

POTASSIUM FIXATION BY CLAY MINERALS DURING HYDROTHERMAL TREATMENT

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Abstract—The amount of K fixed in K- and Ca-saturated montmorillonite, vermiculite (trioctahedral), rectorite-type and IMII-ordered mica/montmorillonites was measured as a function of time (1–64 days), temperature (25°–300°C), pH (6.0, 9.7, and 10.7), and K-concentration (0.02 and 1.0 M) in solution. The amount of K fixed by the clays generally increased with increasing temperature, pH, and K-concentration and reached saturation in response to each experimental condition in 5 or 6 days. The K-montmorillonite and K-vermiculite fixed considerable amounts of K even at 25°C. Fixed K in montmorillonite increased with an increase of the layer charge which is also influenced significantly by the interlayer cation. In detail, the behavior in K-fixation was specific to each clay.

The type of structural transformation with K-fixation was different for each clay. In montmorillonite, especially, the type of transformation was related to the cationic composition of the system; in K homoionic system, montmorillonite transformed rapidly into illite/montmorillonite with about 40% expandable layers at 300°C and in a mixed cation system with Ca and K, it reacted gradually to random illite/montmorillonites with increasing temperature. These data indicate that the cation-exchange process of a natural pore solution plays an important role in the gradual transformation of detrital montmorillonite to illite.

Key Words—Diagenesis, Fixation, Hydrothermal, Interstratification, Montmorillonite, Potassium, Rectorite.

INTRODUCTION

It is well known that specific cations are fixed in the interlayer of clay minerals such as montmorillonite and vermiculite (Mackenzie, 1963; Grim, 1968). In most previous studies, cation fixation was examined using oven-dried clays. Several factors affect cation fixation, e.g., octahedral occupancy, layer charge, properties of the solvent, and properties of the cations (Marshall, 1964). The layer charge required for fixation of alkali cation was predicted quantitatively by Eberl (1980) on the basis of an interplay between cation hydration energy and layer charge, assuming that the charge on interlayer sites can be represented as a sphere of equivalent electric field strength.

Of those cations that become fixed, K is of greatest interest to most geologists and clay mineralogists. Montmorillonite transforms to illite through a series of interstratified phases in sedimentary basins (Burst, 1959, 1969; Perry and Hower, 1970; Weaver and Beck, 1971; Hower *et al.*, 1976; Yeh and Savin, 1977), and in hydrothermal environments (Steiner, 1968; Browne and Ellis, 1970; Eslinger and Savin, 1973; Inoue *et al.*, 1978). During the transformation, exchangeable cations such as Na⁺ and Ca²⁺ in the interlayer of montmorillonite are replaced by K⁺ from the pore solution, and the K⁺ is gradually fixed.

Eberl and Hower (1976) and Roberson and Lahann (1981) studied the structural change from smectite to illite in the laboratory from a kinetic point of view. The effects of interlayer cations on the reaction of montmorillonite to interstratified phases were also examined

by Eberl (1978a, 1978b). In addition, Lahann and Roberson (1980) determined the effect of solution chemistry for the dissolution of Si from montmorillonite under hydrothermal conditions.

The purpose of the present investigation was to determine the factors that control the amount of K fixed by clay minerals under hydrothermal conditions, and to clarify the mechanism of K-fixation. A final goal was a better understanding of the mechanism of illitization of montmorillonite through interstratified intermediates during burial diagenesis.

MATERIALS AND METHODS

Four clays were employed in this study: montmorillonite from Aterazawa in Yamagata Prefecture, Japan; trioctahedral vermiculite from Palabora in South Africa; a rectorite-type regularly interstratified mineral with 50% expandable layers from Goto Mine, Nagasaki Prefecture, which contained sericite and pyrophyllite as major impurities; and an interstratified illite/montmorillonite similar to the IMII-ordered type (Reynolds and Hower, 1970) from Seigoshi Mine, Shizuoka Prefecture. The interstratified illite/montmorillonite contained about 20% expandable layers and small amounts of quartz and goethite as impurities. The rectorite-type interstratified mineral initially contained significant amounts of Na and Ca as well as K fixed in the interlayer position (Tables 1 and 2). All samples were saturated with K⁺ or Ca²⁺.

Hydrothermal experiments were carried out in Morrey-type reaction vessels of approximately 11-ml capac-

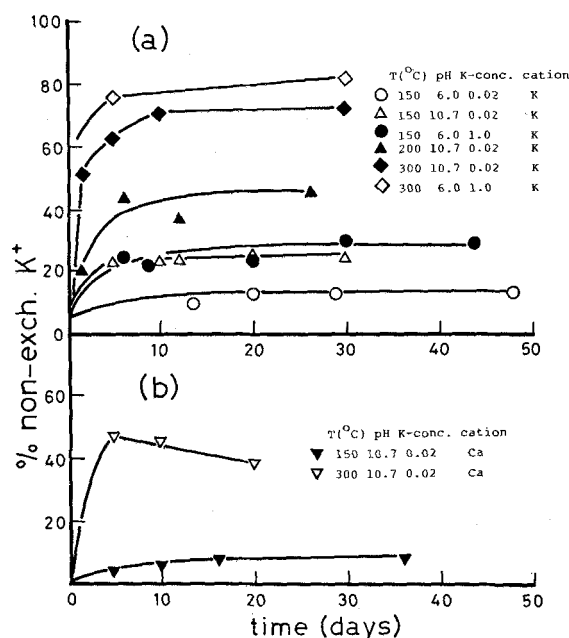


Figure 1. Percentage of non-exchangeable K vs. time for (a) K- and (b) Ca-montmorillonites under various temperatures, initial pHs, and K-concentrations.

ity and Teflon reaction vessels of approximately 22-ml capacity at 100°, 150°, 200°, and 300°C. The internal pressure was the vapor pressure of H₂O at the temperatures of the experiment. About 200 mg of starting materials and about 21 ml of reaction solution were put in the Teflon vessels; the same solid : solution ratio was used for the autoclave experiments. The initial pH of the solution was 6.0, 9.7 or 10.7; and the cation concentration was 0.02 or 1.0 M of K⁺, as the chloride or hydroxide. The hydrothermally treated clay was washed with distilled water, dried at room temperature, and stored in 100 ml of 0.1 N SrCl₂ solution at room temperature for a week. Under the conditions, most of exchangeable cations in the interlayer of clays were substituted by Sr. The Sr-substituted clays were analyzed for Sr, K, Ca, and Na by atomic absorption spectroscopy; the bulk chemical compositions for some of the specimens were also determined. The percentage of expandable layers in the Sr-substituted products was determined after ethylene glycol treatment, and the relation between X-ray powder diffraction (XRD) peaks and percentage of expandable layers was calculated using the Kakinoki and Komura equation (Sato, 1973).

EXPERIMENTAL RESULTS

Effect on non-exchangeable K

Changes in the percentage of non-exchangeable K (%NEK) under the various experimental conditions are summarized in Table 1. %NEK represents the amount

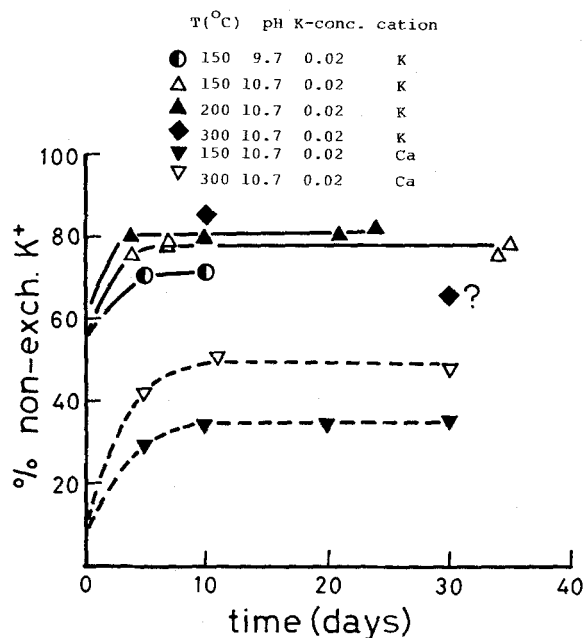


Figure 2. Percentage of non-exchangeable K vs. time for K-(solid curves) and Ca- (dashed curves) vermiculites under various temperatures, initial pHs, and K-concentration.

of non-exchangeable K ion divided by the total amount of interlayer cations times 100. In montmorillonite and vermiculite, small amounts of Na and Ca were retained after Sr-substitution, as shown in the table, but the Na and Ca contents in K-saturated specimens cannot be correlated with temperature or reaction time; therefore, their effects are neglected in the following discussion.

The %NEK values in K- and Ca-montmorillonites are plotted against time in Figure 1. In K-montmorillonite, the %NEK values increased with increasing temperature, pH, and initial K-concentration in solution; they leveled off after reaction for about 5 or 6 days. The change of %NEK in Ca-montmorillonite was similar to that in K-montmorillonite, but the %NEK values in the former stayed smaller than those in the latter under the same experimental conditions. In detail, Ca-montmorillonite did not fix K at room temperature, whereas some K-fixation took place in K-montmorillonite (Table 1). The %NEK in Ca-montmorillonite at 300°C increased for 5 days and then decreased.

In general, the final change of %NEK in the vermiculites (Figure 2) was nearly the same as that in the montmorillonites, but at room temperature, it was larger in K-vermiculite than in K-montmorillonite. A decrease in %NEK in Ca-vermiculite was not observed at 300°C.

Figure 3 shows the change of %NEK in the rectorite-type and IMII-ordered phases. The %NEK values did not increase in either the K- or Ca-saturated rectorite-type specimen at T = 100°–150°C, pH = 6.0–10.7, and K-concentration = 0.02 M, but increased at 300°C in

Table 1. Experiments determining percentage of non-exchangeable K ion.

Specimen	T(°C)	Initial pH	Initial conc. of K ion (M)	Duration (day)	Interlayer cations (meq/100 g)				sum.	% Non-exch. K ion	% Exp. layer
					Sr	K	Na	Ca			
K-mont.	25				65.4	4.1	1.3	—	70.8	5.8	100
Ca-mont.	25				72.1	—	—	2.3	74.4	0.0	100
K-verm.	25				63.5	77.2	1.3	—	142.0	54.4	100
Ca-verm.	25				106.4	9.4	10.0	6.4	132.2	7.1	100
K-mixed G ¹	25				16.8	126.4	18.7	17.8	179.7	70.3	50
K-mixed S ²	25				16.6	123.0	19.0	—	158.6	77.6	20
K-mont.	150	6.0	0.02	13	62.1	7.5	2.3	—	71.9	10.4	100
	150	6.0	0.02	20	62.9	10.4	6.1	—	79.4	13.1	100
	150	6.0	0.02	29	55.3	9.0	3.9	—	68.2	13.2	100
	150	6.0	0.02	48	65.2	10.9	2.9	—	79.0	13.8	100
	150	10.7	0.02	6	58.8	20.5	3.9	—	83.2	24.6	100
	150	10.7	0.02	9	59.0	17.9	4.2	—	81.1	22.1	100
	150	10.7	0.02	20	58.2	19.8	5.8	—	83.8	23.6	100
	150	10.7	0.02	30	45.7	21.7	3.2	—	70.6	30.7	100
	150	10.7	0.02	43	57.3	24.3	2.3	—	83.9	29.0	100
	150	6.0	1.0	5	36.0	11.9	2.6	—	50.5	23.6	100
	150	6.0	1.0	10	39.9	13.6	3.9	—	57.4	23.7	100
	150	6.0	1.0	12	65.0	21.3	1.9	—	88.2	24.2	100
	150	6.0	1.0	20	50.6	18.8	3.6	—	73.0	25.8	100
	150	6.0	1.0	30	46.1	17.5	3.4	—	67.0	26.1	100
	200	10.7	0.02	1	49.5	20.8	7.4	21.0	98.7	21.1	>90
	200	10.7	0.02	6	43.3	37.7	3.9	—	84.9	44.4	>90
	200	10.7	0.02	12	38.6	26.0	5.5	—	70.1	37.1	>90
	200	10.7	0.02	26	37.4	37.9	5.5	—	80.8	46.9	>90
	300	9.7	0.02	9	36.2	85.7	6.4	—	128.3	66.8	~40
	300	10.7	0.02	1	37.0	78.5	10.7	25.0	151.2	51.9	~50
	300	10.7	0.02	5	34.0	56.3	—	—	90.3	62.3	~40
	300	10.7	0.02	10	24.0	59.7	1.0	—	84.7	70.5	~40
	300	10.7	0.02	30	33.1	96.6	4.2	—	133.9	72.1	~40
	300	6.0	1.0	5	32.6	99.8	tr.	—	132.4	75.4	~40
	300	6.0	1.0	30	22.6	97.7	—	—	120.3	81.2	~30
Ca-mont.	150	10.7	0.02	5	70.3	3.0	4.2	—	77.5	3.9	100
	150	10.7	0.02	10	62.9	4.0	—	1.8	68.7	5.8	100
	150	10.7	0.02	16	53.7	5.5	10.0	17.8	87.0	6.3	100
	150	10.7	0.02	36	50.0	5.7	4.8	10.0	70.5	8.1	~95
	300	9.7	0.02	9	40.4	23.9	12.2	27.4	103.9	23.0	~90
	300	10.7	0.02	5	49.0	56.7	2.9	12.8	121.4	46.7	~90
	300	10.7	0.02	10	47.6	59.3	2.9	22.4	132.2	44.9	~80
	300	10.7	0.02	20	43.5	48.6	1.3	35.6	129.0	37.7	~70
K-verm.	150	9.7	0.02	5	36.6	98.0	1.3	3.2	139.1	70.5	50
	150	9.7	0.02	10	33.5	88.2	1.9	—	123.6	71.4	50
	150	10.7	0.02	4	38.0	128.2	2.9	—	169.1	75.8	50
	150	10.7	0.02	7	30.0	126.8	4.8	—	161.6	78.5	50
	150	10.7	0.02	7	33.5	119.8	3.2	—	156.5	76.6	50
	150	10.7	0.02	34	21.5	92.3	8.7	—	122.5	75.4	50
	150	10.7	0.02	35	40.1	174.1	4.8	—	219.0	79.5	50
	200	10.7	0.02	4	29.6	126.2	1.6	—	157.4	80.2	50
	200	10.7	0.02	10	14.5	112.5	15.2	—	142.2	79.1	50
	200	10.7	0.02	21	13.9	84.5	6.5	—	104.9	80.6	50
	200	10.7	0.02	24	19.1	104.0	3.6	—	126.8	82.1	50
	300	10.7	0.02	10	12.8	162.4	—	15.3	190.5	85.3	<5
	300	10.7	0.02	30	43.2	105.5	3.5	10.0	162.2	65.1	<5
Ca-verm.	150	10.7	0.02	5	99.6	46.7	9.0	3.6	158.9	29.4	
	150	10.7	0.02	10	77.0	44.8	6.1	3.2	131.1	34.2	
	150	10.7	0.02	20	58.1	43.3	23.5	—	124.9	34.7	
	150	10.7	0.02	30	81.8	48.4	1.6	2.9	134.7	35.9	
	300	10.7	0.02	5	36.8	57.8	6.1	37.8	138.5	41.7	
	300	10.7	0.02	11	39.7	60.1	4.5	12.8	117.1	51.3	
	300	10.7	0.02	30	14.1	94.2	6.1	85.9	199.5	47.2	

Table 1. Continued.

Specimen	T(°C)	Initial pH	Initial conc. of K ion (M)	Duration (day)	Interlayer cations (meq/100 g)					% Non-exch. K ion	% Exp. layer
					Sr	K	Na	Ca	sum.		
K-mixed G	100	6.0	0.02	9	17.4	129.8	19.0	25.3	191.5	67.8	50
	100	6.0	0.02	20	17.4	130.0	17.7	24.6	189.7	68.5	50
	100	6.0	0.02	29	21.7	133.6	20.9	24.6	200.8	66.5	50
	100	6.0	0.02	41	17.0	131.5	19.6	24.6	192.7	68.2	50
	150	6.0	0.02	19	18.2	134.7	18.7	26.4	198.0	68.0	50
	150	6.0	0.02	28	17.8	127.9	18.4	20.3	184.4	69.4	50
	150	6.0	0.02	34	18.4	132.4	18.7	26.4	195.9	67.6	50
	150	6.0	0.02	48	17.4	129.6	18.7	26.4	192.1	67.5	50
	150	10.7	0.02	7	17.8	129.2	20.3	24.6	191.9	67.3	50
	150	10.7	0.02	11	18.2	132.8	61.0	26.0	238.0	55.8	50
	150	10.7	0.02	20	17.8	130.9	18.0	19.6	186.3	70.3	50
	150	10.7	0.02	28	19.7	129.8	22.2	7.1	178.8	72.6	50
	150	10.7	0.02	41	19.4	129.2	18.0	21.0	187.6	68.9	50
	300	10.7	0.02	10	12.4	114.0	11.6	16.0	138.0	82.6	~50
	300	10.7	0.02	20	15.7	147.1	5.2	16.0	184.0	80.0	~50
300	10.7	0.02	27	17.6	123.8	0.6	5.0	147.0	84.2	~50	
Ca-mixed G	150	10.7	0.02	19	15.9	121.5	16.8	24.2	178.4	68.1	50
	150	10.7	0.02	36	13.7	93.8	14.2	21.0	142.7	65.7	50
	150	10.7	0.02	49	18.2	127.9	15.1	29.6	190.8	67.0	50
	150	10.7	0.02	64	15.1	123.6	13.5	21.4	173.6	71.2	50
K-mixed S	100	6.0	0.02	10	16.5	124.5	20.6	—	161.6	77.0	20
	100	6.0	0.02	22	15.5	122.8	19.6	—	157.9	77.8	20
	100	6.0	0.02	31	16.5	122.1	20.0	—	158.6	77.0	20
	100	6.0	0.02	45	21.1	123.6	19.3	—	164.0	75.4	20
	150	10.7	0.02	5	16.3	123.2	18.4	—	157.9	78.0	20
	150	10.7	0.02	11	16.8	129.2	21.6	—	167.6	77.1	20
	150	10.7	0.02	29	17.0	128.5	20.3	—	165.8	77.5	20
	150	10.7	0.02	33	17.2	125.3	21.6	—	164.1	76.4	20
	300	10.7	0.02	10	16.3	140.5	19.3	—	176.1	79.8	~20

¹ K-interstratified mineral from Goto Mine.

² K-interstratified mineral from Seigoshi Mine.

the K-saturated specimen (Figure 3a). The %NEK value in the IMII-ordered phase was nearly invariant up to 150°C and increased only slightly at 300°C (Figure 3b).

As shown in Figures 1–3, the %NEK values in the clays tend to attain a saturation at short reaction time under the respective experimental conditions. For determining the exact temperature dependence of the saturated %NEK in the clays, the corrected %NEK ($\Delta\%$ NEK) at pH = 10.7 and K-concentration = 0.02 M are plotted against ΔT ($=T - 25^\circ\text{C}$) in Figure 4. $\Delta\%$ NEK represents a difference between %NEK values at T°C and 25°C. The increase of $\Delta\%$ NEK with increasing ΔT is accelerative in the montmorillonites (Figure 4a) and decelerative in the vermiculites (Figure 4b). In addition, the %NEK value in K-montmorillonite was greater than that in Ca-montmorillonite at a given temperature, but the reverse was found in the vermiculites. The increase of %NEK in the rectorite-type specimen was greater than in the IMII-ordered specimen.

Effect on $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios

The bulk chemical compositions of the reaction products at pH = 10.7 and K-concentration = 0.02 M are given in Table 2. The Fe_2O_3 and MgO contents of the montmorillonites remained nearly constant during the reactions at any temperature. The SiO_2 content decreased gradually during the reaction at a given temperature. The Al_2O_3 content increased with increasing temperature and tended to increase slightly during the reaction at a given temperature. As a result, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios in the products (Table 2) decreased with increasing temperature and only slightly during the reaction. The decrease in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the K-montmorillonite was more than that in the Ca-montmorillonite at 300°C.

In the vermiculites, the SiO_2 , Al_2O_3 , and Fe_2O_3 contents increased and, contrary to that of MgO, decreased with increasing temperature. The change of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is uncertain because of a lack of data. On the basis of a few analyses (Table 2), the $\text{SiO}_2/\text{Al}_2\text{O}_3$

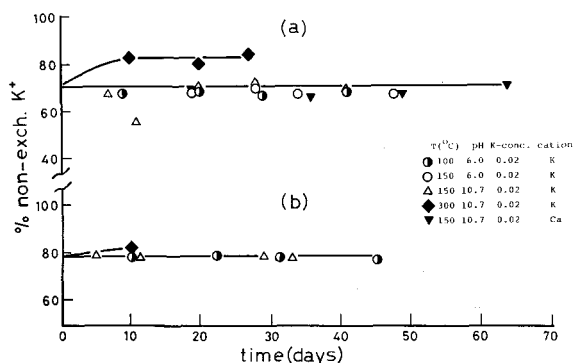


Figure 3. Percentage of non-exchangeable K vs. time for K- and Ca-interstratified specimens under various temperatures, initial pHs, and K-concentration. (a) rectorite-type specimen, (b) IMII-ordered specimen.

ratios in both the rectorite-type and IMII-ordered phases decreased.

Structural change with increasing %NEK

Representative XRD patterns of the reaction products are shown in Figures 5–7.

K-montmorillonite. The percentage of expandable layers in the run products from the K-saturated montmorillonite at 25°–200°C decreased only slightly, although the basal reflections changed slightly (Figures 5b and 5c). At 300°C, the expandability decreased to about 40–50%. In the 300°C product (Figure 5d), an ordered illite/montmorillonite with an about 30-Å peak for a one-day run was associated with a randomly interstratified illite/montmorillonite with greater expandability. For a 30-day run at 300°C (Figure 5e), an ordered illite/montmorillonite with a 27.5-Å peak and a random product with about 70–80% expandable layers were produced. In a preliminary run of K-montmorillonite at 400°C, the product had an expandability less than 30% and was associated with K-feldspar and quartz. Neither kaolinite nor pyrophyllite was formed at any temperature.

At a K-concentration of 1.0 M, the percentage of expandable layers decreased to about 30–40% at 300°C. The product was also associated with a small amount of a random illite/montmorillonite with greater expandability (Figure 5f).

Ca-montmorillonite. The expandability of the Ca-saturated montmorillonite changed only slightly up to 150°C. At 300°C (Figure 5g), the first order reflection shifted from 17.3 Å in the initial to 16.4 Å in the product. When the specimen was resaturated by K⁺, the first order reflection shifted to 11.6 Å at ambient RH and to 14.3 Å on glycolation. These shifts suggest that high-charged montmorillonite formed because high-charged smectites tend to have smaller basal spacings for a given 00l reflection than do smectites with lower layer charge (Brindley, 1966). In addition, an enhancement

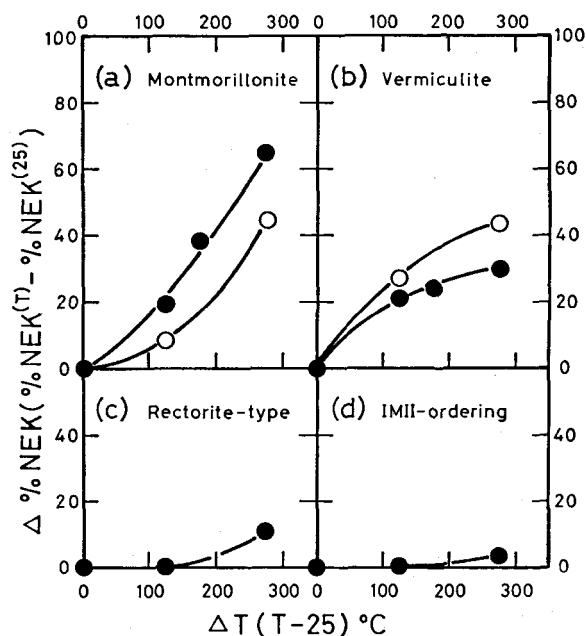


Figure 4. Temperature dependence on increase of saturated %NEK in (a) montmorillonite, (b) vermiculite, (c) rectorite-type interstratified phase, and (d) IMII-ordering illite/montmorillonite at pH = 10.7 and K-concentration = 0.02 M. Solid and open circles indicate K- and Ca-specimens, respectively.

of the background at $<5^{\circ}2\theta$, indicates that the specimen has a random interstratification (Weir *et al.*, 1975). The product at 300°C is illite/montmorillonite with about 70% expandable layers as determined from the relation between the 00l peak position and expandability (Sato, 1973).

The product at 300°C was associated with other phases having major peaks at 9.03, 5.61, 3.42, and 2.93 Å. These data suggest the presence of wairakite-type and heulandite-type Ca-zeolites, though the identification is not certain. In the Ca-montmorillonite runs (Table 1), the retention of Ca²⁺ tended to increase gradually with increasing temperature and run time. Most of the remaining Ca²⁺ probably concentrated in the associated zeolites rather than in the interlayer position of the clays.

K-vermiculite. In a preliminary test, the basal spacing of vermiculite saturated with either Ca or Sr at room temperature was shifted by ethylene glycol treatment from 14.8 to 15.6 Å and from 15.6 to 16.2 Å, respectively (Figures 6a and 6b), whereas the K-saturated specimen collapsed to 10.6 Å (Figure 6c). In addition, the K-saturated vermiculite had another broad peak at 13.5 Å, and the Ca-saturated vermiculite had extra small peaks at 13.5 and 8.27 Å.

After hydrothermal treatment of the K-saturated vermiculite at 150° and 200°C, the 14.5-Å peak of the Sr-substituted specimen split into 15.6- and 13.5-Å peaks

Table 2. Chemical analyses of reaction products at pH = 10.7, and K-concentration = 0.02 M.

Specimen	Temp. (°C)	Duration (day)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ ¹	MgO (wt.%)	CaO	Na ₂ O	K ₂ O	SrO	H ₂ O	Total	SiO ₂ /Al ₂ O ₃ (mole ratio)
Original													
montmorillonite			56.46	19.88	2.20	3.22	0.41	3.35	0.01	—	15.11	100.64	4.82
K-mont.	150	5	56.40	19.44	1.98	3.13	—	0.08	0.56	1.86	16.60	100.05	4.91
	150	12	55.94	18.94	1.84	3.06	—	0.12	0.64	2.06	16.98	99.58	5.01
	150	20	55.34	19.35	2.17	3.29	—	0.11	0.88	2.61	16.72	100.47	4.85
	150	30	54.57	19.13	1.93	3.17	—	0.11	0.82	2.38	17.11	99.22	4.83
K-mont.	200	1	55.34	19.76	2.38	2.92	0.59	0.23	0.98	2.56	15.73	100.49	4.75
	200	6	54.23	20.62	1.93	3.36	—	0.12	1.77	2.24	16.41	100.68	4.47
	200	12	54.03	19.72	1.87	3.12	—	0.17	1.24	1.99	15.84	97.98	4.66
	200	26	53.15	20.52	2.00	3.39	—	0.17	1.78	1.93	15.02	97.93	4.40
K-mont.	300	1	53.18	22.16	2.29	3.10	0.70	0.33	3.70	1.91	13.59	100.96	4.08
	300	5	53.31	22.88	2.98	2.90	—	—	2.65	1.76	13.31	100 ²	3.96
	300	30	52.05	24.43	3.23	3.37	—	0.11	3.63	1.74	11.44	100 ²	3.61
Ca-mont.	150	5	56.03	19.07	1.93	2.93	—	0.13	0.14	3.64	16.70	100.57	4.98
	150	10	56.28	19.18	1.80	2.86	0.05	—	0.19	3.26	17.21	100.83	4.98
	150	16	55.54	19.51	2.12	2.90	0.50	0.31	0.26	2.78	17.16	100.08	4.84
	150	36	55.72	19.53	2.05	2.84	0.28	0.15	0.27	2.59	15.84	99.27	4.83
Ca-mont.	300	20	52.52	20.33	2.69	2.88	0.73	0.33	1.20	2.56	16.76	100 ²	4.39
Original													
vermiculite			36.18	9.90	4.90	25.91	0.55	0.06	1.12	—	20.64	99.26	6.21
K-verm.	200	4	37.86	10.94	6.14	22.00	—	0.29	1.71	5.84	16.93	101.71	5.87
	200	10	40.92	9.60	4.69	21.53	—	0.67	1.50	4.12	16.22	99.25	7.23
	200	21	40.23	11.75	4.74	20.47	—	0.40	1.68	2.80	17.21	99.28	5.82
	200	24	39.60	10.80	4.91	22.22	—	0.31	2.06	3.62	17.51	101.03	6.22
K-verm.	300	30	41.54	10.92	6.27	25.10	0.37	0.11	7.49	0.68	7.52	100 ²	6.46
Ca-verm.	300	30	40.32	12.13	6.90	22.79	1.28	0.51	4.31	0.97	10.79	100 ²	5.64
Original													
mixed layer G			50.70	32.36	0.54	0.18	1.10	0.39	6.17	—	7.89	99.33	2.66
K-mixed G	300	27	50.78	33.79	0.33	0.20	0.78	0.68	7.63	0.91	5.81	100 ²	2.55
Original													
mixed layer S			55.50	28.21	1.43	0.48	0.48	0.46	5.99	—	8.63	101.18	3.33
K-mixed S	300	10	51.77	33.56	1.99	0.43	—	0.59	5.81	0.68	8.71	100 ²	2.62

¹ Fe₂O₃ as total Fe.

² The wt. % SiO₂ was obtained by subtracting the wt. % of the other oxides from 100%.

after ethylene glycol treatment. In addition, very weak peaks at 25.2 and 8.6 Å were noted (Figure 6d). Thus, the products at 150° and 200°C consisted of the expanded 15.6-Å layers attributed to vermiculite and a small proportion of an interstratified phase of 10-Å (mica) and 15.6-Å (vermiculite) layers giving 25.2-Å, 13.5-Å, and 8.6-Å reflections. The intensity of the 15.6-Å peak diminished gradually with run time, but the 13.5-Å peak became more intense and shifted somewhat toward a high angle. At 300°C, the 15.6-Å peak disappeared, and the basal spacing shifted to 10.2 Å (Figure 6e). K-feldspar and quartz were formed in a preliminary run of the K-saturated vermiculite at 400°C, pH = 10.7, and K-concentration = 0.02 M.

Ca-vermiculite. The basal reflection of the product from the Ca-saturated vermiculite at 150°C split into 13.3- and

11.2-Å peaks after ethylene glycol treatment (Figure 6f). With increasing temperature, the 11.2-Å peak shifted toward a high angle, but the 13.3-Å peak shifted toward a low angle. At 300°C, the 11.2- and 13.3-Å peaks shifted to 10.3 Å and 15.7°A, respectively (Figure 6g). These observations suggest that the products consisted of vermiculite and an interstratified phase.

Interstratified phases. Structural changes in the rectorite-type and IMII-ordered phases were undetected up to 150°C. At 300°C, only a slight peak shift was observed in the K-saturated rectorite-type specimen (Figure 7b), and the ordering was unchanged. In the K-saturated IMII-ordered specimen, at 300°C, the 11.6-Å peak decreased in intensity and the 9.8-Å peak was sharpened (Figure 7d). The expandability of both the rectorite-type and IMII-ordered phases decreased only slightly.

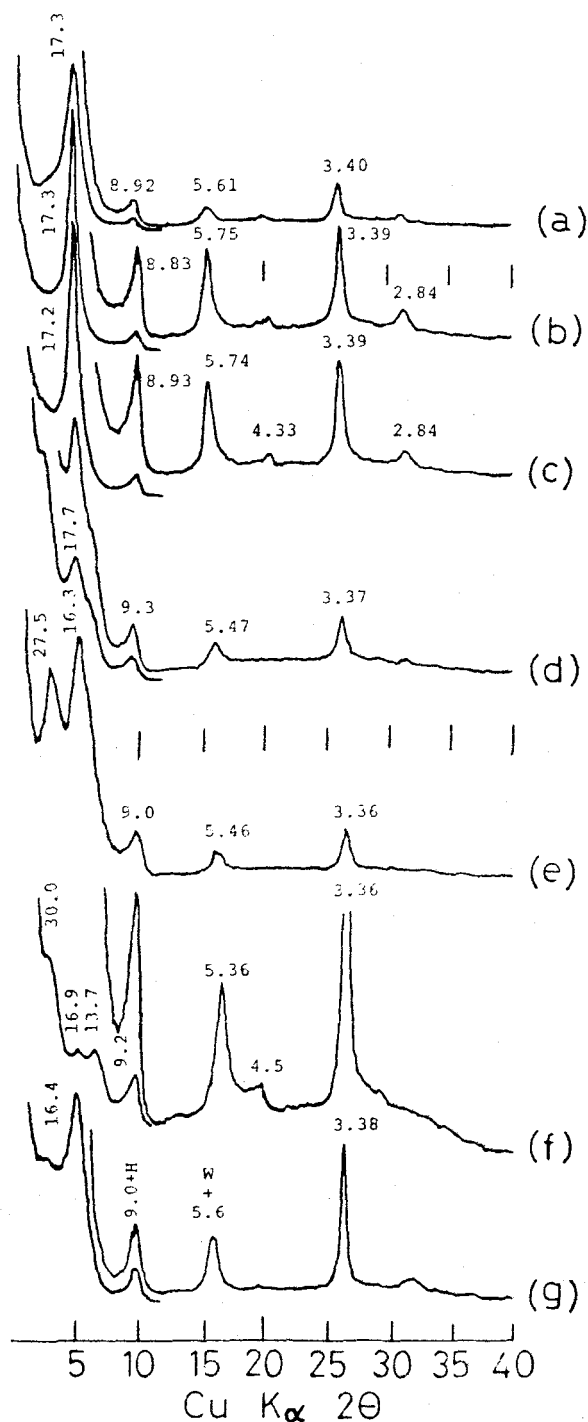


Figure 5. Representative X-ray powder diffraction patterns of hydrothermal products from K- and Ca-montmorillonites after Sr-substitution and glycolation. (a) original K-montmorillonite, (b) K-montmorillonite, 150°C, 10.7, 0.02 M, 43 days, (c) K-montmorillonite, 200°C, 10.7, 0.02 M, 26 days, (d) K-montmorillonite, 300°C, 10.7, 0.02 M, 1 day, (e) K-montmorillonite, 300°C, 10.7, 0.02 M, 30 days, (f) K-montmorillonite, 300°C, 6.0, 1.0 M, 30 days, (g) Ca-montmorillonite, 300°C, 10.7, 0.02 M, 20 days. H = heulandite; W = wairakite.

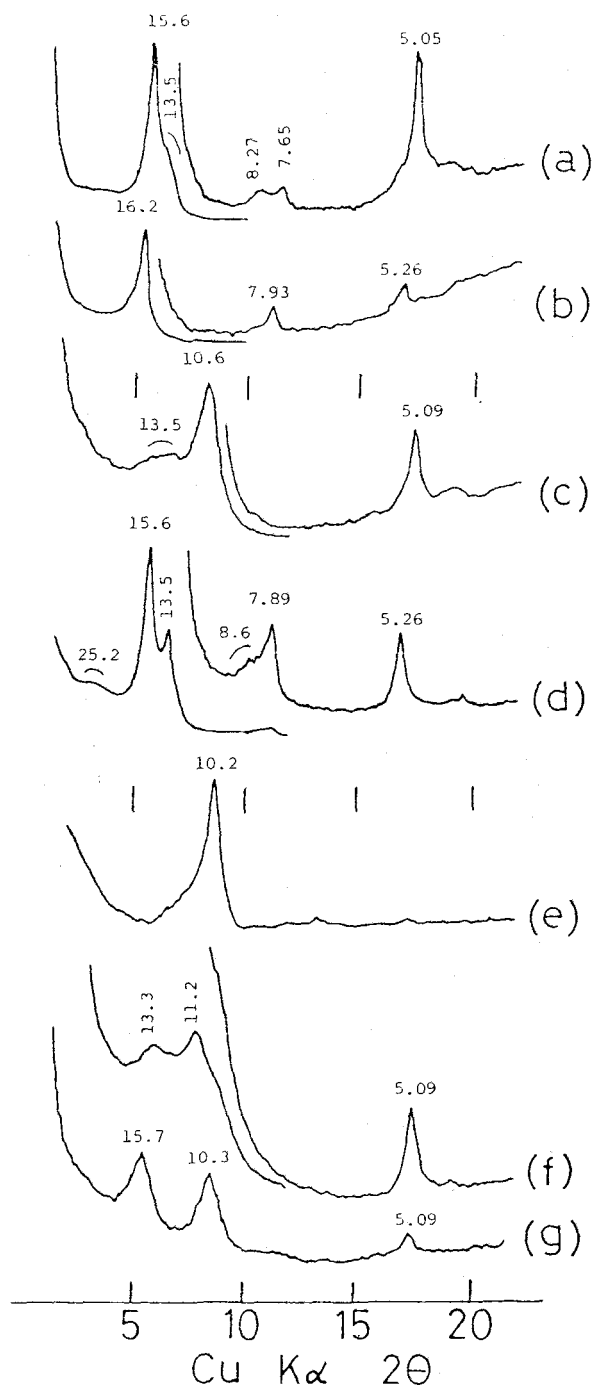


Figure 6. Representative X-ray powder diffraction patterns of hydrothermal products from K- and Ca-vermiculites after Sr-substitution ((d)–(g)) and glycolation ((a)–(g)). (a) original Ca-saturated vermiculite, (b) original Sr-saturated vermiculite, (c) original K-saturated vermiculite, (d) K-vermiculite, 200°C, 10.7, 0.02 M, 24 days, (e) K-vermiculite, 300°C, 10.7, 0.02 M, 10 days, (f) Ca-vermiculite, 150°C, 10.7, 0.02 M, 30 days, (g) Ca-vermiculite, 300°C, 10.7, 0.02 M, 30 days.

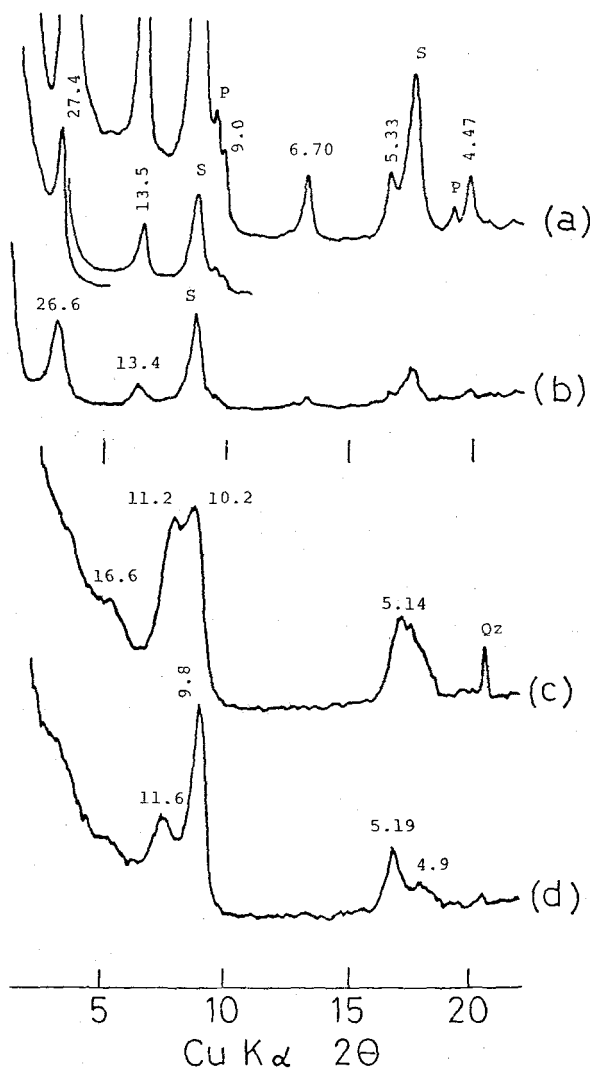


Figure 7. Representative X-ray powder diffraction patterns of hydrothermal products from rectorite-type and IMII-ordering interstratified minerals after Sr-substitution and glycolation. (a) original K-rectorite-type specimen, (b) K-rectorite-type specimen, 300°C, 10.7, 0.02 M, 27 days, (c) original K-IMII-ordered specimen, (d) K-IMII-ordered specimen, 300°C, 10.7, 0.02 M, 10 days. S = sericite, P = pyrophyllite, Qz = quartz.

DISCUSSION

Meaning of change in the SiO_2/Al_2O_3 ratio

If cation-exchange reactions in the interlayer position were the only reactions to take place in the present study, the SiO_2/Al_2O_3 ratios of the products would not vary during hydrothermal treatment because the experiments were conducted in a closed vessel. On the contrary, the SiO_2/Al_2O_3 ratio tended to decrease with increasing temperature in the montmorillonite and the interstratified phases runs (Table 2), suggesting that some of montmorillonite layers decomposed during hy-

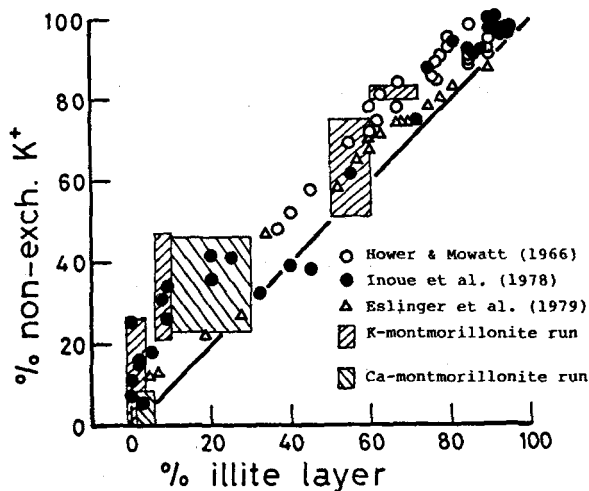


Figure 8. Percentage of non-exchangeable K vs. percentage of illite layer in natural illite/montmorillonites and the products in the present experiment.

drothermal treatment, and that dissolved Al was taken into the remaining montmorillonite layers and exchanged for Si at the high pH. In natural rocks, the extra Al and Si in the solution would ultimately precipitate as a cement. However, quartz and K-feldspar formed at 400°C, and neither kaolinite nor pyrophyllite was produced at any temperature in the present study. The silica lost from the solid run products presumably remained in solution. Thus, the lower SiO_2/Al_2O_3 ratios of the products approximately represents the increase of layer charge due to the substitution of Al for Si. This interpretation is supported by the increase in the total amount of interlayer cations with increasing temperature (Table 1).

Mechanism of K-fixation by clays

In general, cation fixation is thought to take place when the cation dehydrates in the interlayer space of clay and resides directly on the clay surface. In terms of the hydration state of interlayer K, Shainberg and Kemper (1966a, 1966b) indicated that in a clay-solution system, 49% of the K ions in the interlayer of montmorillonite partially dehydrated, even at room temperature, and resided directly on the clay surface. In the present experiment, if the K-fixation takes place in the same manner, the amounts of fixed K in the montmorillonites are smaller than the Shainberg and Kempers' estimate. In addition, the amount of fixed K at room temperature is attributed to the amount of layer charge; the difference in the %NEK values at 25°C between K-montmorillonite and K-vermiculite is due to the difference in primary layer charges in the clays. The amount of K fixed in the montmorillonites increased with rising temperature (Figure 1). Inoue and Minato (1979) demonstrated that the amount of K fixed in K-saturated

montmorillonite is independent of temperature between 80° and 300°C. Accordingly, the increase of amount of fixed K with increasing temperature noted in the present study was caused mostly by the increase of layer charge arising from the substitution of Si by Al in montmorillonite as discussed above.

Eberl (1980) indicated that the layer charge required for the K-fixation with illite formation is -0.77 per $O_{10}(OH)_2$, and distinguished between K-fixation with illite formation and fixation on the surface of lower charged montmorillonite by oven-drying. The relation between %NEK and percentage of illite layers in natural illite/montmorillonites is shown in Figure 8. If K-fixation takes place only in a layer with -0.77 of layer charge, i.e., if %NEK corresponds directly to the percentage of illite layers, the relation between these factors is represented by the line drawn in Figure 8. In fact, the plots are biased in the upper part of the line; the %NEK is greater than the percentage of illite layers in an illite/montmorillonite, meaning that lower charged montmorillonite itself has a real capacity for K-fixation. In order for the illite layer to be detected on the XRD patterns of illite/montmorillonites, however, the %NEK in the interlayer of montmorillonite must exceed a threshold value. This idea is also evident from the changing behavior of the $d(001)$ spacing of K-Ca montmorillonite (Gaultier and Mamy, 1979).

The increase of layer charge in montmorillonite was affected by the interlayer cation; the increase of layer charge in the K-montmorillonite runs was more than that in the Ca-montmorillonite runs at the same temperature (Table 2). The presence of Ca in solution inhibits effectively the substitution of Si by Al in montmorillonite (Lahann and Roberson, 1980). Therefore, the presence of Ca in the interlayer of montmorillonite also retarded the increase of layer charge due to the substitution of Si by Al, which resulted in the smaller %NEK in the Ca-montmorillonite at a given temperature (Figure 4a).

In both ordered interstratified phases, a small increase in the %NEK was recognized at 300°C (Figures 4c and 4d). If the expandable layers in such ordered interstratified phases are identical to the montmorillonite in a property that affects K-fixation, the %NEK would be almost 100% at 300°C. A dissimilarity in a K-fixation property between the montmorillonite and the expandable layer in the ordered interstratified phases means that the expandable layer has some distinct property that affects K-fixation, a property not found in pure montmorillonite. The difference of the increase of Δ %NEK between the montmorillonites and the vermiculites (Figures 4a and 4b) may be due to the different type of reaction between them during hydrothermal treatment (see below).

Structural transformation with K-fixation

Regarding the structural transformation of montmorillonite, Eberl and Hower (1977) and Eberl (1978b) demonstrated that K- and Ca-montmorillonites in each homoionic system transform rapidly and directly to rectorites at specific temperatures. In the present study, a similar type of transformation was observed in the K homoionic system, whereas in the Ca-K mixed cations system, it was not found. In a mixed cations system with Na and K, Na-montmorillonite reacted gradually to random illite/montmorillonites as well (Roberson and Lahann, 1981). Accordingly, the present experimental observations indicate that the type of structural transformation of montmorillonite is influenced greatly by the cationic composition in the reaction system; in a single cation system, montmorillonite transforms rapidly and directly to an ordered interstratified phase at a specific temperature for each cation, while in a mixed cations system, it reacts gradually through random interstratified phases. This difference is caused by the fact that the transformation in a mixed cations system is accompanied by an exchange reaction between cations having different hydration energy. Furthermore, the experimental results indicate that the gradual transformation of detrital montmorillonite to illite is affected significantly by the cation-exchange process for a natural pore solution.

The different types of transformations noted for the montmorillonite and the ordered interstratified phases in the present study indicate that the expandable layers in rectorite and IMII-ordered illite/montmorillonite are more stable than montmorillonite even at high temperature. This is evident from natural and experimental assemblages of Na- or Ca-rectorites and IMII-ordered illite/montmorillonites, indicating that they formed at fairly high temperature (Eberl and Hower, 1977; Eberl, 1978b; Hower *et al.*, 1976; Inoue *et al.*, 1978).

In the vermiculites, the transformation of K-vermiculite to mica proceeds through a regular interstratification of vermiculite and mica layers (Figure 6). The transformation took place below 300°C, and at 300°C the regular interstratified phase finally converted to a mica. The reaction trend in the Ca-vermiculite runs is probably similar to that in the K-vermiculite runs, though the reaction rate is slower because a considerable amount of primary interlayer Ca remains at 300°C (Table 1). The formation of a regular interstratified phase in the vermiculite as in the present experiment was also observed in Ca-K exchange reactions of vermiculite at 35°–150°C (Inoue, unpublished data). Sawhney (1967) attributed this transformation behavior to the polarization effects of a collapsed layer for an adjacent expanded layer.

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Резюме—Количества К, фиксированного в К- и Са-насыщенных монтмориллоните, вермикулите (треугольчатом), и слюде/монтмориллоните типа ректорита и ИМII-упорядоченной, измерялось в зависимости от времени (от 1 до 64 дней), температуры (от 25° до 300°C), pH (6,0, 9,7, и 10,7) и концентрации К (0,02 и 1,0 М) в растворе. Количество К, фиксированного глинами, в основном увеличивалось с увеличением температуры, pH, и концентрации К и достигало насыщения в каждом экспериментальном условии в течение 5 или 6 дней. К-монтмориллонит и К-вермикулит фиксировали значительные количества К даже при 25°C. Количество К, фиксированного в монтмориллоните, увеличивалось с увеличением слойного заряда, который также подвергался значительно влиянию межслойного катиона. В особенности поведение процесса фиксации К было специфическое для каждой глины. Особенно, в монтмориллоните, тип трансформации зависел от катионного состава системы; в одноионной системе К монтмориллонит быстро трансформировался в иллит/монтмориллонит с около 40% расширяющихся слоев при 300°C, а в системе со смешанными катионами Са и К, монтмориллонит видоизменялся постепенно при увеличении температуры в неупорядоченный иллит/монтмориллонит. Эти данные указывают на то, что процесс обмена катионов естественных поровых растворов играет важную роль в постепенной трансформации детритального монтмориллонита в иллит. [E.C.]

Resümee—Die K-Menge, die an K- und Ca-gesättigten Montmorillonit, Vermiculit (trioktaedrisch), und Montmorillonit vom Reaktor-Typ und IMII-geordneten Glimmer/Montmorillonit gebunden ist, wurde in Abhängigkeit von Zeit (1–64 Tage), Temperatur (25°–300°C), pH-Wert (6,0, 9,7, und 10,7), und K-Konzentration (0,02 und 1,0 m) der Lösung untersucht. Die K-Menge, die an Tone gebunden wird, steigt im allgemeinen mit zunehmender Temperatur, steigendem pH, und steigender K-Konzentration und erreicht den Sättigungszustand, in Abhängigkeit von den jeweiligen experimentellen Bedingungen, nach 5 bis 6 Tagen. K-Montmorillonit und K-Vermiculit binden beachtliche K-Mengen selbst bei 25°C. Die an Montmorillonit gebundene K-Menge wächst mit zunehmender Schichtladung, die ebenfalls beachtlich durch die Zwischenschichtkationen beeinflusst wird. Im einzelnen ist die K-Bindung für jeden Ton spezifisch.

Die Art der strukturellen Umwandlung durch die K-Bindung war bei jedem Ton anders. Bei Montmorillonit war die Art der Umwandlung von der Zusammensetzung der Kationen im System abhängig; im reinen K-System wandelte sich der Montmorillonit rasch in Illit/Montmorillonit um mit etwa 40% bei 300°C expandierbaren Lagen. In einem gemischten Kationensystem mit Ca und K wandelte sich der Montmorillonit allmählich mit zunehmender Temperatur in unregelmäßige Illit/Montmorillonit-Wechselagerungen um. Diese Ergebnisse deuten darauf hin, daß der Ionenaustausch mit einer natürlichen Porenlösung eine wichtige Rolle bei der allmählichen Umwandlung von detritischem Montmorillonit in Illit spielt. [U.W.]

Résumé—La quantité de K fixée dans la montmorillonite saturée de K et de Ca, dans la vermiculite (trioc-taédrale), et dans les montmorillonites/mica du type rectorite et ordonnées-IMII a été mesurée en fonction du temps (1–64 jours), de la température (25°–300°C), du pH (6,0, 9,7, et 10,7) et de la concentration en K (0,02 et 1,0 M) en solution. La quantité de K fixée dans les argiles a généralement augmenté proportionnellement à la température, au pH et à la concentration en K, et a atteint la saturation vis à vis de chaque condition expérimentale en 5 ou 6 jours. La montmorillonite-K et la vermiculite-K ont fixé des quantités considérables de K même à 25°C. K fixé dans la montmorillonite a augmenté proportionnellement à la charge de couche qui est aussi influencée de manière significative par le cation intercouche. En détail, le comportement dans la fixation de K était spécifique pour chaque argile.

Le genre de transformation structurale avec la fixation de K était différent pour chaque argile. Dans la montmorillonite, spécialement, le genre de transformation était apparenté à la composition cationique du système; dans un système homoionique K, la montmorillonite s'est rapidement transformée en illite/montmorillonite avec à peu près 40% de couches expansibles à 300°C, et dans un système mélangé avec Ca et K, elle a réagi graduellement en des illite/montmorillonites quelconques proportionnellement à une augmentation de température. Ces données indiquent que le procédé d'échange de cations d'une solution naturelle de pores joue un rôle important dans la transformation graduelle de montmorillonite detritique en illite. [D.J.]