitization should occur. If the intrusion takes place in the presence of water, however, the thermal energy of the dike should produce significant illitization in the adjacent smectitic rock.

The application of these experimental results to natural media may not be limited to unsaturated porous rocks, however, because some pores may be filled with non-aqueous fluids, such as petroleum or natural gas, which do not participate in the clay dissolution-transport-crystallization process. According to Levorsen (1967) a mixture of water and oil in pore spaces produces a film of water on mineral grains which isolates the petroleum from the mineral grains. Thus, the effect on diffusion length and tortuosity for aqueous ionic species through the surface film of water in such an environment would be the same as for unsaturated media. Therefore, rocks containing liquid petroleum, natural gas, or some other immiscible fluid in the pore spaces with water (Levorsen, 1967) may experience retardation of the illitization reaction even though the pores are filled with fluid. Porous sediments partly saturated with petroleum or natural gas may provide a good case study to test this hypothesis.

At high pressures, dissolution of minerals is accelerated at grain contacts (Berner, 1971). In addition, nucleation and crystal growth proceed preferentially where grains are in contact (Sunagawa *et al.*, 1975). Furthermore, in environments lacking fluid-saturated pores, reaction, transport, and cementation proceed preferentially in the pore throats, creating what has been termed meniscus cement (Dunham, 1971). This preferential reaction at grain contacts was inferred in the present study. The tendency for the I/S to be poorly

oriented and difficult to disaggregate suggests that cementation reactions proceeded at edge-to-face grain contacts, because that is where the water was located. Thus, the induration of mudrocks by cementation at pore throats and at grain contacts may be accelerated in systems in which the pores are not saturated with water, but rather by air, natural gas, or petroleum. This cementation, accompanied by the recrystallization of the I/S, may contribute to the development of pressure seals and capillary seals in shales (Magara, 1978), processes that proceed simultaneously with illitization of the shale. Interlayer water in smectite is not easily lost during diagenesis (Colten-Bradley, 1987). The timing of illitization and lithification of the shale relative to the loss of interlayer water and the movement of pore fluids during compaction and petroleum generation may partly determine the rate of illitization because of changes in the rock: water ratio.

In summary, the rate and extent of illitization is affected by the abundance of water in the system. Reducing the water content retards illitization, especially if the water content is less than the amount required to saturate pores. Natural environments in which this phenomenon may be important include unsaturated sediments or sediments in which pore spaces are filled with gas or petroleum.

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