

COMPARISON OF RATES OF SMECTITE ILLITIZATION WITH RATES OF K-FELDSPAR DISSOLUTION

Key Words—Dissolution, Illite, Illitization, K-feldspar, Mixed layer, Smectite.

Crystal growth may be limited by transport of ions to a crystal surface, surface reactions (e.g., ion exchange, crystal diffusion, and dehydration), heat supplied to the crystal, or removal of products of the reaction from the crystal (Berner, 1980; Fisher and Lasaga, 1981). Which factors dominate is often difficult to determine because crystal growth may be influenced by several or all of these processes simultaneously. Metamorphic petrologists have outlined methods to determine which process controls crystal growth (Fisher, 1977, 1978). The present paper proposes a calculation scheme that compares rates of two reactions that occur during the transformation of smectite to illite.

BACKGROUND

Many workers have observed that smectite-rich clay minerals react towards illite through intermediate mixed-layer illite/smectite (I/S) in shales that are deeply buried in sedimentary basins (e.g., Weaver and Beck, 1971; Hower *et al.*, 1976; Boles and Franks, 1979). The percentage of illite layers in I/S, herein termed I/S layer composition, increases with burial depth, and stacking order in I/S changes from random to ordered with increasing burial depth. This mineralogical reaction is herein termed smectite illitization.

Above 50°–80°C, rates of smectite illitization in shales increase from near zero to a maximum of ~20% illite layers per 10°C (Perry and Hower, 1970; Boles and Franks, 1979), although illitization has been reported at lower temperatures (Jones and Weir, 1983; Środoń and Eberl, 1984). At more than 60–70% illite layers, the reaction rate usually decreases to <2% illite layers per 10°C (Hower *et al.*, 1976). Data from wells drilled into rocks of widely varying geologic age indicate that increased reaction time enhances illite formation (McCubbin and Patton, 1981; Środoń and Eberl, 1984). In addition, K-rich solutions appear to increase rates of smectite illitization (Boles and Franks, 1979; Howard, 1981; Altaner *et al.*, 1984).

Chemical changes associated with smectite illitization are: (1) K fixation in illite interlayers; (2) an increase in net negative layer charge on the silicate structure (produced chiefly by Al-for-Si substitution); and (3) expulsion of exchangeable cations and water from smectite interlayers. Because K-feldspar decreases in abundance or disappears in rocks that undergo smectite illitization, most workers believe that K-feldspar dissolution within the shale provides a major source of

K during the process (Weaver and Wampler, 1970; Perry, 1974; Hower *et al.*, 1976; Boles and Franks, 1979). The results of the present study show that at temperatures relevant to these reactions, smectite illitization proceeds much more slowly than K-feldspar dissolution.

RATES OF K-FELDSPAR DISSOLUTION

The dissolution rate of feldspar is directly proportional to its exposed surface area (Lagache, 1965; Lin and Clemency, 1981) and pore water pH, at less than a critical and relatively acidic value [$\text{pH} \leq 10.6 - (2300 \div T)$, where T is temperature in kelvins; Helgeson *et al.*, 1984]. Because the water in shales is generally basic ($\text{pH} > 8$; Weaver and Beck, 1971), pore water pH is not included in this kinetic expression for feldspar dissolution. This present paper considers rates of dissolution of feldspar having a single value of surface area; hence, at a particular temperature, the K in the pore water varies directly with time.

Figure 1 presents plots of K concentration in pore water as a function of time for the dissolution of adularia having a surface area of 800 cm²/g at 100° and 200°C, and P_{CO_2} of 6 and 0 bars, respectively (using data from Lagache, 1965). No data are available for 100°C and $P_{\text{CO}_2} = 0$ bars, but the rate constant at these conditions may be calculated using Lagache's rate constants and the Arrhenius equation:

$$E_a = -\frac{\Delta \ln k_d}{\Delta 1/T} \cdot R, \quad (1)$$

where E_a = activation energy, k_d = rate constant for feldspar dissolution, and R = gas constant.

The dissolution reaction has an activation energy of 7.95 kcal/mole (calculated using data at 100° and 200°C and $P_{\text{CO}_2} = 6$ bars). Assuming that the activation energy for dissolution at $P_{\text{CO}_2} = 0$ bars is the same as that at $P_{\text{CO}_2} = 6$ bars, values of 36, 20, and 7 ppm K/yr (corresponding to dissolution rates at 100°, 80°, and 50°C and $P_{\text{CO}_2} = 0$ bars) are predicted using this approach.

RATES OF SMECTITE ILLITIZATION

A kinetic expression for smectite illitization presented in terms of decreasing amount of smectite layers in I/S is:

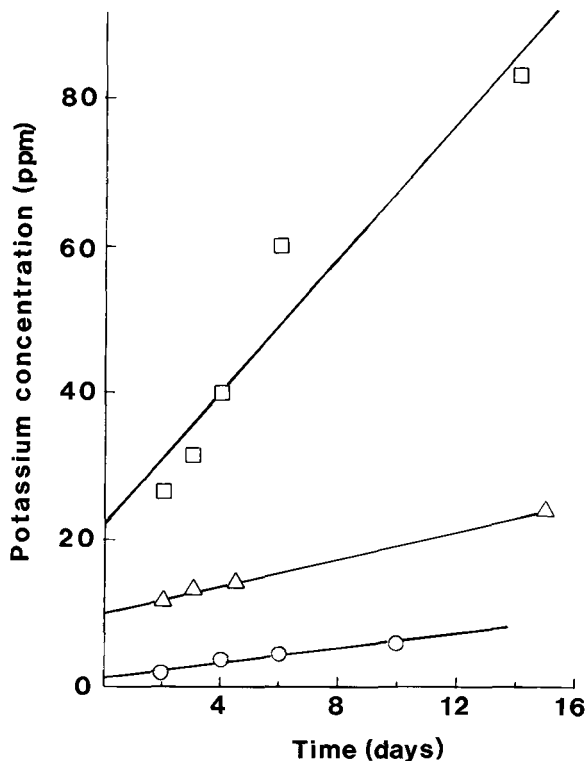


Figure 1. K concentration as a function of time. Data are from adularia (specific area = 800 cm²/g) dissolution experiments of Lagache (1965). Circles represent measurements at 100°C and P_{CO₂} = 6 bars; triangles represent measurements at 200°C and P_{CO₂} = 0 bars; squares represent measurements at 200°C and P_{CO₂} = 6 bars.

$$\frac{\partial c^{sm}}{\partial t} = -k_i(c^{sm})^\alpha (c^K/c^{Na})^\beta, \quad (2)$$

(Pytte, 1982), where c^{sm} = fraction of smectite layers in I/S, c^K/c^{Na} = ratio of K to Na concentrations in pore water, α and β are constants which when added together equal the order of the reaction, and k_i = illitization rate constant. Rate constant $k_i = Ae^{-E_a/RT}$, where A = frequency factor. McCubbin and Patton (1981) presented a similar kinetic expression without the c^K/c^{Na} term.

Table 1. Rate constants for the dissolution of adularia.¹

Temperature (°C)	Rate constant at (ppm K/yr)	
	P _{CO₂} = 6 bars	P _{CO₂} = 0 bars
50	36 ³	6.8 ³
80	105 ³	20 ³
100	189 ²	36 ³
200	1830 ²	347 ²

¹ Determined for adularia with a specific area of 800 cm²/g.

² Measured by Lagache (1965).

³ Calculated, this study.

Table 2. Kinetic parameters for smectite illitization used in this study.

Reaction order	Activation energy (kcal/mole)	Frequency factor (sec ⁻¹)	Source
First	22.5	1.0	McCubbin and Patton (1981)
Fourth	27	2.3 × 10 ⁴	Pytte (1982)
Fifth	30	1.0 × 10 ⁶	Pytte (1982)
Sixth	33	5.2 × 10 ⁷	Pytte (1982)

Table 2 lists kinetic parameters for smectite illitization that were used in the present study. To compare rates of feldspar dissolution with rates of smectite illitization, Eq. (2) must be rewritten in terms of K uptake in I/S rather than in terms of decreasing smectite content, and must be expressed in terms of loss of K from pore water instead of gain of K in I/S.

The proportion of smectite layers in I/S and the K₂O content of a rock are related by the K₂O content of pure illite and the amount of I/S in the rock. Assuming that the K₂O content of pure illite is 9.07 wt. % (similar to the Silver Hill illite from Hower and Mowatt, 1966) and that the rock consists of 50% total I/S clay minerals, the following relations result:

$$c^{sm} = 1 - \frac{c^{K_2O}}{4.53\% K_2O} \quad (3)$$

and

$$\delta c^{sm} = - \frac{\delta c^{K_2O}}{4.53\% K_2O}, \quad (4)$$

where c^{K_2O} = wt. % K₂O in the rock.

To equate changes in K₂O of the rock to changes in K of the pore water, differences in density, volume, and concentration units (wt. % K₂O vs. ppm K) between rock and pore water must be included. The following relation holds,

$$\delta c^K = -Z\delta c^{K_2O}, \quad (5)$$

where

Table 3. Rates of K loss from pore water (ppm K/yr) caused by illitization of smectite at different temperatures.¹

Temperature (°C)	Sixth order	Fifth order	Fourth order	First order
50	2.3 × 10 ⁻³	4.7 × 10 ⁻³	1.2 × 10 ⁻²	1.7 × 10 ⁻²
80	0.11	0.20	0.41	0.26
100	0.52	0.95	2.1	1.1
200	3.3	15	85	112

¹ See text for other values assumed. Four sets of kinetic parameters were used.

$$Z = \frac{\rho_r}{\rho_{pw}} \cdot \frac{1 - \phi}{\phi} \cdot \frac{2AW_K}{AW_{K_2O}} \cdot \frac{10^6 \text{ ppm}}{10^2 \text{ wt. \%}}$$

and $c^K = K$ concentration in pore water (ppm), ρ_r and ρ_{pw} = densities of the rock and pore water, respectively, ϕ = porosity and AW = atomic or molecular weight of the species of interest. Substituting Eqs. (4) and (5) into Eq. (2) produces the following expression for the rate of change in K concentration in pore water caused by smectite illitization:

$$\frac{\partial c^K}{\partial t} = (4.53\% K_2O)Z(c^K/c^{Na})^\beta k_i (c^{sm})^\alpha \quad (6)$$

Pytte (1982) assumed that the c^K/c^{Na} ratio in pore water is controlled by equilibrium between K-feldspar and albite and listed the following values for c^K/c^{Na} at different temperatures: 3.4×10^{-2} at 50°C, 6.5×10^{-2} at 80°C, 0.1 at 100°C, and 0.4 at 200°C. For these calculations $\beta = 1$, $\phi = 0.1$, and rock and pore water densities of 2.6 and 1.0 g/cm³, respectively, were assumed. For the first-order equation, $\beta = 0$ (assumed by McCubbin and Patton, 1981). In addition, 100% smectite layers at 50°C, 80% smectite layers at 80°C, 60% smectite layers at 100°C, and 10% smectite layers at 200°C were assumed.

Table 3 lists rates of change in K concentration of pore water, $\partial c^K/\partial t$, caused by smectite illitization. At 50°C these rates range from 2.3 to 17×10^{-3} ppm/yr, at 80°C they range from 0.11 to 0.41 ppm K/yr, at 100°C they range from 0.52 to 2.1 ppm K/yr, and at 200°C they range from 3.3 to 112 ppm K/yr. Fifth- and sixth-order kinetic parameters for smectite illitization appear to model illitization rates best in nature (Pytte, 1982; Altaner, 1985). For all four temperatures, the $\partial c^K/\partial t$ values of smectite illitization that use fifth- or sixth-order kinetic parameters lie at the lower end of the ranges listed above.

DISCUSSION

Between 50° and 200°C rates of K uptake caused by smectite illitization were found to be much slower than rates of K release by K-feldspar dissolution (Tables 1 and 3), implying that the rate of K-feldspar dissolution should not limit the rate of smectite illitization. Slow transport of K (Parachoniak and Środoń, 1973; Velde and Brusewitz, 1982; Altaner *et al.*, 1984) or paucity of K-bearing minerals in a smectite-rich rock (Weaver and Beck, 1971), however, may still limit the rate of smectite illitization.

In these calculations, dissolution rates are used from experiments which were far from equilibrium. As the fluid approaches saturation with respect to feldspar, dissolution rates decrease by a factor of 2–3 (Helgeson and Murphy, 1983). Dissolution rates would be faster than those calculated both for dissolution in acidic

solutions and for dissolution of K-feldspar with more surface area than that was used in the experiments by Lagache (1965).

The illitization term $\partial c^K/\partial t$ is a maximum value because I assumed a low porosity, a low pore-water density, a high rock density, and that one half of the shale consists of I/S. Thus, even in the extreme case, the fact that the illitization term is much smaller than the dissolution term clearly indicates that K-feldspar dissolution does not limit rates of illitization.

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