ALTERATION OF SMECTITE IN A SYSTEM INCLUDING ALANINE AT HIGH PRESSURE AND TEMPERATURE

HIDEO HASHIZUME, HIROHISA YAMADA, AND HIROMOTO NAKAZAWA

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, 305 Japan

Abstract—Transformation of montmorillonite was experimentally investigated using a model system of montmorillonite-alanine at 100 MPa and up to 500°C. Sodium-montmorillonite changed to a mixed layer mineral of sodium- and ammonium-montmorillonites (Na/NH$_4$-Mnt) in the temperature range from 150 to 400°C. Ammonium ions were the decomposition product of alanine above 150°C. The Na/NH$_4$-Mnt transformed to regularly and randomly interstratified minerals of NH$_4$-montmorillonite and NH$_4$-mica (o. NH$_4$-Mnt/NH$_4$-Mic and d. NH$_4$-Mnt/NH$_4$-Mic) at 400°C. These mixed layered minerals transformed to ammonium-mica at 500°C. Ammonium-analcime appeared and coexisted with the smectites at temperatures over 200°C, and with albite for those over 400°C.

In comparison with the results of previous experiments in which there was no organic component, the present results revealed that (1) some uncommon mineral phases appeared by replacement of sodium ions in montmorillonite with ammonium ions, i.e., NH$_4$-Mic, o. and d. NH$_4$-Mnts, o. and d. NH$_4$-Mnt/ NH$_4$-Mics, and (2) ammonium-analcime appeared. The mineral assemblages and alteration sequences correspond better with those observed in the natural system than those known from experimental results in aluminosilicate-water system.

Key Words—Alanine, Albite, Ammonium-analcime, Ammonium-mica, Ammonium-montmorillonite, Diagenesis, High pressure, X-ray diffraction.

INTRODUCTION

In sediment diagenesis, constituent minerals pass through several phases: e.g., smectite transforms to a mica (illite) through a smectite/mica mixed layered mineral (e.g., Velde *et al* 1986, Inoue 1991, Aoyagi and Shimoda 1991), and clinoptilolite, a zeolite, transform to albite through analcime (e.g., Boles 1971, Utada 1985, Iijima 1986, Sasaki 1991). Many workers have experimentally studied the illitization of smectite and the transformations of zeolite (e.g., Boles 1971, Eberl 1976, Eberl *et al* 1978, Colten 1986, Yau *et al* 1987, Whitney 1990, Yamada *et al* 1991, Chermak 1993). Their interests were mainly the effects of the water content, alkali ions, pressure and temperature on the illitization. There are, however, some organic components in a natural sediment on the ocean floor. Changes in the sedimentary materials were affected by their coexistence with the organic matters and their decomposed products (Juster *et al* 1987, Williams and Ferrell, Jr. 1991). NH$_4$-bearing minerals such as tobelite, buddingtonite and ammonium-illite may be related with the diagenetic change of sedimentary materials (Higashi 1982, Erd *et al* 1964, Stevenson and Dhariwal 1959). It is, however, difficult to assess this effect in natural samples, because the organic matter might have disappeared by decomposition to a final gas phase prior to collection and analysis of the sediment.

In the present paper, a model material of an ocean floor sediment with organic matter is treated at high pressure and temperatures. A mixture of smectite and alanine is used as a model sediment. Some differences in the alteration products of smectite coexisting with and without alanine will be discussed comparing the results of XRD analysis of the present experimental products with those previously known. Alteration processes of some uncommon mineral phases will also be discussed.

EXPERIMENTAL

The starting material was a mixture of natural montmorillonite commercially available (Kunipia-F, Kunimine Co.) which was fractionated from Tertialy pyroclastic rocks (Tsukinuno mine, Yamagata Prefecture, Japan) and a reagent grade alanine (Sigma). The exchangeable cations of montmorillonite had been analyzed as Na$^+$ (81.5%), Ca^{2+} (14.4%), Mg^{2+} (3.2%) and K$^+$ (0.9%). The ratio of montmorillonite/alanine was 4/1 by weight (1/1 by mole). Two types of samples were prepared: (A) the starting materials (150 mg) with 15 mg of distilled water, and (B) those without water. Before sealing in gold tubes, the air was replaced by nitrogen gas to prevent oxidation of the sample.

A hydrothermal apparatus of rapid-quenching type was used throughout the investigation (Yamada *et al* 1988). A sample was held at the desired temperature and pressure from 5 to 10 days. The temperatures examined were at 50°C intervals from room temperature to 500°C. The pressure was 100 MPa. After the hydrothermal treatment, the samples were quenched to room temperature within 30 seconds.

The run products were analyzed by X-ray powder

184

diffraction (XRD) (using CuKα radiation and operating at 40kV and 20mA) for samples randomly oriented on a zerobackground quartz plate, preferentially oriented with water on a glass slide and preferentially oriented with ethylene glycol. The diffraction angle (2θ) was calibrated using a tetradecanol as an external standard (Brindley 1981). Morphology of the product was observed by scanning electron microscopy (Akashi DS-130).

For more detailed identification, minerals <2 μm in size were separated by hydraulic elutriation. They were analyzed by infrared (IR) absorption spectra as well as by XRD as described above. Before IR spectra measurement, the run products were washed and centrifuged for several times to remove the adsorbate on the samples. Every supernatant was checked by ninhydrine reaction and Nessler's reagent to check the complete wash-out of the adsorbates.

RESULTS

Run products, with and without water, showed almost the same phase assemblage at the same pressure and temperature conditions. Thus, the phases identified by XRD are presented only for the case without water (Table 1). Some typical XRD patterns are shown in Figure 1. The XRD patterns necessary for identification of phase appeared are shown in Figure 2.

Description of the identified phases

(1) Alanine. The starting materials, montmorillonite and alanine, were unchanged up to 100°C (Figure 1, A and B). At 150°C, the peak of alanine in the XRD pattern started to decrease and completely disappeared above 200°C (Figure 1, C and D). Parallel to this observation, the sample treated above 150°C included a gas phase that was ejected when the capsules were opened (Table 1). Alanine was thus stable only at temperatures lower than 150°C.
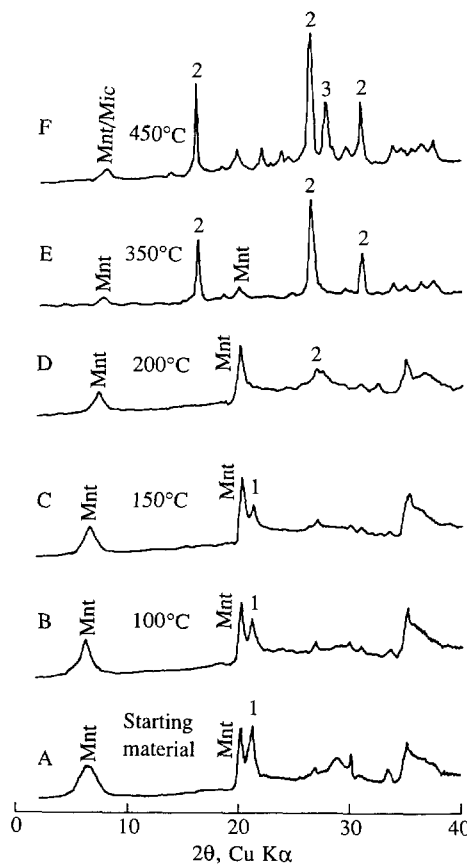
(2) Montmorillonite. Montmorillonite did not change

Figure 1.   Typical XRD patterns of samples treated at different temperatures. Mnt, montmorillonite. 1, alanine. 2, NH4-analcime. 3, albite. Mnt/Mic, interstratified mineral of montmorillonite and mica. Mic, mica.

up to 100°C (Figure 2, B). Its basal spacing was about 13.4 Å measured at 72% relative humidity and was increased to 16.6 Å by ethylene glycol treatment (Figure 2, (a), B). Montmorillonite treated in the range from 150 to 250°C showed a basal spacing of about 12.5 Å

Table 1.   Phases identified in run products.

Temp °C	Time day	Phases
26	7	Na-Mnt, Ala
100	7	Na-Mnt, Ala
150	7	d.Na/NH4-Mnt, Ala, G
200	10	d.Na/NH4-Mnt, NH4-Anl, G
250	9	d.Na/NH4-Mnt, NH4-Anl, G
300	8	d.Na/NH4-Mnt, o.Na/NH4-Mnt, NH4-Anl, G
350	6	d.Na/NH4-Mnt, NH4-Anl, G
400	7	d.Na/NH4-Mnt, o.NH4-Mnt/NH4-Mic, d.NH4-Mnt/NH4-Mic, NH4-Anl, G
450	6	o.NH4-Mnt/NH4-Mic, d.NH4-Mnt/NH4-Mic, NH4-Mic, NH4-Anl, Ab, G
500	5	d.NH4-Mnt/NH4-Mic, NH4-Mic, NH4-Anl, Ab, Qz, uk, G

Na-Mnt, sodium-montmorillonite. Ala, Alanine. d.Na/NH4-Mnt, randomly interstratified mineral of sodium- and ammonium-montmorillonite. o.Na/NH4-Mnt, regularly interstratified mineral of sodium- and ammonium-montmorillonite. NH4-Anl, ammonium-analcime. NH4-Mic, ammonium-mica. d.NH4-Mic/NH4-Mnt, randomly interstratified mineral of ammonium-mica and ammonium-montmorillonite. o.NH4-Mic/NH4-Mnt, randomly interstratified mineral of ammonium-mica and ammonium-montmorillonite. Ab, albite. Qz, quartz. G, gas phase. uk, unknown phase.
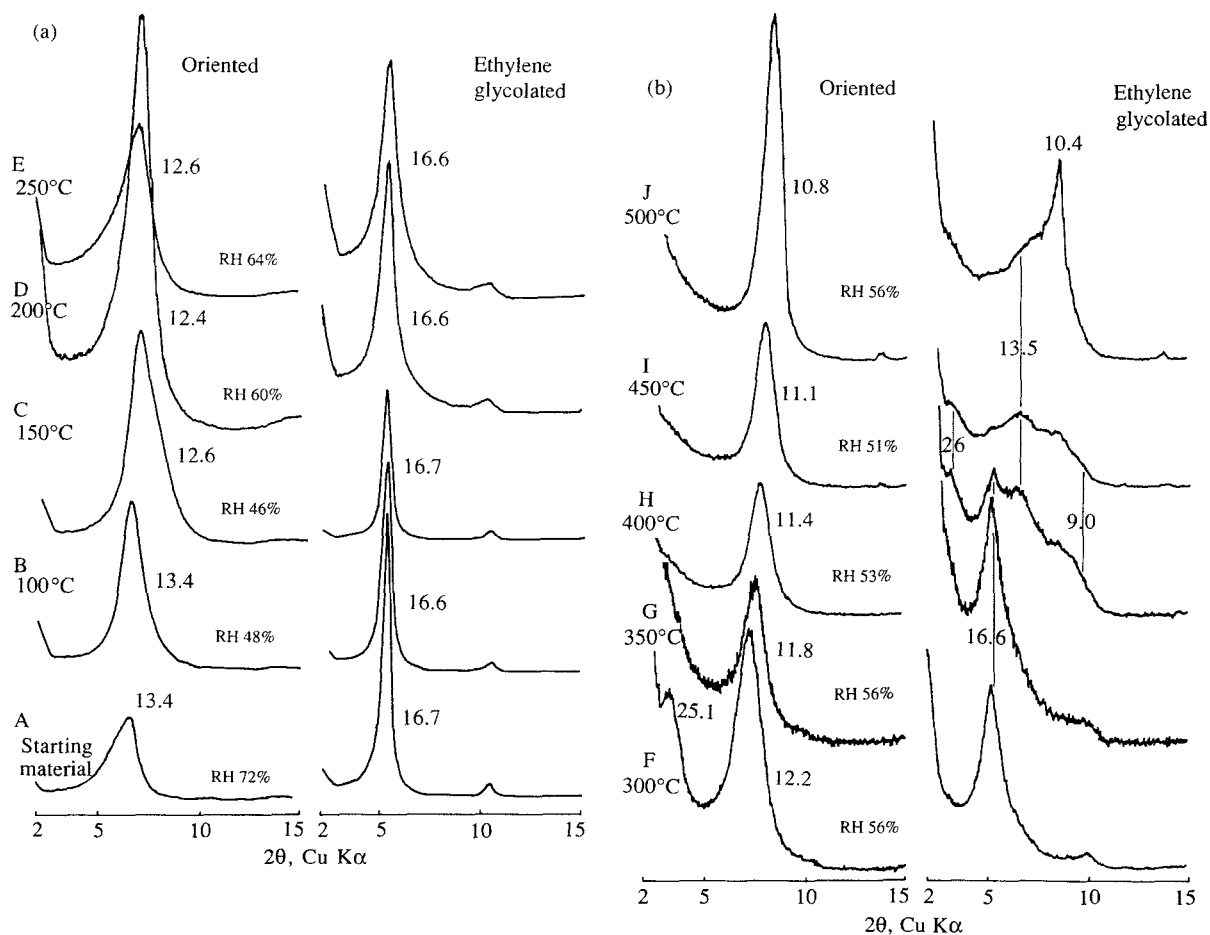
Figure 2.   Detailed XRD patterns of samples treated at different temperatures (a) starting material and from 100 to 250°C and (b) from 300 to 500°C. The water-oriented samples (left) and those ethylene glycolated (right). RH, relative humidity. The numbers at XRD peaks are d- values in Å.

in a relative humidity between 44 and 64% (Figure 2, (a), C, D and E). The basal spacing was increased to about 16.6 Å by ethylene glycol treatment. At 300 and 350°C, montmorillonite showed smaller basal spacings of 12.2 and 11.8 Å, respectively. These expanded to 16.3 and 16.6 Å by ethylene glycol treatment (Figure 2, (b), F and G).

The smaller basal spacing is interpreted as follows: The basal spacing of sodium-montmorillonite (Na-Mnt) is 13.4 Å in a relative humidity of 56% and that of ammonium-montmorillonite (NH₄-Mnt) is 11.5 Å (this is obtained by ion exchange of sodium ion with ammonium ion in our preparation). The random interstratification of the Na- and NH₄-Mnts forms a basal spacing in the range from 13.4 to 11.5 Å depending on the Na⁺/NH₄⁺ ratio. The ethylene glycol intercalation expands the spacing in the range from 16.9 to 16.6 Å. The "smaller" spacing observed is, thus, an indication of such a random stratification. This will be discussed later in more detail. Intercalation of ammonium ions was confirmed in IR absorption spectra at about 1400

cm⁻¹ that was observed only on the samples treated above 150°C.

A sample treated at 300°C showed a broad peak with a d-value of 25.1 Å in the XRD pattern (Figure 2, (b), F). The peak was reasonably assigned to that of the regularly interstratified sodium- and ammonium-montmorillonite (o. Na/NH₄-Mnt), because the spacing corresponded well to the sum, about 24.9 Å, of the inter-layer spacings of Na- and NH₄-Mnts.

(3) Ammonium-mica. The 500°C sample showed a slightly broad peak at 10.8 Å before ethylene glycol treatment but the peak was split to a sharp peak at 10.4 Å and that of broad at 13.5 Å by the treatment (Figure 2, (b), J). The basal spacing of 10.4 Å agreed well with that of tobelite, an ammonium-mica which does not intercalate ethylene glycol (Higashi 1982). The XRD observation described above is explained well that there are two phases, i.e., an ammonium-mica and a randomly interstratified ammonium-montmorillonite and ammonium-mica that are described below.

(4) Regularly and randomly interstratified ammonium-montmorillonite and ammonium-mica. A regularly interstratified ammonium-montmorillonite and ammonium-mica (o. NH_4-Mnt/NH_4-Mic) appeared in the samples treated at 400 and 450°C. The phase was identified by its XRD peak at about 26 Å for ethylene glycol treated samples (Figure 2, (b), H, right). Because the peaks are small and in an extremely low angle region, the precision of the d-value is not expected higher than ± 1 Å. Taking this into account, the spacing corresponds to the sum, 27 Å, of the basal spacings of NH_4-Mnt, 16.6 Å, and of NH_4-Mic, 10.4 Å, when those samples were treated by ethylene glycol. A higher order reflection, 003, may be seen as a broad shoulder at about 9 Å in the same figure. For the sample treated with water, the superstructure reflections may not be observed because their intensities are decreased by replacement of ethylene glycol with water, which results in a smaller difference between structure units of montmorillonite and mica and results in smaller F(001). The broad peak at 11.4 Å of the XRD pattern (Figure 2, (b), H, left) is, therefore, interpreted as an overlapped peak of the 002 of the o. NH_4-Mnt/NH_4-Mic (10.7 Å) and of the 001 of the disordered NH_4/Na-Mnt (d. NH_4/Na-Mnt, 11.9 Å).

A randomly interstratified ammonium-montmorillonite and ammonium-mica (d. NH_4-Mnt/NH_4-Mic) appeared in the samples treated at 400, 450 and 500°C. The phase was identified on the basis of the XRD observation (Figure 2, (b), I and J). The peak at 13.5 Å for the ethylene glycolated samples corresponds well to that of randomly interstratified layers of 16.6 Å (NH_4-Mnt) and 10.4 Å (NH_4-Mic). The former, NH_4-Mnt appeared individually at lower temperature, 400°C. The latter, NH_4-Mic appeared also at higher temperature, 500°C. The d. NH_4-Mnt/NH_4-Mic is an intermediate phase of them. The XRD peaks, 11.4, 11.1 and 10.8 Å, of water treated samples are well explained as overlapped peaks of the d. NH_4-Mnt/NH_4-Mic and d. NH_4/Na-Mnt (400°C), d. and o. NH_4-Mnt/NH_4-Mic (450°C) and d. NH_4-Mnt/NH_4-Mic with NH_4-Mic (500°C).

(5) Ammonium-analcime. The ammonium-analcime appeared above 200°C (Figure 1, from D to F). The d-values and diffraction intensities are listed for the present product at 350°C and for a previously known ammonium-analcime in Table 2 (A) (Barren and Derny 1961, Sheppard and Gude 1973). Those of analcime are also shown as a reference.

(6) Albite. A small amount of albite appeared in the run products at 450 and 500°C (Figure 1F). For the case where water was included in the starting material, albite appeared above 400°C. The X-ray diffraction data of the run product at 450°C and of the previously known albite are listed in Table 2 (B) (Smith 1956). The agreement of them indicates that albite does not
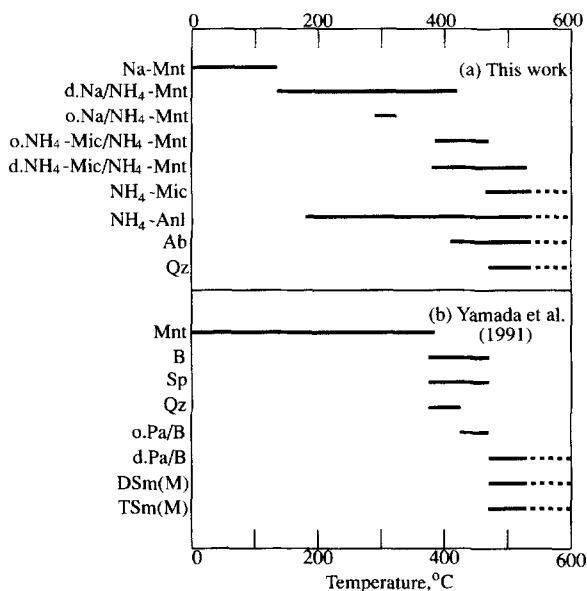

Figure 3. Schematic illustration of phases which appeared at different temperatures. (a) this work, (b) Yamada *et al* (1991). Na-Mnt, sodium-montmorillonite. Ala, alanine. NH_4-Mnt, ammonium-montmorillonite. d.Na/NH_4-Mnt, randomly interstratified mineral of sodium- and ammonium-montmorillonite. o.Na/NH_4-Mnt, regularly interstratified mineral of sodium- and ammonium-montmorillonite. o.NH_4-Mnt/NH_4-Mic, regularly interstratified mineral of ammonium-montmorillonite and ammonium-mica. d.NH_4-Mnt/NH_4-Mic, randomly interstratified mineral of ammonium-montmorillonite and ammonium-analcime. NH_4-Anl, ammonium-analcime. NH_4-Mic, ammonium-mica. Ab, albite. Qz, quartz. B, beidellite. Sp, saponite. o.Pa/B and d.Pa/B, regularly and randomly interstratified mineral of paragonite and beidellite, respectively. DSm(M), dioctahedral smectite with octahedral charges. TSm(M), trioctahedral smectite with octahedral charges.

take substitution of sodium by ammonium ion. This is consistent with a previous report that albite did not give the evidence of ammonium substitution at 200 MPa and 600°C (Barker 1964).

DISCUSSION

Alteration of smectite in coexistence with organic molecules

The temperatures of formation of all phases which appeared in the present experiments are schematically represented in Figure 3a. Those previously known in a montmorillonite-water system are shown for comparison (Figure 3b, Yamada *et al* 1991). The applied pressures were the same for both experiments, i.e., 100 MPa.

In the present system, (1) o. and d. NH_4/Na-Mnts, (2) o. and d. NH_4-Mic/NH_4-Mnt and (3) NH_4-analcime are new observations. Moreover, (4) the alteration sequence of smectite with increases in temperature is different with previous experiments of Mnt-

Table 2. X-ray diffraction data of samples treated at (A) 350 and (B) 450°C, analcime, ammonium-analcime and albite.

(A) 350°C product		NH$_4$-Anl[1]		Anl[2]		(B) 450°C product		NH$_4$-Anl		Ab[3]	
d(A)	I	d(A)	I	d(A)	I	d(A)	I	d(A)	I	d(A)	I
11.1	9					10.7	10				
5.51	69	5.54	90	5.58	90	6.36	3			6.39	20
5.46	47									5.94	2
4.76	7	4.81	30	4.84	36	5.49	72	5.54	80		
4.45	14					4.77	4	4.81	30		
		3.63	10	3.66	22	4.46	23				
3.39	86	3.39	100	3.42	100	4.00	19			4.03	16
3.37	100									3.86	8
3.02	5	3.02	10			3.73	14			3.78	25
2.88	47	2.89	60	2.92	80					3.68	20
2.75	2									3.66	16
2.65	13	2.66	10	2.68	34	3.61	8			3.63	10
2.57	8									3.51	10
2.47	11	2.49	30	2.50	30					3.48	2
2.39	10	2.40	10	2.42	20	3.38	100	3.39	100	3.38	8
2.20	5	2.20	20	2.22	18	3.19	48			3.20	100
2.14	2			2.16	4					3.15	10
				2.11	5	3.00	8	3.02	10		
				2.02	4					2.96	10
				1.94	5					2.93	16
1.88	7	1.88	20	1.90	22	2.87	52	2.89	60	2.78	8
				1.86	15					2.84	2
1.84	4			1.83	1					2.79	2
				1.74	38	2.64	15	2.66	10	2.64	6
1.72	14			1.71	12	2.57	15			2.56	8
1.67	4			1.68	13					2.54	2
				1.66	6	2.50	15	2.49	30	2.51	2
1.58	2			1.59	12					2.50	6
1.49	2			1.49	4	2.46	13			2.46	6
				1.48	7					2.44	4
1.46	2			1.46	2					2.43	2
								2.40	10	2.41	2
						2.38	12			2.39	4
										2.32	4
										2.28	2
						2.18	6	2.20	20	2.19	4
										2.13	8
										2.12	6
										2.08	2
										2.04	2
										2.00	2
										1.98	4
										1.93	2
						1.87	8	1.88	20	1.89	8
						1.83	8				
						1.77	5				
						1.71	16	1.72	40		
						1.57	3	1.57	4		
						1.50	5				

NH$_4$-Anl: ammonium-analcime, Anl: analcime, Ab: albite.
[1] Barrer and Denny, I. (1961).
[2] Sheppard and Gude (1973).
[3] Smith (1956).

water system: smectite → mica/smectite mixed layer mineral (M/S) → mica in the present system whereas a three-minerals coexisting phase appeared between Mnt and M/S in previous report (Yamada *et al* 1991). The present observations are rather consistent with the phase changes of smectite and zeolite estimated from the natural occurrences, indicating the effect of coex-

isting organic molecules or the decomposed compounds (e.g., Aoyagi and Shimoda 1991, Sasaki 1991). These are shown schematically in a diagram together with the present results (Figure 4). In the diagram some details such as a finer classification of smectite as o. and d. Na/NH$_4$-Mnt are neglected for convenience of comparison.

The diagram shows that the orders of alteration sequence, smectite → M/S → mica and analcime → albite, in the present results agree well with natural observations. However, transformation temperatures are considerably higher in the experimental results. The temperature difference may be attributed to the difference in the duration of experimental run, seven days, which was much shorter than that in the natural system. Gotoh *et al* (1988) showed that ammonium-analcime was formed from NH_4-Mnt during a long time duration of 150 days at 2 MPa and 240°C, but was not for 50 days at the same condition. Tsunashima *et al* (1975) synthesized an ammonium-mica from an aluminosilica gel with glysine or lysine above 300°C for four to eight days. The temperature is also much higher than that of natural observation. The duration time might, therefore, be a parameter to decrease the transformation temperatures.

The d. Na/NH_4-Mnt showed an interesting feature in its change as a function of temperature. As seen in Figure 2, from C (150°C) to H (400°C), the basal spacing decreases from 12.6 to 11.4 Å indicating that the number of the ammonium layers increases at higher temperatures by the ion-exchange reaction between sodium and ammonium ions. The starting temperature, 150°C, corresponds to that of alanine decomposition to ammonium and simple hydrocarbons. Sodium ions in Na-Mnt can be replaced by the ammonium ions above that temperature. Below 300°C, the ion-exchange is not significant as shown by the slight decrease in the basal spacing (about 12.5 Å, Figure 2, C and D). Above 300°C, the ion-exchange is obvious in the change of the basal spacing (Figure 2, F and G, H) and at 350°C, sodium ions in Na-Mnt are almost completely replaced by ammonium ions, so that the d-spacing reaches to 11.4 Å of ammonium-montmorillonite. At 300°C, a regular interstratification of sodium- and ammonium-montmorillonites (o. Na/NH_4-Mnt) appeared (Figure 2F). This indicates that (1) the ratio of Na^+/NH_4^+ ions in montmorillonite becomes comparable at that temperature and (2) the ion-exchange occurs layer by layer and does not statistically in an interlayer.

The mixed layer minerals of ammonium-montmorillonite and ammonium-mica

It is well known that by the cation exchange and cation fixation of potassium in smectite the randomly and regularly interstratified illite and smectite results (e.g., Inoue *et al* 1987). Because of the similarity in the ionic radius of the ammonium ion (1.48 Å) with that of potassium (1.38 Å) rather than sodium (0.95 Å), it may be reasonable that the ammonium ion plays a similar role to that of potassium. Sucha and Širáňová (1991) showed experimentally that the rates of fixation of both potassium and ammonium ions in smectite
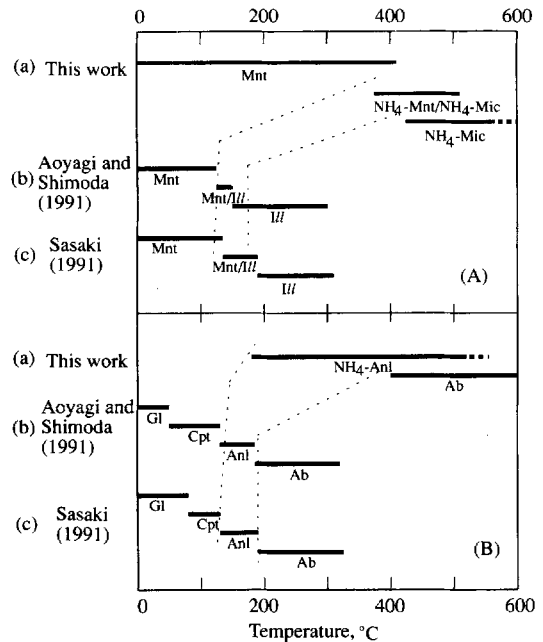

Figure 4. Comparison of mineral assemblages observed in (a) the present experiment and in (b) and (c) field observations. (A) Montmorillonite and mica minerals and (B) Zeolite. Mnt, sodium-montmorillonite and mixed layer mineral of sodium- and ammonium-montmorillonite. NH_4-Mnt/NH_4-Mic, the mixed layer mineral of ammonium-montmorillonite and ammonium-mica. NH_4-Mic, ammonium-mica. Mnt/Ill, the mixed layer of montmorillonite and illite. Ill, illite. NH_4-Anl, ammonium-analcime. Ab, albite. Gl, volcanic glass. Cpt, clinoptilolite. Anl, analcime.

were the same, and that the same number of illite layers was formed for the same number of cycles of wetting and drying with potassium and ammonium solutions. Therefore, it is quite reasonable that the mixed layer minerals of ammonium-smectite and mica (o. and d. NH_4-Mnt/NH_4-Mic) were formed in the present experiment above 400°C. The present result illustrates well that the ion-exchange and the fixation do not occur simultaneously, but the former occurs at lower temperature to form the sodium- and ammonium-mixed layer smectite and the latter occurs to form the mixed layer minerals of ammonium-smectite and mica above 400°C.

Ammonium-analcime and albite

Formation of ammonium-analcime from ammonium-montmorillonite has been known in the experimental study (Gotoh *et al* 1988). In the present study, ammonium-analcime of cubic shape was observed in the SEM images. Such a euhedral form of crystal is an evidence that the mechanism of its growth is a solution growth. Any other mechanism can not explain the euhedral form of analcime than that montmorillonite was dissolved into aqueous solution from which analcime precipitated. Because analcime was not observed in the

previous experiment in the system of montmorillonite and water, the organic molecules coexisting with montmorillonite may play a role in the dissolution of montmorillonite.

Transformation of analcime to albite with increasing temperature has been also known from natural evidence (Campbell and Fyfe 1965, Thompsom 1971). This is confirmed in the present experiment above about 400°C. There is no evidence in the XRD pattern that albite contains ammonium ion (Table 2, B). This is consistent with the previous experiment which was unsuccessful in substituting an ammonium ion for a sodium and potassium ion in alkali feldspars at 200 MPa and around 650°C (e.g., Barker 1964).

ACKNOWLEDGMENTS

REFERENCES

Aoyagi, K., and S. Shimoda. 1991. Diagenesis in argillaceous sediments and rocks. *Nendo Kagaku* 31: 23–31 (in Japanese with English abstract).

Barker, D. S. 1964. Ammonium in alkali feldspars. *Amer. Miner.* 49: 851–858.

Barren, R. M., and P. J. Derny. 1961. Hydrothermal chemistry of the silicates. Part IX. Nitrogenous aluminosilicates. *J. Chem. Soc.* 1961: 971–982.

Boles, J. R. 1971. Synthesis of analcime from natural heulandite and clinoptilolite. *Amer. Miner.* 56: 1724–1734.

Brindley, G. W. 1981. Long-spacing organics for calibrating long spacings of interstratified clay mineral. *Clays & Clay Miner.* 29: 67–68.

Campbell, A. S., and W. S. Fyfe. 1965. Analcime-albite equilibria. *Am. J. Sci.* 263: 807–816.

Chermak, J. A. 1993. Low temperature experimental investigation of the effect of high pH KOH solution on the opalinus shale, Switzerland. *Clays & Clay Miner.* 41: 365–372.

Colten, V. A. 1986. Hydration states of smectite in NaCl brines at elevated pressures and temperature. *Clays & Clay Miner.* 34: 385–389.

Eberl, D. 1976. The reaction of montmorillonite to mixed-layer clay: The effect of interlayer alkali and alkaline earth cations. *Geochim. Cosmoshim. Acta* 42: 1–7.

Eberl, D., G. Whitney, and H. Khoury. 1978. Hydrothermal reactivity of smectite. *Amer. Miner.* 63: 401–409.

Erd, R. C., D. E. White, J. J. Fahey, and D. E. Lee. 1964. Buddingtonite, an ammonium feldspar with zeolitic water. *Amer. Miner.* 49: 831–850.

Gotoh, Y., K. Okada, and N. Otsuka. 1988. Synthesis of ammonium montmorillonite. *Clay Science* 7: 115–127.

Higashi, S. 1982. Tobelite, a new ammonium dioctahedral mica. *Mineral. Jour.* 11: 138–146.

Iijima, A. 1986. Occurrence of natural zeolite. *Nendo Kagaku* 26: 90–103.

Inoue, A. 1991. Factors governing the smectite-to-illite conversion in diagenetic environments. *Nendo Kagaku* 31: 14–22 (in Japanese with English abstract).

Inoue, A., N. Kohyama, R. Kitagawa, and T. Watanabe. 1987. Chemical and morphological evidence for the conversion of smectite to illite. *Clays & Clay Miner.* 35: 111–120.

Juster, T. C., P. E. Brown, and S. W. Bailey. 1987. NH4-bearing illite in very low grade metamorphic rocks associated with coal, northeastern Pennsylvania. *Amer. Miner.* 72: 555–565.

Sasaki, A. 1991. Time-dependence function on diagenetic change. In case of zeolitization in marine sediments. *Nendo Kagaku* 31: 7–13 (in Japanese with English abstract).

Sheppard, R. A., and A. J. Gude III. 1973. Zeolite and associated authigenic minerals in tuffaceous rocks of the Big Study Formation, Mohave County, Arizona. *U.S. Geol. Surv. Prof. Paper* 830: 1–36.

Smith, J. V. 1956. The powder patterns and lattice parameters of plagioclase feldspars. I. The soda-rich plagioclases. *Mineral Mag.* 31: 47–68.

Stevenson, F. J., and A. P. S. Dhariwal. 1959. Distribution of fixed ammonium in soil. *Soil Science Society of America Proceedings.* 121–125.

Sucha, V., and V. Siráñová. 1991. Ammonium and potassium fixation in smectite by wetting and drying. *Clays & Clay Miner.* 39: 556–559.

Thompsom, A. B. 1971. Analcite-albite equilibria at low temperature. *Am. J. Sci.* 271: 79–92.

Tsunashima, A., F. Kanamaru, S. Ueda, M. Koizumi, and T. Matsushita. 1975. Hydrothermal syntheses of amino acid-montmorillonites and ammonium-micas. *Clays & Clay Miner.* 23: 115–118.

Utada, M. 1985. Zoning of authigenic minerals and its genesis. *Nendo Kagaku* 25: 119–125.

Velde, B., T. Suzuki, and E. Nicot. 1986. Pressure-temperature-composition of illite/smectite mixed-layer minerals: Niger delta mudstones and other examples. *Clays & Clay Miner.* 34: 435–441.

Whitney, G. 1990. Role of water in the smectite-to-illite reaction. *Clays & Clay Miner.* 38: 343–350.

Williams, L. B., and R. E. Ferrell Jr. 1991. Ammonium substitution in illite during maturation of organic matter. *Clays & Clay Miner.* 39: 400–408.

Yamada, H., T. Fujita, and H. Nakazawa. 1988. Design and calibration of a rapid quench hydrothermal apparatus. *Jour. Ceramic Soc. Japan* 96: 1041–1044.

Yamada, H., H. Nakazawa, K. Yoshioka, and T. Fujita. 1991. Smectites in the montmorillonite-beidellite series. *Clay Miner.* 26: 359–369.

Yau, Y.-C., D. R. Peacor, E. J. Essene, J. H. Lee, L.-C. Kuo, and M. A. Cosca. 1987. Hydrothermal treatment of smectite, illite, and basalt to 460°C: Comparison of natural with hydrothermally formed clay minerals. *Clays & Clay Miner.* 33: 241–250.