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Hydrothermal reactivity of smectite

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Abstract

Hydrothermal experiments were conducted to explore the effects of changing chemistry, temperature, and pressure on the reaction of smectite, run 1 : 1 with pure water, to mixed-layer clay. At high temperatures trioctahedral smectites are more stable than dioctahedral smectites. For dioctahedral smectites, hydrothermal stability is enhanced by saturation with interlayer cations of greater hydration energy than potassium, and by increased water pressure.

Introduction

Many of the unusual physical and chemical properties of the smectite group of clay minerals are related to the expandable interlayer region. These properties, which include swelling, cation exchange capacity, catalytic activity, and thixotropy, are sometimes diminished or lost during hydrothermal treatment as the smectite reacts to form mixed-layer clay. It is of interest, therefore, from both a geologic and an industrial point of view, to determine the conditions under which smectites are least likely to react. Our experiments explore the effects of chemical composition, temperature, and pressure on the hydrothermal alteration of smectite to mixed-layer clay.

Experimental techniques

A direct comparison between the reactivity of dioctahedral and trioctahedral smectites was made by saturating each type of clay with various interlayer cations and then subjecting them to identical hydrothermal conditions. Trioctahedral starting materials included a natural saponite from Karolihof, Switzerland (<2 micron size fraction) saturated with K, Na, Ca, or Mg; a natural saponite from the Amargosa Valley, Nevada (<2 micron fraction); and gels of potassium and magnesium saponite composition, $Mg_3Si_{3.67}Al_{0.33}O_{10}(OH)_2X^+_{0.33}$, where X^+ is the exchangeable cation. Dioctahedral starting materials were the Wyoming bentonite (<2 micron fraction, Moll *et al.*, 1975) saturated with K, Na, Ca, or Mg, and a gel of potassium montmorillonite composition, $Al_2Si_{3.67}Al_{0.33}O_{10}(OH)_2K_{0.33}$. Gels were prepared by the method of Hamilton and Henderson (1968).

Hydrothermal runs were prepared by introducing 30 mg of clay or gel and 30 μl of pure water into gold tubes (20 mm long, 2.5 mm I.D.) which were then welded shut. These charges were heated in large hot-seal autoclave reaction vessels or in small cold-seal reaction vessels. The former generated maximum pressures of approximately 0.3 kbar, and the latter were maintained at 0.5 or 2 kbar by equilibration with a large reservoir (see Eberl and Hower, 1976). All vessels were heated in resistance furnaces, and temperatures were controlled by on–off regulators attached to thermocouples located in wells near or in the base of the vessels.

Run products were oriented on glass slides, glycolated, and X-rayed with a Norelco diffractometer, using Ni-filtered Cu$K\alpha$ radiation. The expandability of mixed-layer illite/smectite was determined by comparison with the calculated patterns of Reynolds and Hower (1970).

Experimental results

The difference in reactivity between dioctahedral and trioctahedral smectite is clearly shown in Tables 1 and 2 and in Figures 1, 2, and 3. At 400°C and autoclave pressure, the K-montmorillonite gel (run 1) and the natural montmorillonites saturated with K, Na, Ca, and Mg (runs 2–5) reacted extensively to form regularly interstratified mixed-layer clay. The saponites run under equivalent conditions did not react (runs 10–18). The effect of interlayer chemistry on the reaction of dioctahedral clays is also shown in Table 1. Montmorillonite with interlayer potassium (run 6) reacted at a lower temperature than did mont-

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Table 1. Montmorillonite autoclave runs

Run no.	Starting material	Temp. (°C)	Time (days)	Run products
1	K-gel*	300 to 485 **	34	illite, cristobalite pyrophyllite
2-5	K, -Na-, Ca- and Mg-montmorillonite***	400	7	mica/smectite, quartz, kaolinite, ± feldspar
6	K-montmorillonite***	300	30	illite/smectite, quartz, kaolinite
7-9	Na-, Ca-, and Mg-montmorillonite***	300	30	montmorillonite, quartz,

* Composition equivalent to $(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2K_{0.33}$.

** Large temperature range due to failure of temperature regulator.

*** Less than 2 micron size fraction of Wyoming bentonite, plus a small amount of quartz.

morillonite saturated with the other cations (runs 7–9). Interlayer chemistry did not affect the reaction of saponite at temperatures below 415°C (Table 2, runs 11–18), but at 500°C the gel of Mg-saponite did react to form a regularly interstratified talc/saponite (Fig. 4 and Table 2, run 19). The reflections labeled 4.59 and 4.57 in Figure 4 are most likely 020 reflections: the basal reflections lie beneath these peaks.

The effect of pressure on the reaction of montmorillonite is shown in Table 3. Increasing water pressure inhibited reaction for all interlayer cations tested, but had the least effect with interlayer potassium (runs 30–31).

Discussion

Reactivity of dioctahedral and trioctahedral smectites

The results of the present study, namely that dioctahedral smectites (beidellite and montmorillonite)

Table 2. Saponite autoclave runs

Run no.	Starting material	Temp. (°C)	Time (days)	Run products
10	K-gel*	300 to 485**	34	saponite
11-14	K-, Na-, Ca- and Mg-saponite***	400	7	saponite
15	K-saponite†	400	7	saponite
16-18	Mg-gel††	250,330,415	9	saponite
19	Mg-gel††	500	9	talc/saponite

* Composition equivalent to $Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2K_{0.33}$.

** See second footnote, Table 1.

*** Less than 2 micron Karolihof saponite.

† Less than 2 micron Amargosa saponite.

†† Composition equivalent to $Mg_3(Si_{3.67}Al_{0.33})O_{10}(OH)_2Mg_{0.165}$.

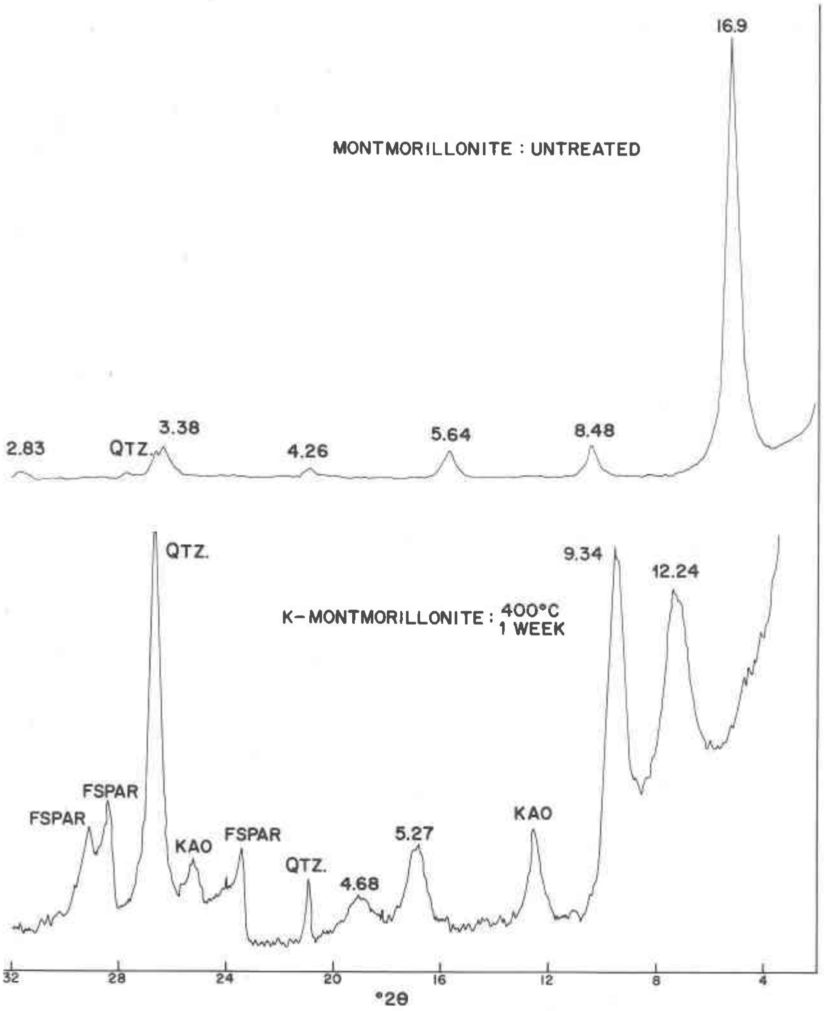

Fig. 1. X-ray diffractograms of <2 micron natural (top) and hydrothermally-treated K-saturated Wyoming bentonite (bottom). Numbered peaks on the lower diffractogram refer to layer spacings for the illite/smectite. Samples treated with ethylene glycol.

readily react to form mixed-layer clays whereas trioctahedral smectites (saponite and hectorite) resist alteration, corroborate the results of previous studies. Eberl and Hower (1976, 1977) found that K- and Na-saturated and supersaturated beidellites and montmorillonites reacted readily to form mixed-layer clays at 2 kbar, and that, in some instances, the reaction commenced at temperatures as low as 150°C, with the degree of reaction increasing with increasing temperature and/or time. By contrast, Koizumi and Roy (1959) identified trioctahedral smectites which were stable up to 850°C at 1 kbar, Iiyama and Roy (1963) found that saponite of the proper composition would remain unreactive up to at least 850°C at 1 kbar, and Sand (1955) and Ames and Sand (1957) determined that hectorite could exist up to 750°C at 1 kbar pressure. In addition, Carmen (1974) synthesized an expandable phase which persisted to temperatures of 1000°C at 5 kbar pressure. Clearly, smectites are not necessarily low-temperature minerals. Dioctahedral varieties may react to form mixed-layer clays at relatively low temperatures, but trioctahedral smectites may persist to high temperatures. Whether or not trioctahedral smectites are stable in a thermodynamic sense at these temperatures is not known.

A comparison between the reactivity of dioctahedral and trioctahedral smectites occurring in nature is difficult. The dioctahedral smectites are by far the most common of the natural smectites, and studies of their reactions include the investigations of Burst (1959, 1969), Perry and Hower (1970), Weaver and Beck (1971), and Hower *et al.* (1976), all of whom studied the mixed-layer products of burial diagenesis. They found that montmorillonite reacts to form

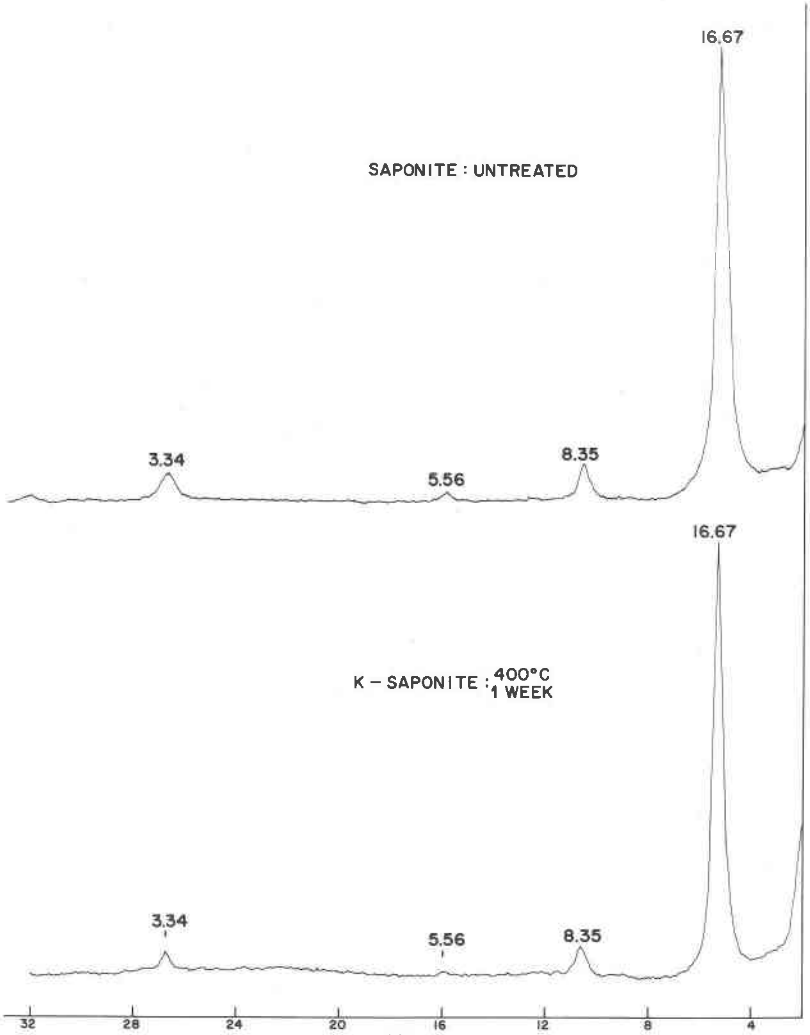

Fig. 2. X-ray diffractograms of <2 micron natural (top) and hydrothermally-treated K-saturated Karolihof saponite (bottom). Samples saturated with ethylene glycol.

mixed-layer illite/smectite at depth. Reaction begins in the Gulf Coast geosyncline at temperatures as low as 50°C (Perry and Hower, 1970). Natural examples of trioctahedral mixed-layer clays with saponite as a layer constituent have been reported, for example, by Earley *et al.* (1956), Earley and Milne (1956), and Wiewiora and Szpila (1975). The reactions which formed these clays are not known in detail, and there is little data to indicate that they developed from saponite starting material.

The greater stability of trioctahedral smectites can be related to mechanisms for the formation of mixed-layer clay. A smectite layer in a clay crystallite will convert to a mica-like layer when electrostatic attraction between the negatively charged 2:1 layers and the positive interlayer cation becomes greater than the attraction between the cation and its shell of hydrating water molecules. The net negative charge on the 2:1 layers may be increased by: (1) the substitution of Al^{3+} for Si^{4+} in the tetrahedral layer, (2) the substitution of Mg^{2+} and/or Fe^{2+} for Al^{3+} in the octahedral layer, and (3) by the reduction of Fe^{3+} (Perry and Hower, 1970). Other mechanisms can also be visualized, such as the substitution of Li^{+} for Mg^{2+} or B^{3+} for Si^{4+}. An increase in the negative layer charge by these mechanisms must be electrically balanced by an increase in the concentration of interlayer cations. The hydrothermal studies of Eberl and Hower (1976) show that the first mechanism proceeds spontaneously for a dioctahedral smectite in the absence of an external source of aluminum. Aluminum and interlayer cations for the reaction are presumably

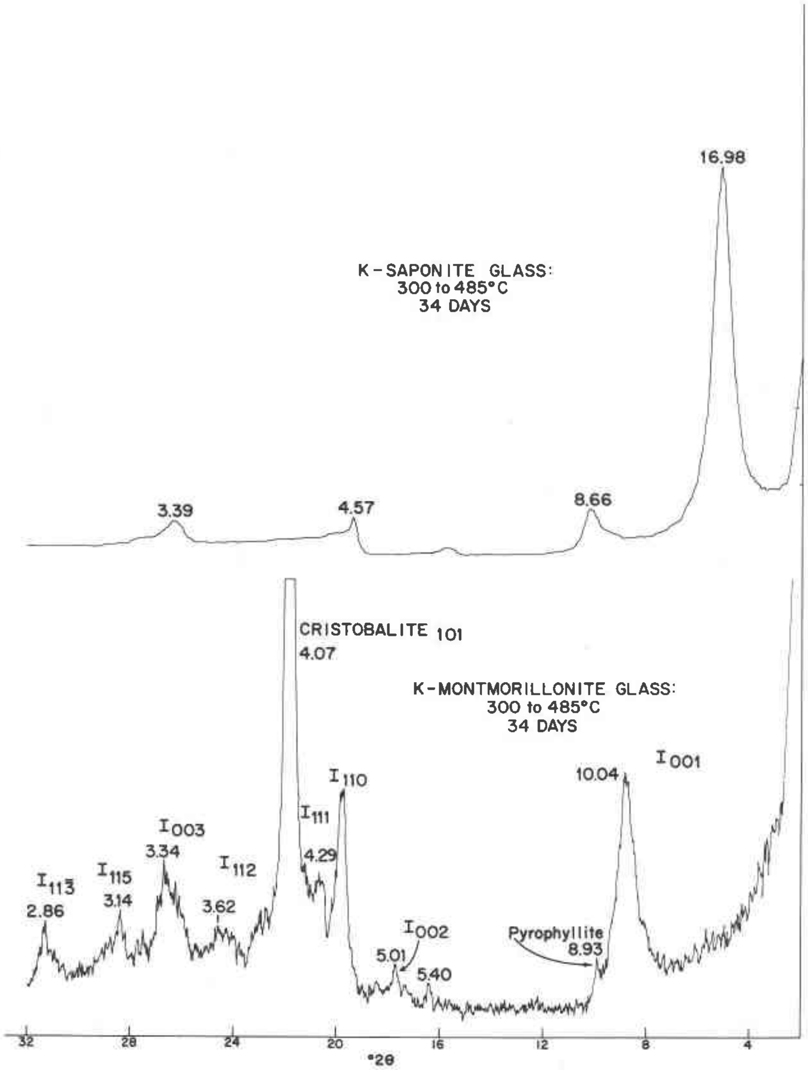

Fig. 3. X-ray diffractograms of run products for gels of K-saponite and K-montmorillonite compositions treated under identical hydrothermal conditions. "*I*" refers to illite peaks. Samples treated with ethylene glycol.

supplied by a dissolution of some of the smectite. The first mechanism also operates in the Gulf Coast geosyncline, where aluminum and potassium are supplied by the dissolution of potassium feldspar (Hower *et al.*, 1976).

Theoretically, trioctahedral smectites of ideal composition should not be able to react via the above mechanisms. In an ideal saponite, the only aluminum present is a small amount (ideally about 0.33 equivalents per half unit cell) which accounts for the layer charge originally found in the saponite. Even if all of this aluminum was concentrated in some crystallites to build an illite layer charge, the number of such collapsed layers would be so few as to be unobservable. Clearly, if this mechanism is to work on saponites, the aluminum must be derived from some source other than the saponite itself. In fact, Koizumi and Roy (1959) demonstrated that aluminum in excess of that required for the saponite composition will cause synthetic saponites to react at temperatures as low as 260°C, and unpublished experiments by the present authors demonstrate that natural saponites may also be induced to react by the addition of aluminum.

The substitution of Mg^{2+} for Al^{3+} in the octahedral sheet is not possible in the trioctahedral smectites, since the octahedral sheet already has a full complement of divalent or monovalent cations. Ames and

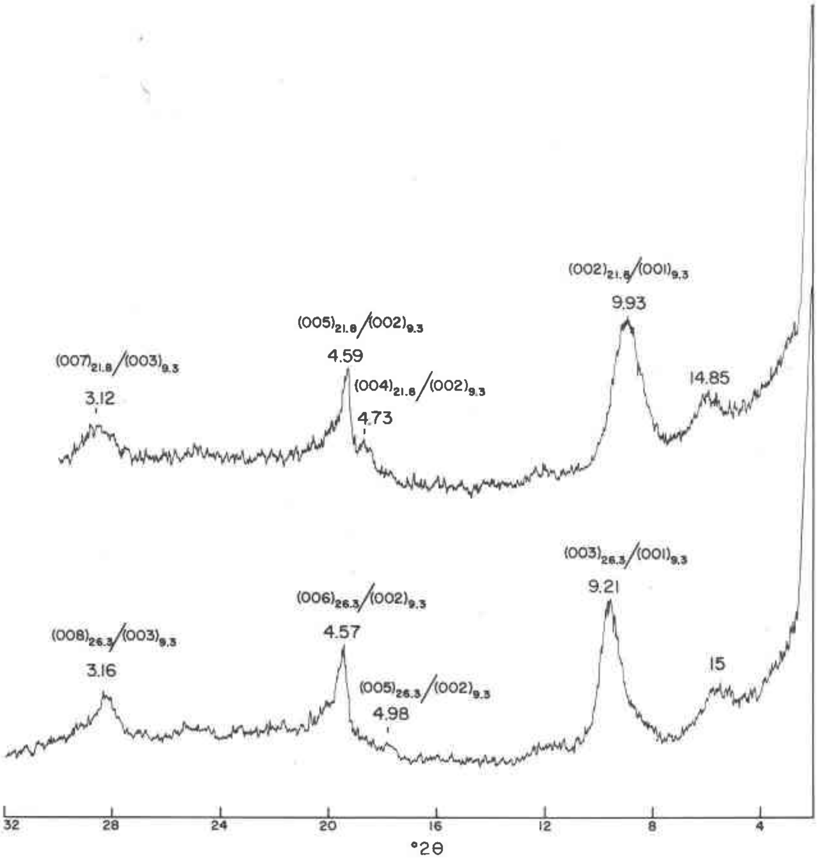

Fig. 4. An ordered mixed-layer talc/saponite produced in run 19 (Table 2). Air-dried (top) and ethylene glycol treated (bottom).

Sand (1958) and Sand and Ames (1957) have also suggested that smectite stability is enhanced when all cation sites are thus occupied.

Finally, the mechanisms involving the reduction of ferric iron and the substitutions of Li^+ and B^{3+} can be disregarded, since the starting materials were not run in a reducing environment and probably do not contain sufficient amounts of Li^+ and B^{3+} to significantly affect layer charge. It is clear that trioctahedral smectites do not react as readily as the dioctahedral smectites because they do not possess the charge building options inherent in a clay system rich in aluminum.

Mixed-layer clays may also be formed by reactions which reduce layer charge rather than increase it. Reduced layer charge leads to a structure in which hydrated interlayer cations are not required for charge balance, thereby giving rise, for example, to a pyrophyllite- or talc-like layer. Mixed-layer clays have been formed experimentally by this mechanism. A Ca-saturated montmorillonite heated with excess Al^{3+} (as a chloride) in a $CaCl_2$ solution (0.5N) was transformed into an ordered mixed-layer pyrophyllite/smectite at 330°C (Eberl, in preparation), and a magnesium saponite gel formed an ordered talc/saponite at 500°C (Fig. 4, and Table 2, run 19). As was mentioned previously, Iiyama and Roy (1963) found that there is an ideal composition which optimizes saponite stability. An Al/Mg ratio in excess of this ideal composition leads to the formation of mica–saponite by the charge building mechanism, and a lower ratio gives rise to talc/saponite by charge reduction.

The influence of interlayer chemistry

These experiments show that interlayer chemistry strongly affects the temperature of reaction for montmorillonite (Table 1). The effect of interlayer alkali and alkaline-earth cations on the reaction was studied in more detail by Eberl (1978). It was found that montmorillonites saturated with cations of low hydration energy (K^+, Rb^+, Cs^+) would react at 300°C and autoclave pressures in 30 days, whereas those saturated with cations of higher hydration energy would not. At 400°C and autoclave pressures, mont-

Table 3. Pressure effect on the reaction of Wyoming montmorillonite

Run no.	Starting material	Temp. (°C)	Time (days)	Pressure (kbar)	Run products
20-21	Na-mont	400	7 and 30	A**	rectorite, kaolinite, quartz
22	Na-mont	405	17	0.5	smectite, rectorite, kaolinite, albite, quartz
23	Na-mont	405	17	2	smectite, quartz
24	Na-mont	507	21	2	montmorillonite, quartz
25	Li-mont	500	7	A	tosudite (chlorite/smectite), kaolinite, quartz
26	Li-mont	507	21	2	smectite, quartz
27-28	Ca-mont	400	7 and 30	A	Ca-rectorite, kaolinite, quartz, smectite
29	Ca-mont	495	19	2	smectite, quartz
30	K-mont	400	8	A	illite/smectite (35%)***, kaolinite, quartz
31	K-mont	400	8	2	illite/smectite (50%)***, pyrophyllite, quartz

* See third footnote, Table 1.
** Autoclave pressure, See text.
*** Percent smectite layers.

morillonite reacted no matter what the interlayer cation. Blatter (1974) also noted the inhibiting effect of Na^+, Ca^{2+}, and Mg^{2+} on the reaction. He found that the transformation of montmorillonite into a less expanded phase was greatly retarded at 200°C in solutions having low K^+/Mg^{2+}, K^+/Ca^{2+}, or K^+/Na^+ ratios, and that the divalent cations were more effective than Na^+ in blocking reaction.

The blocking effect of cations of high hydration energy may either be a kinetic effect or reflect equilibrium. In either case, the lack of reaction is probably related to the amount of negative charge on the 2:1 layers required to dehydrate the interlayer cation. Sodium, for example, will be more strongly hydrated than potassium in the interlayer region of a montmorillonite, and will therefore require a greater layer charge to form a mica-like layer. The 2:1 lattice will require a charge of −0.8 equivalents per $O_{10}(OH)_2$ to dehydrate potassium and a charge greater than −1.2 to dehydrate sodium (Garrels and Tardy, in preparation). These layer charges are reflected in the compositions of the minerals illite, which has a layer charge of −0.8 equivalents per $O_{10}(OH)_2$ (Hower and Mowatt, 1966), and rectorite, which most likely has a charge on the paragonite-like layers greater than −1.0 (Eberl and Hower, 1977). The higher the layer charge required for dehydration, the more Al^{3+} must substitute for Si^{4+} in the tetrahedral layer, a substitution which is probably the rate-limiting step for the reaction (Eberl and Hower, 1976). From an equilibrium viewpoint, the greater the layer charge requirement, the more positive the free energy of reaction at 25°C. For example, the free energy change for the conversion of an ideal beidellite layer into an ideal illite or paragonite layer can be calculated using the thermochemical approximations of Tardy and Garrels (1974), taking into account a correction for interlayer cation hydration (Garrels and Tardy, in preparation). For the reaction:

$$2.42\ K_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2 + 1.42\ H_2O =$$
$$K_{0.8}Al_2(Si_{3.20}Al_{0.8})O_{10}(OH)_2 + 1.42\ Al_2Si_2O_5(OH)_4 + 2.84\ SiO_2 \qquad (1)$$

ΔG^0 at 25°C is + 2.8 kcal/mole, whereas for the reaction:

$$3.03\ Na_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2 + 2.03H_2O = NaAl_2(Si_3Al)O_{10}(OH)_2 + 2.03\ Al_2Si_2O_5(OH)_4 + 4.06\ SiO_2 \quad (2)$$

ΔG^0 is + 11.4 kcal/mole. Since ΔG^0 for reaction (2) at 25°C is four times more positive than that for reaction (1), it seems likely, assuming roughly similar values for ΔS^0 with increasing temperature, that ΔG^0 for reaction (1) will become negative at a lower temperature than will that for reaction (2), an inference that is consistent with the experimental results.

The pressure effect

The effect of pressure on the transformation of smectite (Table 3) could be a function of either phase equilibrium or kinetic effects. From an equilibrium viewpoint the change in free energy with pressure is $(\delta\Delta G/\delta P)_T = \Delta V$. A positive ΔV would lead to an increase in the free energy of reaction with increasing pressure for a given temperature. Such a ΔV is expected if interlayer H_2O is significantly denser than pore H_2O at the experimental temperatures. Carmen (1974) has offered evidence for the denser nature of interlayer water at elevated temperatures and pressures in dehydration experiments run on a Na-vermiculite-like phase. Calculations show that increasing the pressure from 1 bar to 2 kbar at 500°C would raise ΔG for the conversion of beidellite to rectorite by about 2.2 kcal/mole, assuming a constant specific volume for interlayer water of 15 cm^3/mole (after Carmen, 1974), and a value of 26.1 cm^3/mole for pore water under the experimental conditions (Burnham *et al.*, 1969). Presumably the pressure effect would not be as great for clays reacting in brine.

A smaller pressure effect on the reaction is expected with interlayer potassium than with cations of greater hydration energy, since potassium cannot impart as strong a structure to water, a prediction born out by the experiments (Table 3, runs 30–31). If the pressure effect is an equilibrium effect related to the difference in density between interlayer and pore H_2O, then there must exist a crossover temperature at which pressure has no effect on the reaction, since interlayer water in montmorillonite is less dense than pore water at room temperature (Bradley, 1959). Below the crossover temperature, high pressure would lead to a more negative ΔG.

Conclusions

It is clear that smectite is not necessarily a low-temperature mineral. Trioctahedral smectite is stable at high temperatures, whereas dioctahedral smectite will react. The hydrothermal stability of dioctahedral smectite can be increased both by saturation with interlayer cations of hydration energy greater than potassium, and by increased water pressure. It is not clear whether smectite stability at elevated temperatures is an equilibrium or a kinetic phenomenon.

The results of this study are directly applicable only to smectites run in hydrothermal systems in a 1 : 1 ratio with pure water. Changing the solution composition may change the patterns of reaction. For example, adding the sodium ion would change the reaction previously written for the formation of a paragonite layer to:

$$1.29\ Na_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2 + 0.57\ Na^+ = NaAl_2(Si_3Al)O_{10}(OH)_2 + 1.73\ SiO_{2(aq)} + 0.57\ H^+.$$

When the reaction is written in this manner, it can be seen that smectite stability depends on the activity of $SiO_{2(aq)}$, Na^+, and H^+ in solution, a result clearly demonstrated, for example, in the theoretical activity diagrams of Helgeson *et al.* (1969), as well as on the parameters of smectite chemistry, temperature, and pressure examined here.

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