

# Diocahedral smectite reactions at elevated temperatures: Effects of K-availability, Na/K ratio and ionic strength

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## ABSTRACT

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Hydrothermal experiments were conducted to measure the effects of K availability, Na/K ratio and ionic strength in chloride solutions on the rate and extent of the reaction of smectite to interstratified illite/smectite. The  $< 2 \mu\text{m}$  fraction of a bentonite was treated hydrothermally at temperatures of 200, 250, 300, 350, 400 and 450°C for run times of up to 30 days in the presence of 0.33, 0.66 and 1.00 equivalents of K per  $\text{O}_{10}(\text{OH})_2$ . The effect of K-content on reaction progress is dramatic at low (0.33 eq.) K concentrations, but diminishes above a concentration of 0.66 equivalents. The effect of K-content is also more important at lower temperatures than at higher temperatures. Addition of K above that required to satisfy the cation exchange capacity of the smectite reduced the amount of chlorite byproduct and produced authigenic K-feldspar at the highest K-concentration.

Similar experiments were run using Na/K equivalent ratios of 0 to 25 and total solution molalities of 0 to 3.75 molal. Because these experiments were small fixed-volume experiments, it was necessary to vary two of the three key variables (K-content, Na/K ratio, ionic strength) simultaneously. The data suggest, however, that K-content has a much stronger effect than either Na/K ratio or ionic strength on illitization reaction progress.

## INTRODUCTION

Smectite is an important clay mineral in geologic environments and in industrial processes. The reaction from smectite to illite via an interstratified illite/smectite (I/S) phase is a widely studied process in diagenetic and hydrothermal environments, and the reaction is sometimes used as a thermal maturation indicator in sedimentary rocks. In addition, when smectite is used as a sealant in engineered environments for the disposal of nuclear waste,

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exposure to elevated temperatures may cause reactions which diminish the effectiveness of smectite as a physical seal and a chemical absorbant.

Previous research has shown that several variables may affect the manner and rate at which smectite is converted to illite. For example, Whitney (1983) and Eberl et al. (1978) demonstrated that magnesium smectites (saponite, hectorite) are much more resistant to hydrothermal reaction than the aluminous smectites (montmorillonite, beidellite). This is an important observation for applications in which a smectite may be selected for its thermal stability. In addition, Eberl (1978a,b) showed that the species of alkaline or alkaline-earth cation occupying the interlayer exchange site in smectite may have a profound effect on the nature and rate of reaction of dioctahedral smectite to interstratified clays. These cation-dependent reactions suggests that interlayer chemistry of the starting smectite may affect the physical integrity of smectite seals as well as the ability of the smectite to retain exchangeable cations introduced into the waste environment.

Whitney and Northrop (1988) and Inoue et al. (1988) explored the mechanisms of the reactions from smectite to I/S and determined that the illitization reaction is not a single reaction, but consists of at least two stages with different reaction mechanisms. Experiments by Whitney (1990) have demonstrated the effectiveness of very small amounts of water in the reaction of smectite to interstratified minerals and suggests that the reactions may be halted only by removing virtually all free molecular water from the system. Furthermore, recent experiments indicate that the texture of the smectite may also play an important role in the rate of reaction (Whitney and Velde, in press): face-to-face contact between smectite flakes may facilitate reactions to other phyllosilicate phases such as illite. The purpose of the present study is to extent the understanding of smectite reactivity at elevated temperatures by investigating the effect of potassium availability (hereafter called K-availability) Na/K ratio and ionic strength of reacting solutions on the rate of reaction of smectite to interstratified illite/smectite.

#### EXPERIMENTAL TECHNIQUES

Experiments were carried out using standard hydrothermal experimental techniques. Approximately 60 mg of smectite was placed in a gold tube (4.5 mm I.D., 5.0 mm O.D.) with 60  $\mu$ l of known experimental fluid and welded shut. Samples were placed in horizontally-oriented cold-seal bombs with filler rods and heated in a tube-type resistance furnace at 100 MPa (1 kbar) at precisely monitored temperatures ( $\pm 1^\circ\text{C}$ ) for predetermined periods of time. Each sample was weighed before and after treatment to detect any leakage; leaked samples were discarded. A range of experiments was conducted for each composition so that reaction at a particular temperature was monitored for several reaction times.

TABLE 1

Experimental conditions and results for K-availability experiments

Sample #	K (eq per $O_{10}(OH)_2$ )	Temp ( $^{\circ}C$ )	Time (days)	% Illite in I/S
D130	0.33	250	0	0
D131	0.33	250	1	10
D139	0.33	250	3	15
D133	0.33	250	14	22
D13T	0.33	250	21	27
D134	0.33	250	30	28
D140	0.33	300	0	0
D141	0.33	300	1	25
D149	0.33	300	3	32
D142	0.33	300	7	42
D143	0.33	300	14	43
D14T	0.33	300	21	48
D144	0.33	300	30	49
D150	0.33	350	0	0
D15Y	0.33	350	0.33	38
D151	0.33	350	1	45
D159	0.33	350	3	54
D152	0.33	350	7	56
D153	0.33	350	14	60
D15T	0.33	350	21	60
D154	0.33	350	30	63
D160	0.33	400	0	0
D16Y	0.33	400	0.33	55
D161	0.33	400	1	57
D169	0.33	400	3	62
D162	0.33	400	7	65
D163	0.33	400	14	73
D16T	0.33	400	21	75
D164	0.33	400	30	78
D170	0.33	450	0	0
D17Y	0.33	450	0.33	60
D171	0.33	450	1	67
D179	0.33	450	3	77
D172	0.33	450	7	85
D173	0.33	450	14	87
D17T	0.33	450	21	91
D174	0.33	450	30	93
D230	0.66	250	0	0
D23Y	0.66	250	0.33	20
D231	0.66	250	1	24
D239	0.66	250	3	31
D232	0.66	250	7	33
D233	0.66	250	14	37
D23T	0.66	250	21	38
D234	0.66	250	30	47
D240	0.66	300	0	0
D24Y	0.66	300	0.33	30
D241	0.66	300	1	35

TABLE 1 (Continued)

Sample #	K (eq per $O_{10}(OH)_2$ )	Temp (°C)	Time (days)	% Illite in I/S
D249	0.66	300	3	46
D242	0.66	300	7	56
D24T	0.66	300	21	63
D244	0.66	300	30	66
D250	0.66	350	0	0
D25Y	0.66	350	0.33	50
D251	0.66	350	1	63
D259	0.66	350	3	64
D252	0.66	350	7	65
D253	0.66	350	14	68
D25T	0.66	350	21	70
D254	0.66	350	30	70
D260	0.66	400	0	0
D26Y	0.66	400	0.33	60
D261	0.66	400	1	71
D269	0.66	400	3	72
D262	0.66	400	7	74
D263	0.66	400	14	82
D26T	0.66	400	21	84
D264	0.66	400	30	86
D270	0.66	450	0	0
D271	0.66	450	1	82
D279	0.66	450	3	83
D272	0.66	450	7	90
D273	0.66	450	14	92
D27T	0.66	450	21	93
D274	0.66	450	30	95
D330	1	250	0	0
D33Y	1	250	0.33	20
D331	1	250	1	23
D339	1	250	3	29
D332	1	250	7	31
D333	1	250	14	38
D334	1	250	30	48
D340	1	300	0	0
D34Y	1	300	0.33	30
D341	1	300	1	37
D349	1	300	3	52
D342	1	300	7	60
D343	1	300	14	64
D34T	1	300	21	62
D344	1	300	30	65
D350	1	350	0	0
D35Y	1	350	0.33	60
D351	1	350	1	66
D359	1	350	3	67
D352	1	350	7	69
D353	1	350	14	70

TABLE 1

Sample #	K (eq per $O_{10}(OH)_2$ )	Temp ( $^{\circ}C$ )	Time (days)	% Illite in I/S
D35T	1	350	21	70
D354	1	350	30	73
D360	1	400	0	0
D36Y	1	400	0.33	67
D361	1	400	1	73
D369	1	400	3	75
D362	1	400	7	78
D363	1	400	14	85
D36T	1	400	21	87
D370	1	450	0	0
D37Y	1	450	0.33	75
D371	1	450	1	86
D379	1	450	3	87
D372	1	450	7	92
D373	1	450	14	93
D37T	1	450	21	95
D374	1	450	30	96

After hydrothermal treatment, each capsule was opened by cutting the end off and squeezing the sample into a small agate mortar. A few drops of distilled water were added and the clay sample was gently disaggregated with a pestle. The dispersed sample was transferred to a glass slide with an eyedropper and allowed to dry. Each sample was examined by X-ray powder diffraction air-dried and after saturation with ethylene glycol. In all cases, the run products consisted of I/S and the proportion of layer types was determined by comparison with calculated patterns generated using the computer program NEWMOD (R.C. Reynolds, Hanover, NH, 1980).

The smectite used in the experiments was the  $< 2 \mu m$  fraction of SWY-1, a bentonite standard from the Source Clay Minerals Repository (van Olphen and Fripiat, 1979). Solutions were mixed from NaCl and KCl in appropriate amounts to give the compositional scheme shown in Table 1 (K-only experiments) and Table 2 (Na/K and ionic strength experiments). Na/K ratios in Table 2 are computed on an equivalent/equivalent (eq./eq.) basis. Although it is desirable to vary only one parameter at a time (K-availability, Na/K ratio, or ionic strength), limitations of experimental volumes often required that two of the three parameters be varied simultaneously.

## RESULTS

### *K-availability*

The effect of K-availability on the rate and extent of the reaction of smectite to I/S was investigated in two ways. First, a set of samples were treated

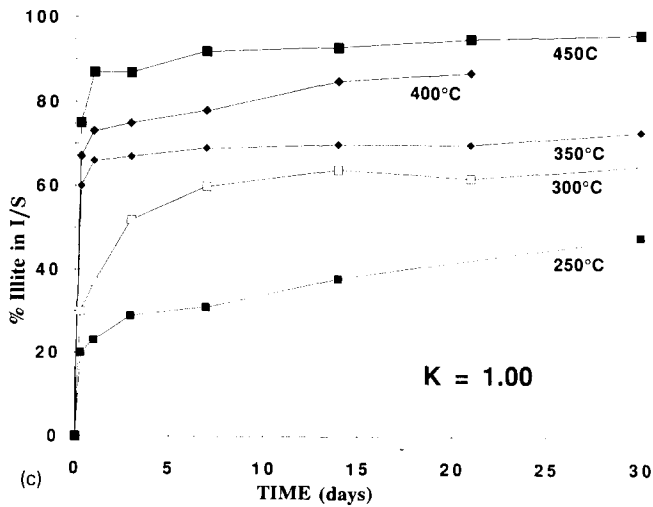
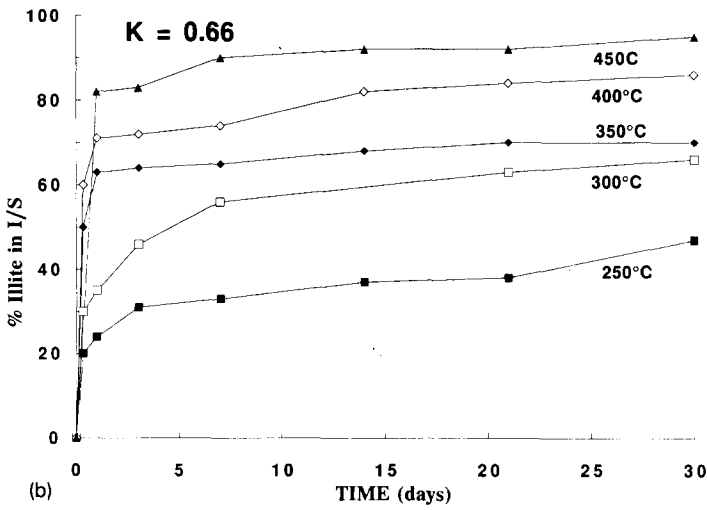
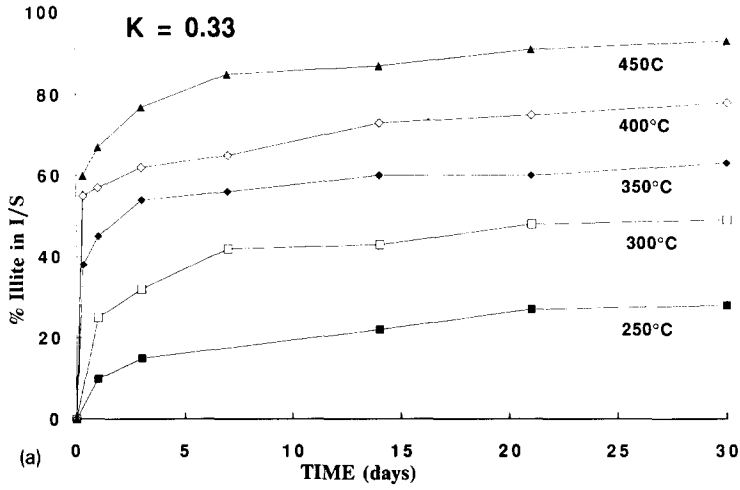
TABLE 2

Experimental conditions and resulting illite layer proportions for I/S

Sample #	Temp (°C)	Time (days)	K per O <sub>10</sub> (OH) <sub>2</sub>	Na/K ratio	Conc. (molal)	% illite in I/S
E122	200	7	0.33	1	0.75	15
E123	200	14	0.33	1	0.75	15
E124	200	30	0.33	1	0.75	20
E132	250	7	0.33	1	0.75	15
E134	250	30	0.33	1	0.75	18
E141	300	1	0.33	1	0.75	27
E142	300	7	0.33	1	0.75	38
E143	300	14	0.33	1	0.75	38
E151	350	1	0.33	1	0.75	40
E161	400	1	0.33	1	0.75	60
E163	400	14	0.33	1	0.75	73
E222	200	7	0.66	1	2.25	10
E223	200	14	0.66	1	2.25	10
E224	200	30	0.66	1	2.25	15
E232	250	7	0.66	1	2.25	30
E233	250	14	0.66	1	2.25	32
E234	250	30	0.66	1	2.25	33
E241	300	1	0.66	1	2.25	40
E242	300	7	0.66	1	2.25	50
E243	300	14	0.66	1	2.25	60
E251	350	1	0.66	1	2.25	60
E261	400	1	0.66	1	2.25	72
E263	400	14	0.66	1	2.25	82
E322	200	7	0.99	1	3.75	8
E323	200	14	0.99	1	3.75	12
E324	200	30	0.99	1	3.75	15
E332	250	7	0.99	1	3.75	25
E333	250	14	0.99	1	3.75	27
E334	250	30	0.99	1	3.75	30
E341	300	1	0.99	1	3.75	39
E342	300	7	0.99	1	3.75	58
E343	300	14	0.99	1	3.75	70
E351	350	1	0.99	1	3.75	70
E361	400	1	0.99	1	3.75	75
E363	400	14	0.99	1	3.75	87
E422	200	7	0.07	5	0.15	5
E423	200	14	0.07	5	0.15	5
E424	200	30	0.07	5	0.15	5
E432	250	7	0.07	5	0.15	5
E433	250	14	0.07	5	0.15	5
E434	250	30	0.07	5	0.15	5
E441	300	1	0.07	5	0.15	5
E442	300	7	0.07	5	0.15	5
E443	300	14	0.07	5	0.15	5
E451	350	1	0.07	5	0.15	5
E461	400	1	0.07	5	0.15	7
E522	200	7	0.11	5	0.75	8
E532	200	14	0.11	5	0.75	5

TABLE 2

Sample #	Temp (°C)	Time (days)	K per O <sub>10</sub> (OH) <sub>2</sub>	Na/K ratio	Conc. (molal)	% Illite in I/S
E524	200	30	0.11	5	0.75	10
E532	250	7	0.11	5	0.75	8
E533	250	14	0.11	5	0.75	8
E534	250	30	0.11	5	0.75	10
E541	300	1	0.11	5	0.75	10
E542	300	7	0.11	5	0.75	11
E543	300	14	0.11	5	0.75	12
E551	350	1	0.11	5	0.75	13
E561	400	1	0.11	5	0.75	18
E622	200	7	0.22	5	2.25	14
E623	200	14	0.22	5	2.25	12
E624	200	30	0.22	5	2.25	16
E632	250	7	0.22	5	2.25	14
E633	250	14	0.22	5	2.25	8
E634	250	30	0.22	5	2.25	16
E641	300	1	0.22	5	2.25	30
E642	300	7	0.22	5	2.25	30
E651	350	1	0.22	5	2.25	30
E663	400	14	0.22	5	2.25	70
E722	200	7	0.33	5	3.75	14
E723	200	14	0.33	5	3.75	14
E724	200	30	0.33	5	3.75	15
E732	250	7	0.33	5	3.75	17
E733	250	14	0.33	5	3.75	19
E734	250	30	0.33	5	3.75	20
E741	300	1	0.33	5	3.75	30
E742	300	7	0.33	5	3.75	30
E751	350	1	0.33	5	3.75	36
E761	400	1	0.33	5	3.75	55
E763	400	14	0.33	5	3.75	75
E822	200	7	0.05	25	2.25	5
E823	200	14	0.05	25	2.25	5
E824	200	30	0.05	25	2.25	6
E832	250	7	0.05	25	2.25	6
E833	250	14	0.05	25	2.25	6
E834	250	30	0.05	25	2.25	6
E841	300	1	0.05	25	2.25	8
E842	300	7	0.05	25	2.25	8
E851	350	1	0.05	25	2.25	5
E861	400	1	0.05	25	2.25	19
E863	400	14	0.05	25	2.25	62
E922	200	7	0.08	25	3.75	7
E924	200	30	0.08	25	3.75	9
E932	250	7	0.08	25	3.75	9
E933	250	14	0.08	25	3.75	11
E934	250	30	0.08	25	3.75	15
E941	300	1	0.08	25	3.75	13
E942	300	7	0.08	25	3.75	15
E951	350	1	0.08	25	3.75	16
E961	400	1	0.08	25	3.75	34
E963	400	14	0.08	25	3.75	70





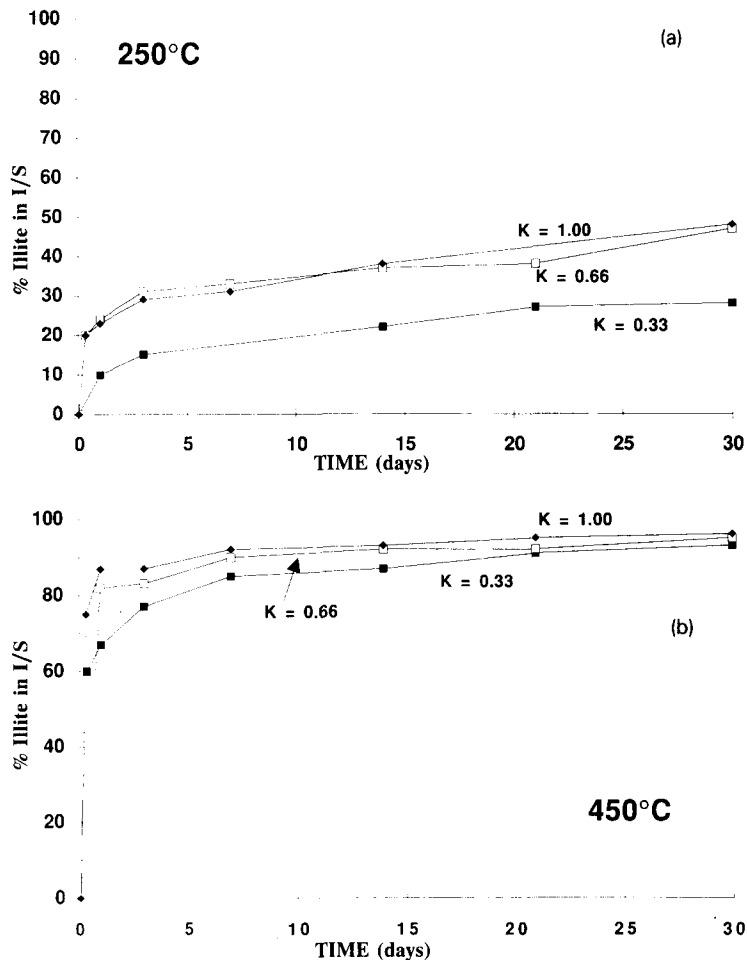


Fig. 2. Proportion of illite layers in interstratified illite/smectite (I/S) as a function of time for each run temperature for different potassium contents at 250°C (a) and 450°C (b).

Fig. 1. Reaction trends for illitization with potassium content of 0.33 equivalents (a) 0.66 equivalents (b) and 1.00 equivalents per  $O_{10}(OH)_2$  (c).

hydrothermally with only K as the interlayer cation (0.33 equivalents per  $O_{10}(OH)_2$ ). To test the effect of K-availability, identical experiments were conducted with two and three times as much K (Table 1). The proportion of illite layers in the I/S, as a function of time and temperature, for each of the K-only experiments is shown in Fig. 1. The reaction proceeds according to the same trends as observed by Whitney and Northrop (1988) and Whitney (1990). Initially, illite proportion increased rapidly but then slowed dramatically with increasing time.

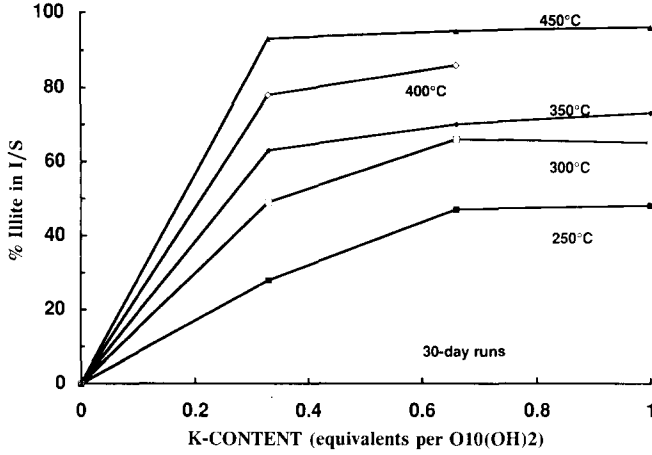


Fig. 3. The effect of K-content on the extent of illitization for different temperatures after 30 days.

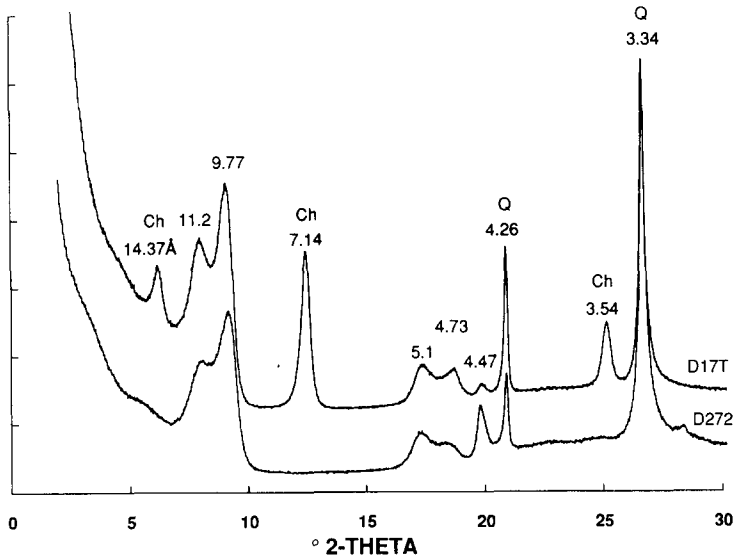


Fig. 4. X-ray powder diffraction patterns for illitic I/S run products with 0.33 equivalents of K per O<sub>10</sub>(OH)<sub>2</sub> and 0.66 equivalents of K per O<sub>10</sub>(OH)<sub>2</sub> showing the effect of excess K on the inhibition of chlorite formation. Q=quartz, Ch=chlorite, all unlabelled peaks are for I/S.

Comparison of the reaction trends for the different K concentrations is shown in Fig. 2. At 250°C (Fig. 2a), the difference between 0.33 equivalents per O<sub>10</sub>(OH)<sub>2</sub> and 0.66 equivalents is significant. Doubling the amount of K approximately doubled the proportion of illite layers in the I/S. However, additional K [1.00 equivalent per O<sub>10</sub>(OH)<sub>2</sub>] had little additional affect. At

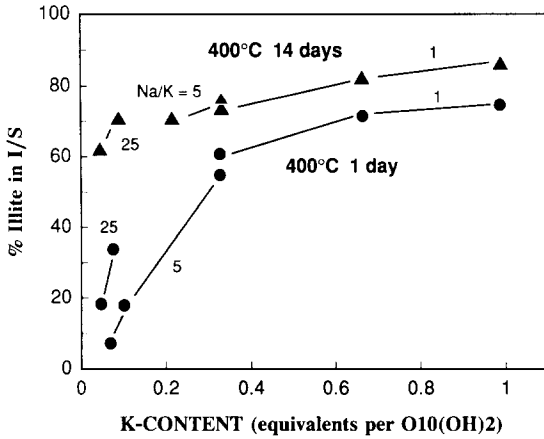


Fig. 5. The effect of K content on the extent of illitization for times of 1 day and 14 days at 400°C. Increasing K content has a strong effect on the extent of the reaction and the effect is strongest at smaller K content. For a particular K content, the Na/K ratio appears to have a minor additional effect.

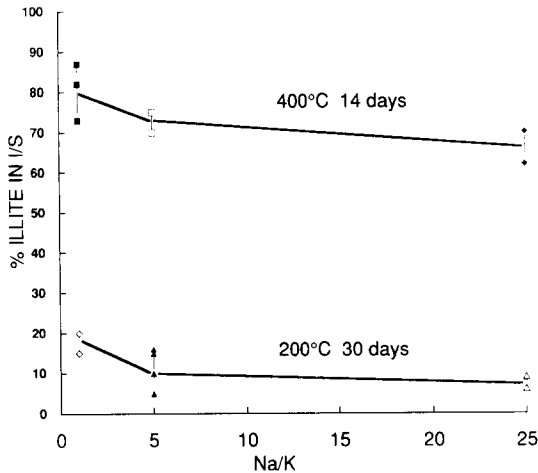


Fig. 6. The effect of Na/K ratio on the extent of the illitization reaction for two temperature-time combinations. For each value of Na/K, the range of values represents different amounts of K present. The effect of Na/K is minor, but measurable.

higher temperatures (Fig. 2b), the amount of K in the system had relatively less effect on the extent of the illitization reaction, especially at longer run times. The effect of K-content for the longest run time (30 days) is summarized in Fig. 3. As Whitney and Northrop (1988) observed, the addition of K in excess of the cation exchange capacity of the starting smectite also retards the formation of chlorite as a byproduct (Fig. 4). In addition to the

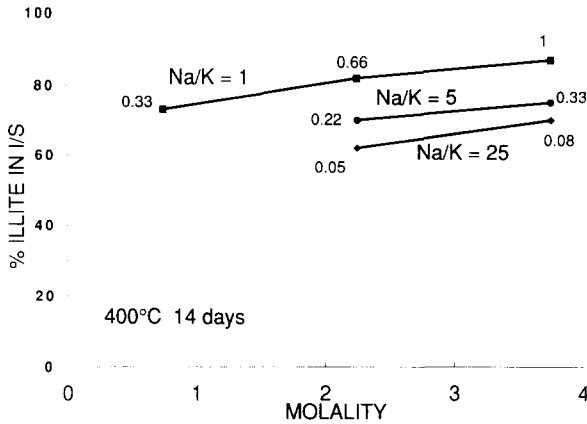


Fig. 7. The effect of ionic strength of the reacting fluids on the extent of illitization after 14 days at 400°C. Na/K ratios are given for each curve, and the numbers by each data point represent the amount of K present in each run [in equivalents per  $O_{10}(OH)_2$ ]. The extent of illitization is approximately the same for each K content, regardless of total solution molality.

production of I/S, small amounts of adularia were also precipitated in the longest runs of the most K-rich [1.00 eq./ $O_{10}(OH)_2$ ] experiments.

In experiments containing mixed Na-K fluids, reaction progress depended upon K-availability and, to a lesser extent, on Na/K ratio. Figure 5 shows the effect of increasing K-availability on the extent of the reaction at two run times at 400°C. The reaction extent clearly increased with K-availability, but there was apparently only a minor effect from the Na/K ratio. In addition, the magnitude of the effect of K-availability decreased as K concentration increased. At the highest K concentrations, adularia formed in addition to the I/S, suggesting that the bulk composition of the high-K experimental run lay within the K-feldspar stability field.

### *Na/K ratio*

Although the Na/K ratio of the reacting solutions may effect reaction progress to some extent, it appears to play a less important role than K-availability. A plot of the proportion of illite layers developed for two time-temperature combinations shows little significant change with increasing Na/K ratio (Fig. 6). Only at very low Na/K values did the reaction appear to progress significantly further, but that is within the range of higher K-content. Thus, it appears that K-availability is the primary factor affecting the reaction progress, while Na/K plays a secondary role.

### *Ionic strength*

The experiments designed to test the effects of ionic strength on the reaction produced ambiguous results, largely because it was not possible to vary only K-availability or only Na/K as a function of solution molality. Figure 7 suggests that increasing molality produced increased illitization for each Na/K ratio, but close examination again reveals that the proportion of illite layers in I/S increased in proportion to the K content. This was demonstrated in Fig. 5. Thus, ionic strength also appears to be of minor importance to the reaction progress relative to K-availability.

### DISCUSSION

Previous work on the reactivity of smectite to I/S has shown that the reaction consists of at least two stages, marked by different reaction mechanisms. Whitney and Northrop (1988) and Inoue et al. (1988) suggested that the first stage of the reaction might consist of an isomorphous transformation of smectite layers into illite layers, whereas the second stage of the reaction is dissolution/precipitation. More recent data (Whitney and Velde, in press) suggests that both stages of the reaction proceed by dissolution/precipitation mechanism, but that the first stage (> 50% expandable layers) is the dissolution of primary smectite layers and precipitation of secondary illite layers, whereas the second stage of the reaction (< 50% expandable layers) is dissolution of small illite particles and growth of larger illite particles according to a process called Ostwald ripening (Eberl and Srodon, 1988; Eberl et al., 1990). Although some important aspects of the overall reaction mechanisms remain unclear, it is important to understand that the reaction of smectite to I/S is not a simple, single-step reaction. Not only do several chemical parameters affect the rates of the multiple fundamental reactions, but may even change the reaction mechanisms.

It would clearly be useful to quantify reaction rates for the overall reactions of smectite to I/S. Illitization reaction curves cannot be fit with first-order or second-order rate laws, but can be fit approximately with fourth- or fifth-order kinetic rate laws (Whitney and Northrop, 1988). Huang et al. (1991) have expressed the reaction in terms of smectite layers ( $S^2$ ) and K content, based on their experimental studies. Pytte and Reynolds (1989), examining the reaction in a natural setting, used a similar expression but used K/Na instead of K and suggested a sixth-order rate law for the overall reaction. Such a forced fit does not adequately describe the overall reaction because of the existence of multiple fundamental reaction mechanisms. Pytte and Reynolds (1989) suggests, in fact, that the overall reaction, while described by an approximately sixth-order rate law, actually consists of a series of reactions with lower-order rate laws. Thus, trying to fit this complicated, multiple-step re-

action with a kinetic expression using a single rate law becomes an exercise of questionable value.

Nevertheless, it is necessary to identify the key variables affecting reaction progress and to gain some quantitative measure of their relative importance. Hower (1981) has concisely described these key variables in general terms: temperature, pressure, pore fluid composition, bulk chemistry of the clay, specific composition of the smectite and time. Studies in both experimental and natural systems have demonstrated that temperature and time are prime variables in the reaction of smectite to interstratified clays (e.g., Eberl and Hower, 1976; Pollastro, 1990). The role of solution parameters is less clear.

The presence of K is a prerequisite for illite formation (Eberl, 1978b; Howard and Roy, 1985), but investigators have suggested that K-availability is a first-order kinetic effect in illitization (Pytte and Reynolds, 1989; Huang et al. 1991). The present experiments suggest that K-content produces a second-order (or higher) effect when illitization is viewed as a single reaction. Again, the overall reaction does not proceed via a single reaction mechanism, so such a formulation must be applied cautiously.

Natural bentonitic smectites have relatively low Na/K ratios. For example, bentonite samples from diverse geologic ages and geographic settings exhibit Na/K ratios of 4.66, 3.73 and 0.56 eq./eq. (van Olphen and Fripiat, 1979). Natural fluids exhibit a broader range: seawater has a Na/K ratio of 45 eq./eq. (Drever, 1982) and Tertiary oilfield brines have an average Na/K ratio of 300 eq./eq. In fact, examination of fluids from a variety of geologic settings shows that the Na/K ratios likely to be encountered in natural waters cover a very large range (White et al., 1963). Thus, the Na/K ratios used in the present experiments (0 to 25) do not cover the entire range likely to be encountered in nature, but do permit an evaluation of the more potassic end of the range. Within this range, the Na/K ratio appears to be much less important than the abundance of K. At much larger Na/K ratios, the reaction may follow the Na-rectorite and paragonite series described by Eberl (1978a).

Ionic strength appears to be almost insignificant in affecting the reaction progress. Baronnet (1984) has pointed out that solubility of primary silicate phases can be enhanced by the presence of a "mineralizer", a complexing agent that may or may not contain some elements of the solute. The presence of a mineralizer may enhance the dissolution of primary minerals, thus accelerating crystal growth processes in which dissolution is a rate-limiting step. He adds, however, that chloride solutions do not enhance solubility of silicates sufficiently to affect the dissolution/precipitation processes. Therefore, increasing ionic strength of chloride solutions did not noticeably speed the illitization process in the present experiments. In natural environments where brines are elevated in some other anion such as sulfate, as in certain Texas Gulf Coast brines (Schmidt, 1973), the ionic strength of interstitial brines

may accelerate the reaction. Additional experiments examining the effects of anions other than chloride would help answer this question.

## CONCLUSIONS

The K content of the reacting system must be reduced virtually to zero to stop the smectite-to-illite reaction. When modelling the illitization reaction using single-reaction, "forced-fit" expressions, it appears that K produces a high-order effect on illitization rather than a first-order effect, as previously suggested. Other solution characteristics such as ionic strength and Na/K ratio appear to play a minor role in illitization reaction progress relative to K-content.

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