

This paper is dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday.

SYNTHESIS OF ILLITE-SMECTITE FROM SMECTITE AT EARTH SURFACE TEMPERATURES AND HIGH pH

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ABSTRACT: It is well known that illite-smectite can form from smectite at elevated temperatures in natural and experimental systems. However, the conversion of smectite to illite-smectite is also found in some natural systems that have never been heated. The present experiments show that illite layers can form from smectite by chemical reaction at 35° and 60°C at high solution pH. The rate of this reaction is accelerated by wetting and drying.

The transformation of smectite into illite-smectite (I-S), generally through the formation of intermediate, randomly interstratified (R0) and ordered (R1) mixed-layer I-S phases, occurs during burial diagenesis (e.g. Hower *et al.*, 1976), during regional metamorphism (e.g. Nadeau & Reynolds, 1981), and during hydrothermal alteration (e.g. Jennings & Thompson, 1986). In addition, hydrothermal synthesis experiments have formed illite from smectite at elevated temperatures (e.g. Whitney & Northrop, 1988). Generally, with increasing time and temperature of alteration, I-S becomes progressively less expandable, becomes R1 ordered at about 30–40% expandable, and becomes R3 ordered at ~15% expandable (Moore & Reynolds, 1989).

The expandability of I-S and the appearance of the different types of ordering have been used as geothermometers in sedimentary basins (Hoffman & Hower, 1979; Pollastro, 1990). However, I-S also occurs in rocks that have never been heated. For example, Singer & Stoffers (1980) found illite neof ormation in saline lake sediments. Turner & Fishman (1991) found I-S having a range of expandabilities and ordering types in altered tuff beds contained in a Jurassic lake in the Morrison Formation (eastern Colorado Plateau, USA); these beds were never buried deeply, and did not undergo hydrothermal alteration. The I-S minerals in this deposit form concentric zones with respect to expandability, from highly smectitic clay (70–100% expandable) in the outermost zone, to highly illitic (0–30% expandable) clay in the central zone, with a variety of expandabilities for I-S in the intermediate zone. The authors stated that these zones generally follow a lateral hydrogeochemical gradient, characterized by increasing salinity and alkalinity from the margin of the lake to the centre. The authors concluded that, in the absence of temperature effects, pore-water chemistry exerted a significant control on the smectite to illite reaction.

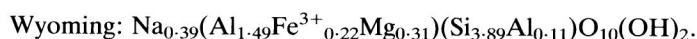
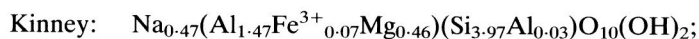
Experiments have shown that one way I-S can form from smectite at the Earth's surface is through wetting and drying (WD) cycles (Eberl *et al.*, 1986). In the presence of K⁺ ions or K-minerals, WD of smectite formed up to ~50% expandable (by X-ray diffraction) R0 I-S.

Reaction progress was proportional to the layer charge of the original smectite. Isotopic and chemical evidence indicated that I-S formed by this mechanism did not undergo chemical reaction, but, rather that illite layers formed in smectite by mechanical rearrangement and irreversible dehydration of high-charge smectite layers around interlayer K^+ . As a part of this study, several experiments were performed in KOH solutions. Illite layer formation at these elevated pH's did not require WD cycles. Chemical and oxygen isotope data for clays reacted in such solutions, but with WD cycles, indicated that the 2:1 layer of the original smectite had undergone dissolution and chemical reaction to yield R0 I-S.

In the present paper, laboratory synthesis experiments were undertaken to explore further the formation of I-S from smectite under highly alkaline conditions with the hope that the results could be applied to the natural setting. Very high pHs were used in order to increase reaction rate.

METHODS

The starting smectites were $<0.1 \mu\text{m}$ fractions of the Kinney bentonite (Khoury & Eberl, 1981) and the Wyoming bentonite (Moll *et al.*, 1975). The Kinney clay is a nearly pure montmorillonite, and the Wyoming clay has a significant component of beidellitic charge. Their structural formulae are (Eberl *et al.*, 1986):



Clay samples weighing 0.5 g were added to 100 ml of basic aqueous solution containing KOH or NaOH with molarities of 0, 0.1, 0.5, 1.0, and 3.0. In addition, some experiments were carried out in 1.0 M KHCO_3 and 1.0 M K_2CO_3 . Reactions were conducted in sealed plastic bottles kept in ovens at 35° and 60°C, with reaction times lasting up to 270 days. The bottles were shaken once a week. In addition, several WD experiments were conducted by mixing 100 ml (for KHCO_3) or 200 ml (for KOH) of 1.0 M solutions with 1.5 g of clay in plastic weighing boats, and then by drying them at 60°C. After drying, fresh distilled water was added, and the drying cycle begun again.

After reaction, samples were washed several times with distilled water, then saturated twice with Sr^{2+} in 0.5 M chloride solutions, and then thoroughly washed until chloride-free. Strontium saturation ensured that all of the K^+ and Na^+ remaining in the clays was non-exchangeable. This saturation also aided X-ray diffraction (XRD) analysis by ensuring 2-component mixed-layering when the samples were glycolated (Eberl *et al.*, 1986, 1987).

Samples were prepared for XRD analysis by drying suspensions on glass slides. These preparations then were glycolated at 60°C overnight. The XRD patterns were obtained using an automated Siemens D500 XRD system employing $\text{Cu-K}\alpha$ radiation, a graphite monochromator, 1° divergence and receiving slits, and Siemens D5000 software. Expandabilities were determined from the difference (Δ) in XRD peak positions for the 001/002 and 002/003 reflections of I-S by the delta two-theta method of Moore & Reynolds (1989, Table 7.3). Expandability was related to Δ by calculating curves using the NEWMOD computer program of R. C. Reynolds, Jr. (available from the author, Dept. of Earth Sciences, Dartmouth College, Hanover, NH, 03755 USA). The default entries in this program were used in the calculation, except that the 16.9 Å and 16.7 Å spacings were used for the swelling layers in Wyoming bentonite and Kinney montmorillonite, respectively. In addition, 9.98 Å was used for K non-expanding layers, and 9.6 Å was used for Na non-

expanding layers. For expandabilities >40%, R0 ordering was used; R1 was used for expandabilities between 40 and 10%, and R3 ordering was used for expandabilities of 10% or less. The curves relating expandability (EXP) to Δ were then fitted to third order polynomial equations ($R^2 = 0.99$ for all equations; regressions contained 11 calculated data points each). The equations are:

$$\text{Kinney (9.98 and 16.7 \AA): EXP} = 1305.1 - 458.6\Delta + 56.78\Delta^2 - 2.44\Delta^3 \quad (1)$$

$$\text{Kinney (9.6 and 16.7 \AA): EXP} = 1576.4 - 579.5\Delta + 74.22\Delta^2 - 3.25\Delta^3 \quad (2)$$

$$\text{Wyoming (9.98 and 16.9 \AA): EXP} = 973.76 - 323.45\Delta + 38.43\Delta^2 - 1.62\Delta^3 \quad (3)$$

$$\text{Wyoming (9.6 and 16.9 \AA): EXP} = 1517.8 - 548.49\Delta + 68.35\Delta^2 - 2.90\Delta^3 \quad (4)$$

Expandabilities calculated from these equations using Δ s measured for unreacted, Sr-saturated, glycolated Kinney and Wyoming starting materials are 94% and 97%, respectively.

Suspensions were dispersed on holey carbon grids for transmission electron microscope (TEM) investigations. Electron microscopy was performed with a Hitachi H800NA TEM operating at 150 kV, fitted with a Kevex Be-window X-ray detector and energy dispersive spectrometer (EDS). Minerals could be identified on the basis of their EDS spectrum.

RESULTS

Results for experiments carried out at 35°C in KOH solutions (Table 1 and Figs. 1 through 3) indicate that both the Kinney and the Wyoming smectite reacted to form randomly

TABLE 1. Results of smectite + KOH experiments at 35°C.

No.	Lab no.	Clay	Molarity	Days	Exp (%)	Comments
1	2K	Kinney	0	118	86	control
2	K9	Kinney	0.1	42	81	
3	8K	Kinney	0.1	118	—	13.8 Å phase
5	K15	Kinney	0.5	42	75	
6	14K	Kinney	0.5	118	92	
7	13K	Kinney	0.5	270	91	contains chloride
8	K21	Kinney	1.0	42	80	
9	20K	Kinney	1.0	118	85	
10	19K	Kinney	1.0	270	83	
11	K27	Kinney	3.0	42	69	
12	26K	Kinney	3.0	118	—	13.3 Å phase
14	2W	Wyoming	0	118	97	control
15	W9	Wyoming	0.1	42	92	
16	8W	Wyoming	0.1	118	97	
17	7W	Wyoming	0.1	270		
18	W15	Wyoming	0.5	42	90	peak at 3.53 Å
19	W14	Wyoming	0.5	118	92	weak higher orders
20	13W	Wyoming	0.5	270	93	
22	20W	Wyoming	0.5	118	93	
24	W27	Wyoming	3.0	42	87	
25	26W	Wyoming	3.0	118	77	
26	25W	Wyoming	3.0	270	74	peak at 12.10 Å

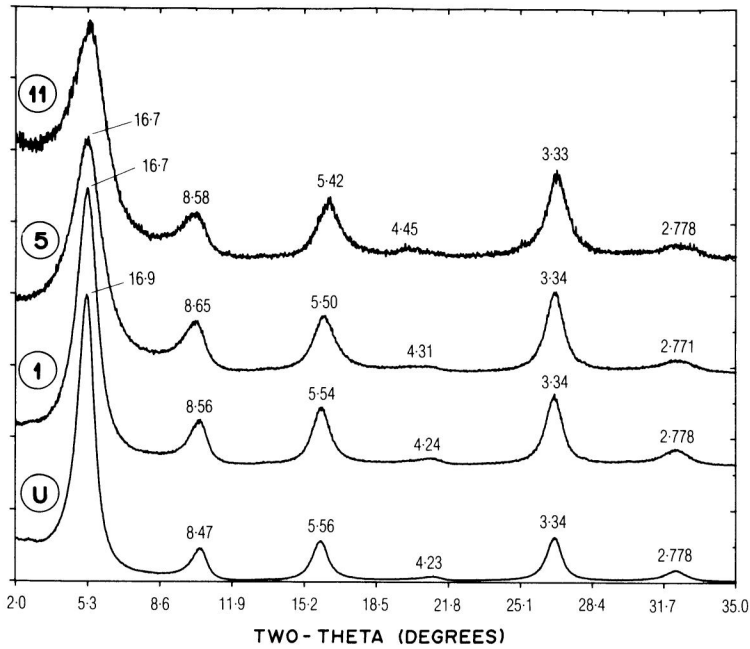


FIG. 1. XRD patterns of Kinney montmorillonite reacted at 35°C in water in KOH solutions. Peaks labelled in Å units. Circled numbers refer to numbered runs in Table 1. U is untreated clay.

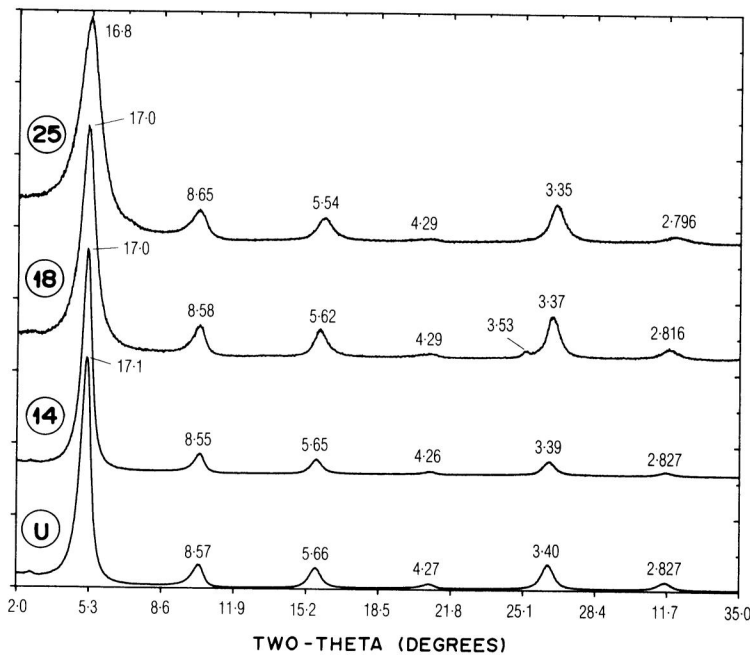


FIG. 2. XRD patterns of Wyoming smectite reacted at 35°C in water and in KOH solutions. Peaks labelled in Å units. Circled numbers refer to numbered runs in Table 1. U is untreated clay.

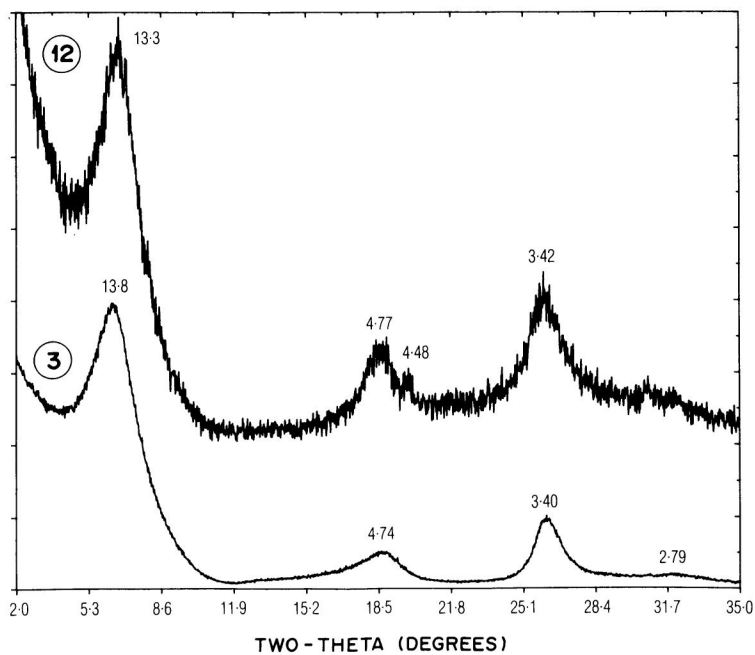


Fig. 3. XRD patterns of 13 Å phases formed from Kinney montmorillonite reacted at 35°C in water and in KOH solutions in runs 3 and 12 (Table 1).

interstratified I-S at Earth surface temperatures. Reaction most likely affected the chemistry of the 2:1 layers, because previous experiments indicated that these smectites will not form illite layers that are stable against Sr^{2+} -exchange simply by K^+ -saturation, and that reaction in KOH solutions will increase smectite layer charge (Eberl *et al.*, 1986).

The XRD maxima for clays in most experiments decreased strongly in absolute intensity with increasing degree of alteration (although this is not evident from the XRD patterns presented because of manipulation of the intensity scale), thereby indicating that clays dissolved during the experiments. There was a general decrease in expandability of R0 I-S with increasing KOH molarity and with increasing reaction time, although this pattern was not completely consistent, and therefore rate constants could not be calculated. The lack of more consistent kinetic results may indicate experimental problems (e.g. the need for more careful control of shaking), or could result from the measurement technique used to follow the reaction (expandability). Expandability can be influenced by several factors, including the thickness of fundamental illite particles that diffract coherently in mixed-layer crystals (MacEwan crystallites), the *ab* area of the fundamental illite particles, and the number of fundamental illite particles that stack on top of each other in MacEwan crystallites (Nadeau *et al.*, 1984; Środoń *et al.*, 1992). Therefore expandability may not be a precise measure of reaction progress, because it is sensitive not only to the amount of illite layers in the sample, but also to the arrangement of these layers on the slide used for XRD.

Chlorite formed in one run (no. 7), as did some minor, unidentified phases in other runs (Table 1) which could not be identified with certainty from the JCPDS XRD file. Efforts to identify these phases were not pursued because they were present in minor amounts, and because they were not of immediate interest for the present experiments. However, the

positions of their XRD peaks are listed in the tables or in the figures. A curious 13 Å phase replaced smectite in the longest runs for the Kinney montmorillonite in the 0.1 and 3.0 M KOH solutions (runs no. 3 and no. 12 in Table 1 and Fig. 3).

The Wyoming clay appears to have been more resistant to illite formation than was the Kinney: the Wyoming reacted to a minimum expandability of 74% after 270 days in 3 M KOH solution, whereas the Kinney reacted to a minimum expandability of 69% after only 42 days in the same type of solution. According to the XRD data, the Kinney even appears to have decreased in expandability by ~8% (from 94–86% expandable) when reacted in pure water without K⁺ present (run no. 1, Table 1). Reaction of the Kinney smectite in pure water proceeded even farther at 60°C (to 70% expandable; run no. 41 in Table 3). The Wyoming smectite showed no tendency to react in pure water at any temperature (runs 14, 34 and 52, Tables 1, 2 and 3).

Results for experiments carried out at 35°C in NaOH solutions (Table 2 and Fig. 4) indicate that both the Kinney and the Wyoming smectite reacted with Na⁺ to form random interstratifications containing Na-non-expanding layers at Earth surface temperatures. The minimum expandability attained in the NaOH system was 81% after 118 days in 0.5 M solution (run 29, Table 2).

Raising the temperature from 35° to 60°C in KOH systems generally increased the rate of illite formation (compare Tables 1, 3 and 4). In the 60°C, 28 day, 3.0 M KOH experiments (Table 3 and Figs. 5 and 6), ordered (R1) I-S appeared for both the Kinney and the Wyoming clays, and expandability decreased to a minimum value for the experiments of 33%. Under these conditions, the Kinney clay formed a mixture of R0 and R1 I-S (Fig. 5, run 47), whereas the Wyoming formed a purely R1 structure, plus a small amount of discrete illite (Fig. 6, run 58). Longer runs of the Kinney and Wyoming clays in the same solutions (3.0 M KOH) at 60°C rendered these clays amorphous (runs 62 and 68, Table 4), indicating that the R1 structures formed in the shorter runs were non-equilibrium products.

A TEM photo (Fig. 7A) of R1 I-S formed from the Wyoming clay in run 58 (Fig. 6) shows a general dissolution texture, with many embayments on the edges of anhedral flakes. The presence of equidimensional, euhedral, authigenic illite crystals, reported previously for

TABLE 2. Results of smectite + NaOH experiments at 35°C.

No.	Lab no.	Clay	Molarity	Days	Exp (%)	Comments
27	K3	Kinney	0	42	89	control
28	K33	Kinney	0.5	42	95	peaks at 3.52, 3.47, 3.02, 4.36 Å
29	32K	Kinney	0.5	118	81	peak at 2.97 Å
30	K39	Kinney	1.0	42	97	peak at 3.53 Å
31	38K	Kinney	1.0	118	89	
32	K45	Kinney	3.0	42	93	
33	44K	Kinney	3.0	118	85	
34	W3	Wyoming	0	51	97	control
35	W33	Wyoming	0.5	42	94	peaks at 3.52, 3.47, 3.01, 4.35, 4.27 Å
36	32W	Wyoming	0.5	118	92	
37	W39	Wyoming	1.0	42	91	
38	38W	Wyoming	1.0	118	85	
39	W45	Wyoming	3.0	42	84	
40	W44	Wyoming	3.0	118	83	

TABLE 3. Experiments conducted for 28 days at 60°C, some with wetting and drying cycles.

No.	Lab no.	Clay	Solution	Cycles	Exp (%)	Comments
41	61	Kinney	water	0	70	control
42	lit. ¹	Kinney	water	10	74	K-saturated
43	63	Kinney	0.5 M KOH	0	80	
44		Kinney	0.5 M KOH	6	—	amorphous
45	64	Kinney	1.0 M KOH	0	62	other phases ²
46	B	Kinney	1.0 M KOH	6	—	amorphous clay, others ³
47	65	Kinney	3.0 M KOH	0	33?	R1 + R0, others (Fig. 5)
48	67	Kinney	1.0 M KHCO ₃	0	92	peaks at 3.43, 3.54, 2.97 Å
49	D	Kinney	1.0 M KHCO ₃	6	57	peak at 2.97 Å
51	C	Kinney	1.0 M K ₂ CO ₃	6	50	peak at 2.97 Å
52	70	Wyoming	water	0	99	control
53	lit. ¹	Wyoming	water	100	97	K-saturated
55	72	Wyoming	0.5 M KOH	0	95	peaks at 7.14, 3.57 Å
56	73	Wyoming	1.0 M KOH	0	87	
57	A	Wyoming	1.0 M KOH	6	—	amorphous clay, others ⁴
58	74	Wyoming	3.0 M KOH	0	33	R1 ordered, others (Fig. 6)

¹ Previous experiment from Eberl *et al.*, 1986.

² Additional peaks at 3.30, 3.34, 3.175, 2.97, 2.74, 3.76 Å

³ Additional peaks at 3.81, 3.43, 3.30, 3.18, 2.97, 2.73 Å

⁴ Additional peaks at 4.52, 4.26, 3.76, 3.44, 3.30, 3.10, 2.97, 2.734, 2.674, 2.611 Å

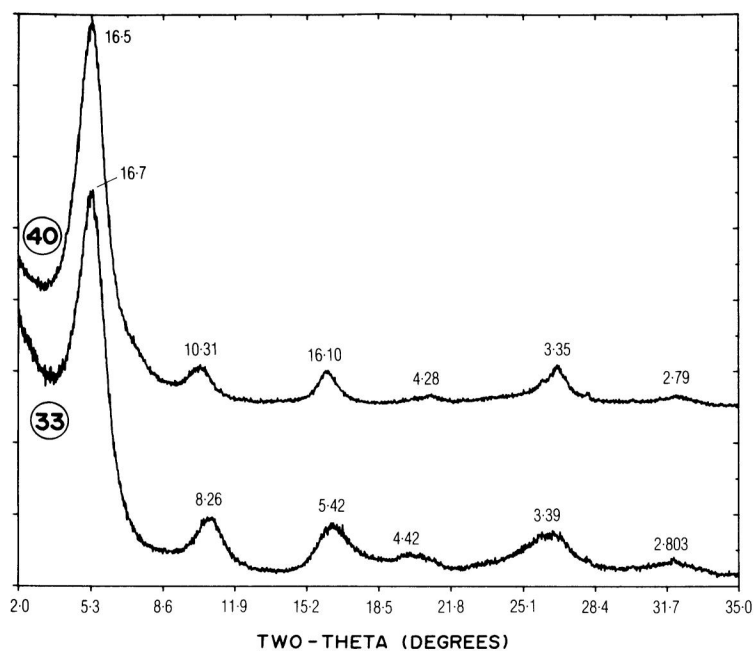


FIG. 4. XRD patterns of Kinney montmorillonite (bottom) and Wyoming smectite (top) reacted at 35°C in NaOH solutions. Peaks labelled in Å units. Circled numbers refer to numbered runs in Table 2.

TABLE 4. Results of smectite experiments at 60°C for 150 days.

No.	Lab no.	Clay	Solution	Exp (%)	Comments
59	62'	Kinney	0.1 M KOH	90	
60	63'	Kinney	0.5 M KOH	88	
61	64'	Kinney	1.0 M KOH	64	trace of R1
62	65'	Kinney	3.0 M KOH	—	amorphous
64	70'	Wyoming	0	97	control
65	71'	Wyoming	0.1 M KOH	92	
68	74'	Wyoming	3.0 M KOH	—	amorphous

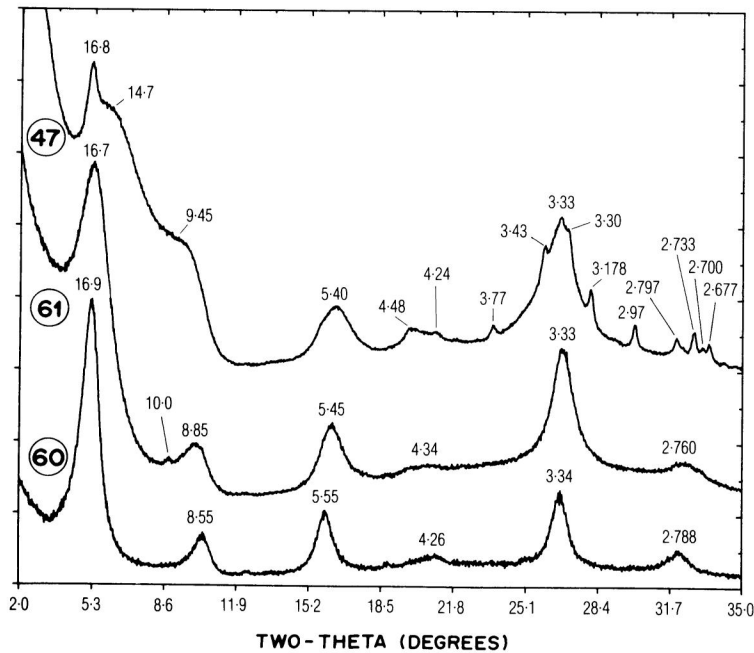


FIG. 5. XRD patterns of Kinney montmorillonite reacted at 60°C in KOH solutions. Peaks labelled in Å units. Circled numbers refer to numbered runs in Tables 3 and 4.

the appearance of R1 ordered I-S in Gulf Coast shales (Freed & Peacor, 1992), was not detected in this run product, thereby suggesting that a mechanism other than neoformation may have been involved in the present experiments. Indeed, Inoue *et al.* (1990) suggested that R1 I-S can form by a solid-state transformation mechanism. Also seen in this product were rare, hexagonal mica grains (Fig. 7B) which are thought to be detrital, because the Wyoming bentonite rock contains detrital biotite (Gene Whitney, US Geological Survey, personal communication).

Because the solution compositions used in the above experiments are unrealistic for natural systems, wetting and drying (WD) experiments were conducted with clay placed initially in 1 M KHCO_3 and K_2CO_3 solutions. During the drying cycle, pH should have been

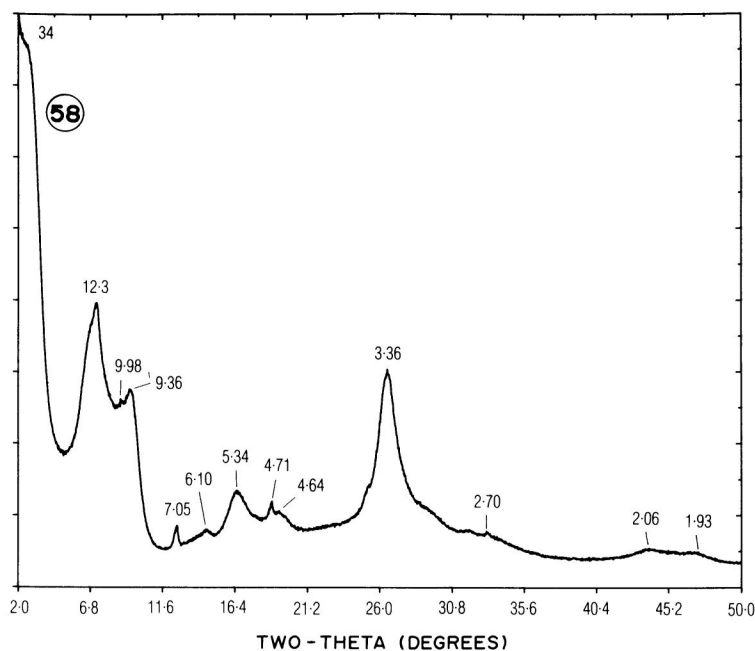


Fig. 6. R1 ordered I-S formed from Wyoming smectite in 3.0 M KOH at 60°C in run no. 58 (Table 3).

buffered in these systems at saturation values, which were measured at room temperature to be 8.82 for the KHCO_3 system and 13.68 for the K_2CO_3 system. The WD experiments made at 60°C with six WD cycles (Table 3) demonstrate that WD effectively increases reaction rate. The WD experiments with KOH rendered the clays amorphous. However, WD experiments with K_2CO_3 for the Kinney clay decreased expandability in I-S to values as low as 50% after only six cycles (run 51 in Fig. 8). Runs of the Kinney in KHCO_3 after 28 days at 60°C with no wetting and drying barely reacted, whereas with wetting and drying a 57% expandable I-S formed (runs 48 and 49, Table 3 and Fig. 8).

CONCLUSIONS

Illite-smectite can form from smectite at Earth surface temperatures at elevated pH. Therefore solution chemistry, as well as temperature, should be considered when making geological interpretations based on the expandability of I-S. Most of the present experiments were conducted in solutions that are geologically unrealistic. However, it would not be unusual for smectite eroded in desert regions to undergo WD cycles in carbonate-bicarbonate-rich waters that contain K^+ ions. Extreme solution chemistries thereby could develop during drying cycles, and, as the experiments demonstrate, readily transform smectite into I-S of lower expandability.

The experimental results may also be applicable to the effect of alkaline flooding for enhanced oil recovery on smectite in reservoir rocks (Kumar *et al.*, 1989; Mohnot *et al.*, 1987), and to the engineering of radioactive waste disposal sites that use smectite in combination with cement barriers in their design (Savage *et al.*, 1992). Cement pore-waters

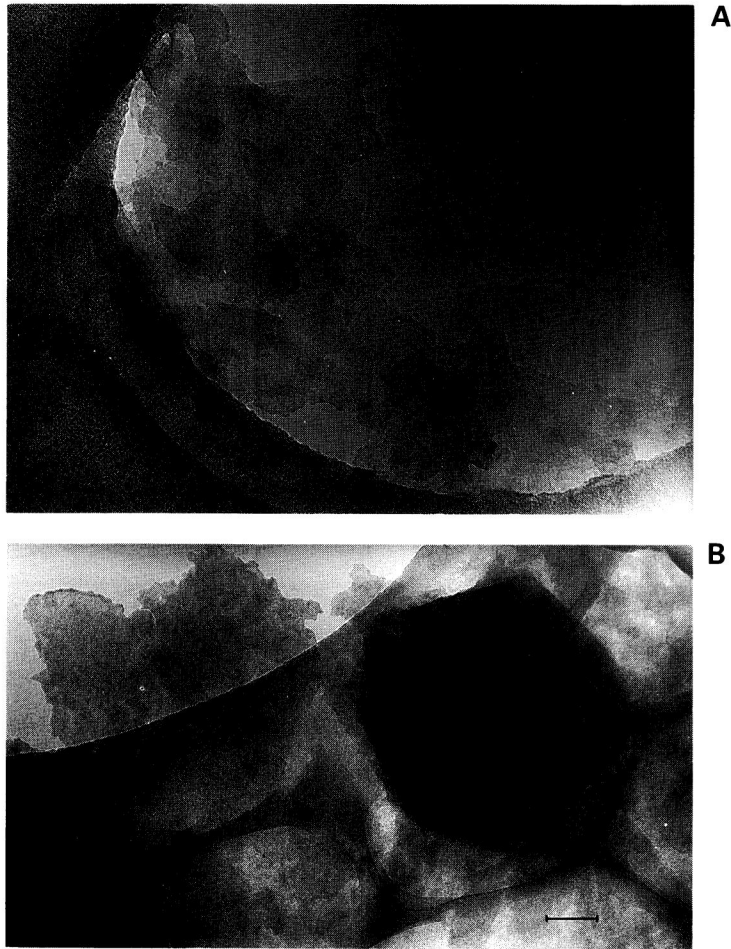


FIG. 7. TEM photos of R1 ordered I-S (A) and detrital (?) biotite (B) found in run no. 58 (Table 3). Samples were photographed on holey carbon grids. Scale bars = 0.1 μm .

have high pH (12.4–13.5), high ionic strength (up to 0.3), and high K- and Na-ion concentrations (Andersson *et al.*, 1989; Lunden & Andersson, 1989). Therefore smectite barriers may lose some of their desirable properties, which include high sorptivity, longevity, and low permeability (Lee & Tank, 1985), by reaction with such waters to form I-S of low expandability and/or amorphous materials.

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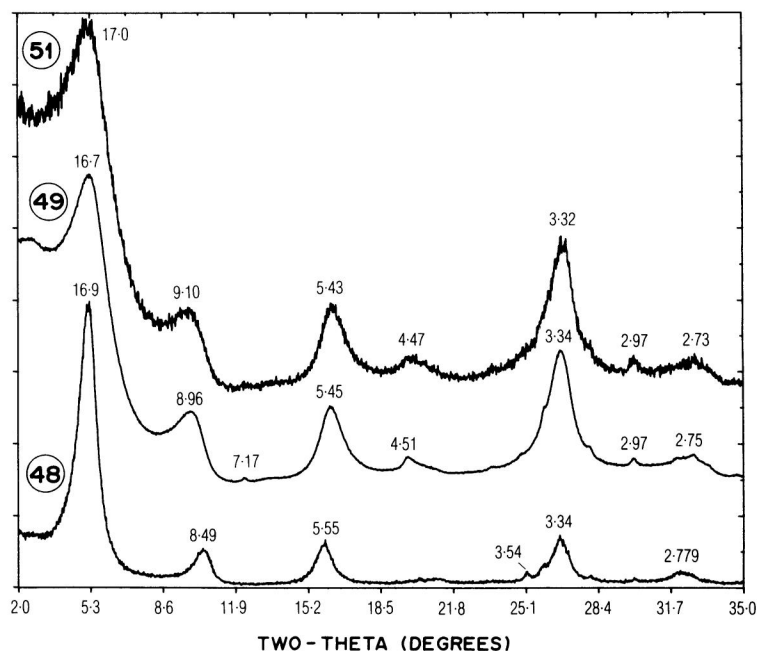


FIG. 8. XRD patterns of Kinney montmorillonite subjected to wetting and drying cycles in KHCO_3 (bottom two patterns) and K_2CO_3 (top pattern) solutions. See Table 3.

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