

DISTRIBUTION OF Ca AND Na IONS IN DIOCTAHEDRAL SMECTITES AND INTERSTRATIFIED DIOCTAHEDRAL MICA/SMECTITES

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Abstract—The structures of 11 smectites and 2 interstratified mica/smectites containing mainly Ca²⁺ and Na⁺ as exchangeable cations in variable ratio were studied under a relative humidity of about 40%. Observed X-ray powder diffraction patterns were compared with diagrams calculated from interstratification models containing 15.2-Å Ca-smectite layers (C), 12.4-Å Na-smectite layers (N), and 10.0-Å mica layers (M) in various combinations. The smectites appear to be a random interstratification of component layers C and N, and display a tendency towards segregation. One of the interstratified minerals studied is a regular interstratification of C and M layers; the other is a regular interstratification of C, N, and M layers, in which N and C layers are randomly distributed in equal proportion and show a tendency towards segregation.

Key Words—Demixing, Exchangeable cations, Interstratified mica/smectite, Relative humidity, Smectite, Water, X-ray powder diffraction.

要旨 — 交換性陽イオンとして主に Ca²⁺ と Na⁺ を様々な量比で含むスメクタイト 11試料と雲母／スメクタイト混合層鉱物 2 試料について相対湿度約 40% の条件下で構造を検討した。測定した X 線回折パターンを 15.2-Å Ca-スメクタイト層 (C)、12.4-Å Na-スメクタイト層 (N) および 10.0-Å 雲母層 (M) の組合せからなる混合層モデルに基づき計算した X 線回折プロファイルと比較した。スメクタイト試料は成分層 C と N とからなり、それらは segregation 寄りのランダム混合層構造を示す。混合層鉱物の一つは成分層 C と M からなる規則混合層構造をとるが、もう一つは同じ比率で存在する C 層と N 層が segregation 寄りのランダムな分布を示す C、N 層と M 層の規則混合層構造であった。

INTRODUCTION

The variation of the basal spacings of smectites as a function of water adsorption has been studied by a number of workers (e.g., Hendricks *et al.*, 1940; Mooney *et al.*, 1952; Zettlemoyer *et al.*, 1955; Fripiat *et al.*, 1965; Keren and Shainberg, 1975). These works indicate that the variation of basal spacings depends chiefly on the chemical difference among interlayer cations, especially between monovalent and divalent cations.

Ca²⁺ and Na⁺ are usually found in smectites as interlayer cations, Ca²⁺ having two layers of molecular water and giving rise to a basal spacing of about 15.5 Å, and Na⁺ having one layer of molecular water and giving rise to a basal spacing of about 12.5 Å (see, e.g., Keren and Shainberg, 1975). Glaeser and Méring (1954) pointed out that these ions tend to occur in a “demixed state,” that is, some interlayer regions are occupied mainly by Ca²⁺ and others mainly by Na⁺. McAtee (1956) analyzed the X-ray powder diffraction (XRD)

patterns of cation-exchanged (Ca,Na)-smectites by a Fourier transform method and found that Ca-montmorillonite and Na-montmorillonite layers are randomly interstratified in the *c** direction of the crystal. On the other hand, Levy and Francis (1975) reported that the interstratification corresponds to a segregated type of structure.

Yoshida (1979) calculated electrostatically the amount of cations that can coexist in an interlayer of a coexisting Ca²⁺ and Na⁺ system of smectite. He concluded that the demixing of Ca²⁺ and Na⁺ occurs readily. On the basis of these data, the variation of the basal spacings of smectite with relative humidity may be interpreted from a knowledge of such interstratified structures containing component layers about 15.5 and 12.5 Å thick. The present paper concerns the evidence for this line of reasoning.

SPECIMENS

The 11 smectites (dioctahedral) and 2 interstratified minerals (dioctahedral mica/smectite) studied are described in Table 1. The diagenetic bentonites from the Tsukinuno and Mizumaki mines contain quartz and feldspars as impurities; a small amount of cristobalite is also present in the Mizumaki specimen studied here.

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Table 1. Localities and modes of occurrence of specimens examined.

Specimen	Locality	Sampling point	Description
T1	Tsukinuno mine, Yamagata Pref.	No. 31 seam, 90 m depth	Massive, pale-gray clay
N1	Mizumaki, Fukuoka Pref.	No. 3 seam, lower part, 90 m depth	Massive, dark-green clay
N2		No. 1 seam, 110 m depth	Greenish-white matrix of dark-green, patched clay
N3		No. 2 seam, 110 m depth	Massive, pale-green clay
M1	Matsuki mine, Akita Pref.	Well A9, 99.4 m depth	White clay in strongly argillized tuff
M2		Well A6, 202.0 m depth	Greenish-brown clay
M3		Well 61, 132.6 m depth	Greenish-white matrix of dark-green, patched clay
M4		Well 100, 208.8 m depth	Green clay in compact mudstone
M5		Well 107, 215.1 m depth	Greenish-gray clay in fine-grained tuff
M6		Well A5, 205.3 m depth	White clay in argillized tuff
M7		Matsuki orebody, 180 m depth	Massive green clay in hanging wall
I1	Matsuki mine, Akita Pref.	Takadate orebody, 180 m depth	Greenish-white clay with silky luster
I2		Matsuki orebody, 150 m depth	Greenish-white clay with silky luster

The Matsuki ore deposit is of the Kuroko type. Smectites from this mine are alteration products of acidic tuffs or lavas; the smectites are considered to be diagenetic and to have been altered hydrothermally during the emplacement of the ore. In this deposit interstratified minerals exist in the clay zone enclosing the ore bodies. Smectite and interstratified minerals (samples I1–I2) from the Matsuki mine were collected from drill cores above the ore body or in the pit. Quartz and feldspar are common in all the smectite specimens studied. Small amounts of pyrite and quartz occur in specimens I1 and I2, respectively.

Each of the specimens was disaggregated by ultrasonics. The $<2\text{-}\mu\text{m}$ fraction was free or almost free from impurities and was used in the following experiments. Chemical analyses were made by a standard wet method; CaO and MgO were determined by a chelatometry using EDTA, and Na₂O and K₂O were determined by flame photometry. The amount of remaining quartz and cristobalite impurities was determined by XRD by the standard addition method. Chemical formulae calculated on the basis of O₁₀(OH)₂ from the analyses of $<2\text{-}\mu\text{m}$ material are shown in Table 2. The octahedral nature of these specimens is indicated by the octahedral population of about 2.00; it was also confirmed by XRD. Interlayer cations are Ca, Na, K, and Mg, but Ca and Na are the main constituents. The Ca/Na atomic ratio ranges from 2 to 0.1. XRD patterns of oriented powders treated with ethylene glycol and glycerol show the basal reflections at submultiples of 16.9–17.0 Å and 17.7–17.8 Å, respectively.

The chemical formulae of the interstratified minerals indicate that they are of the 1:1 regular type, having a component layer of potassium mica. The chemical formulae containing small amounts of Fe and Mg are close

to those of dioctahedral micas from Kuroko deposits, as previously reported by Kodama *et al.* (1969), Shimoda (1972), and Higashi (1974). Specimen I2 contains more interlayer Na than specimen I1.

EXPERIMENTAL

For studies of the hydration behavior of the smectites, XRD basal spacings of the Ca- or Na-saturated clay film of specimen M6 were measured under various relative humidity (RH) conditions. The RH was changed between 0 and 100% at intervals about 20% by changing the concentration of the sulfuric acid. XRD patterns were made when the RH reached equilibrium at each step; the equilibrium state was confirmed by the intensity of 001 reflection becoming constant; usually, it took 30–60 min to achieve equilibrium.

The variation of basal spacings of Ca- or Na-saturated smectite with RH is shown in Figure 1. At 40% RH, the basal spacings of Ca and Na smectites were clearly different from each other, occurring at about 15 Å in the former and at about 12 Å in the latter. At RH $\geq 60\%$, the basal spacing of the Na-smectite expanded nearly to that of the Ca-smectite. Therefore, at this RH, the basal reflections of these smectites nearly overlap one another. On the other hand, at $<20\%$ RH, the expansion of Ca-smectite was minor and close to that of Na-smectite. From the data shown in Figure 1, if an interstratified structure of 12-Å and 15-Å layers could be formed, a RH of about 40% would be most favorable for the formation of the interstratification. On this basis, the RH was controlled at 40% throughout the experiments.

Interstratifications were identified by comparing measured values with those calculated by the method of Kakinoki and Komura (1952, 1954). The technical procedures of the calculation were described in detail

by Watanabe (1977). The X-ray scattering intensity in the reciprocal space along the c^* direction of an interstratified crystal consisting of N layers and n types of layers, can be expressed as follows:

$$I = N \text{ Spur } VF + \sum_{n=1}^{N-1} (N - n) \text{ Spur } VFQ^n + \text{conj.}, \quad (1)$$

where Spur means the sum of the diagonal elements of square matrix, and conj., the complex conjugate of the foregoing terms. The symbols in Eq. (1) are

$$V = \begin{bmatrix} V_1*V_1 & V_1*V_2 & \dots & V_1*V_R \\ V_2*V_1 & V_2*V_2 & \dots & V_2*V_R \\ \vdots & \vdots & \ddots & \vdots \\ V_R*V_1 & V_R*V_2 & \dots & V_R*V_R \end{bmatrix}_R,$$

the matrix of the structure factors,

$$F = \begin{bmatrix} W_1 & 0 & \dots & 0 \\ 0 & W_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & W_R \end{bmatrix}_R,$$

the matrix of the probabilities of finding component layers,

$$P = \begin{bmatrix} P_{11} & P_{11} & \dots & P_{1R} \\ P_{21} & P_{22} & \dots & P_{2R} \\ \vdots & \vdots & \ddots & \vdots \\ P_{R1} & P_{R2} & \dots & P_{RR} \end{bmatrix}_R,$$

the matrix of the junction probabilities of component layers, and

$$Q = \Phi P$$

$$\Phi = \begin{bmatrix} \exp -i\psi_1 & 0 & \dots & 0 \\ 0 & \exp -i\psi_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \exp -i\psi_R \end{bmatrix}_R,$$

the matrix of phase factors. V_i is the layer structure factor of the layer i , W_i the probability of finding the layer i , P_{ij} the probability of finding the layer j after the layer i , and ψ_i the phase shift due to the thickness of the layer i .

As defined by Jagodzinski (1949), the 'Reichweite' is g when the junction probability P_{ij} depends not only on the layer i but also on the combination of the pre-

Table 2. Calculated numbers of atoms on the basis of 22 negative charges.

Specimen	T1	N1	N2	N3	M1	M2	M3	M4	M5	M6	M7	I1	I2
Tetrahedral													
Si	3.76	3.86	3.89	3.87	3.93	3.85	3.75	3.90	3.90	3.89	3.92	3.42	3.51
Al	0.24	0.14	0.11	0.13	0.07	0.15	0.25	0.10	0.10	0.11	0.08	0.58	0.49
Charge	-0.24	-0.14	-0.11	-0.13	-0.07	-0.15	-0.25	-0.10	-0.10	-0.11	-0.08	-0.58	-0.49
Octahedral													
Al	1.79	1.64	1.58	1.59	1.41	1.38	1.42	1.44	1.47	1.53	1.46	1.94	1.84
Fe ³⁺	0.04	0.13	0.14	0.18	0.11	0.19	0.29	0.21	0.13	0.10	0.12	0.05	0.03
Fe ²⁺	0.03	0.01	0.01	0.03	0.03	0.03	0.03	0.01	0.03	0.00	0.02	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Mg	0.15	0.23	0.27	0.20	0.49	0.43	0.32	0.32	0.39	0.36	0.44	0.06	0.10
Sum	2.01	2.01	2.00	2.00	2.04	2.04	2.06	1.99	2.02	1.99	2.04	2.05	1.97
Charge	-0.16	-0.20	-0.30	-0.21	-0.40	-0.37	-0.16	-0.36	-0.35	-0.36	-0.36	+0.01	-0.17
Interlayer													
Ca	0.03	0.03	0.02	0.03	0.10	0.12	0.10	0.13	0.13	0.14	0.15	0.06	0.07
Mg	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.42	0.40
K	0.00	0.03	0.02	0.01	0.02	0.02	0.02	0.03	0.02	0.02	0.05	0.03	0.12
Na	0.32	0.25	0.33	0.25	0.23	0.24	0.17	0.16	0.13	0.15	0.07	0.03	0.12
Charge	0.40	0.34	0.41	0.34	0.47	0.52	0.41	0.47	0.45	0.47	0.44	0.57	0.66

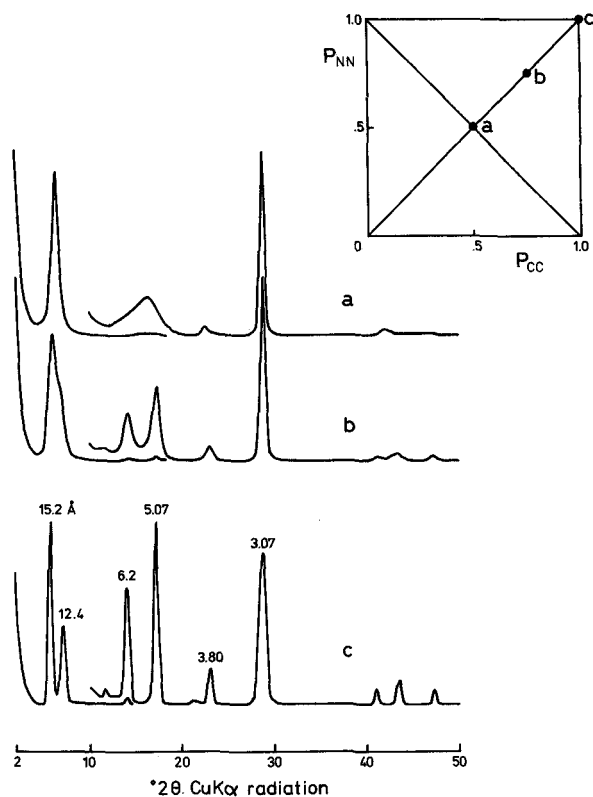


Figure 3. Calculated X-ray powder diffraction profiles for some structure models of (Ca,Na)-smectite. The diagram of P_{CC} vs. P_{NN} shows the probability parameters of interstratified structure of two component system used in the calculation. C = Ca-smectite layer; N = Na-smectite layer; a = 1:1 random interstratification; b = segregation structure corresponding to $P_{CC} = .75$ and $P_{NN} = .75$; c = ideal segregation.

interstratification of Ca- and Na-saturated smectite layers.

XRD line profiles were calculated for some structural models having Reichweite $g = 1$ and the two component system of a Ca-smectite layer (component C) and a Na-smectite layer (component N).

The two-component system has probabilities related by the following equations:

$$W_C + W_N = 1,$$

$$P_{CC} + P_{CN} = 1,$$

$$P_{NC} + P_{NN} = 1,$$

and

$$W_C P_{CN} = W_N P_{NC},$$

where W_C is the probability of occurrence of C, W_N that of N and P_{CC} is the junction probability that C succeeds C. P_{CN} , P_{NC} , and P_{NN} are similarly defined (MacEwan *et al.*, 1961). Six variables exist, but all are fixed if any two are specified.

Generally, the mode of interstratification may be of three types: (1) regular interstratification, (2) random

interstratification, and (3) segregation. For characterizing the interstratified structure, we consider here models having W_C and W_N fixed at 0.5 and various junction probabilities on Sato's diagram (Sato, 1965) (Figure 3). Model a belongs to a completely random type and model b to a partially random type, with a tendency towards segregation. Model c indicates complete segregation.

For $W_C = W_N = 0.5$, calculated XRD profiles show that the reflections at about 5 and 6 Å become weak and diffuse as the interstratification becomes completely random ($c \rightarrow b \rightarrow a$). Intensity ratios of $I(6 \text{ \AA})/I(3 \text{ \AA})$ and $I(5 \text{ \AA})/I(3 \text{ \AA})$ were therefore calculated for 20 models having various probability values ranging from completely random to completely segregated structures ($1 < P_{CC} + P_{NN} < 2$). These values were plotted on Sato's diagram, and two kinds of isopleths of $I(6 \text{ \AA})/I(3 \text{ \AA})$ and $I(5 \text{ \AA})/I(3 \text{ \AA})$ were drawn (Figure 4). Interstratification probabilities can be found as the intersection of two intensity ratio curves on the diagram, if XRD intensities of the three 6-, 5-, and 3-Å reflections are determined. Interstratification probabilities of specimens obtained by this procedure are listed in Table 4. The relation between W_A -values and the observed ratio $Ca^{2+}/(Ca^{2+} + Na^+)$, in which the amounts are given in equivalent weight, yields an essentially straight line (Figure 5). This relationship is evidence for the validity of analytical method mentioned above and indicates that the different XRD patterns of the smectite specimens are due to an interstratified structure, i.e., random interstratification with a tendency towards segregation into two components: 12.4-Å Na-smectite and 15.2-Å Ca-smectite layers.

Interstratification of mica and Ca- and Na-smectite layers

On ethylene glycol solvation, specimens I1 and I2 yielded similar XRD patterns having a nearly integral series of basal reflections (Figure 6). These patterns indicate a regular interstratification of mica and smectite. The proportion of smectite layers in specimens I1 and I2 was estimated to be 35% and 45%, respectively,

Table 4. Probability parameters of interstratified structures of smectites having component layers of 15.2-Å Ca-smectite layer (C) and 12.4-Å Na-smectite layer (N).

Specimen	W_C	W_N	P_{CC}	P_{CN}	P_{NC}	P_{NN}
N1	0.23	0.77	.53	.47	.23	.86
N2	0.21	0.79	.62	.38	.10	.90
N3	0.31	0.69	.44	.56	.25	.75
M1	0.48	0.52	.72	.28	.26	.74
M2	0.42	0.58	.70	.30	.22	.78
M3	0.50	0.50	.73	.27	.27	.73
M4	0.70	0.30	.85	.15	.36	.64
M5	0.64	0.36	.80	.20	.35	.65
M6	0.66	0.34	.83	.17	.33	.67
M7	0.79	0.21	.91	.09	.33	.67

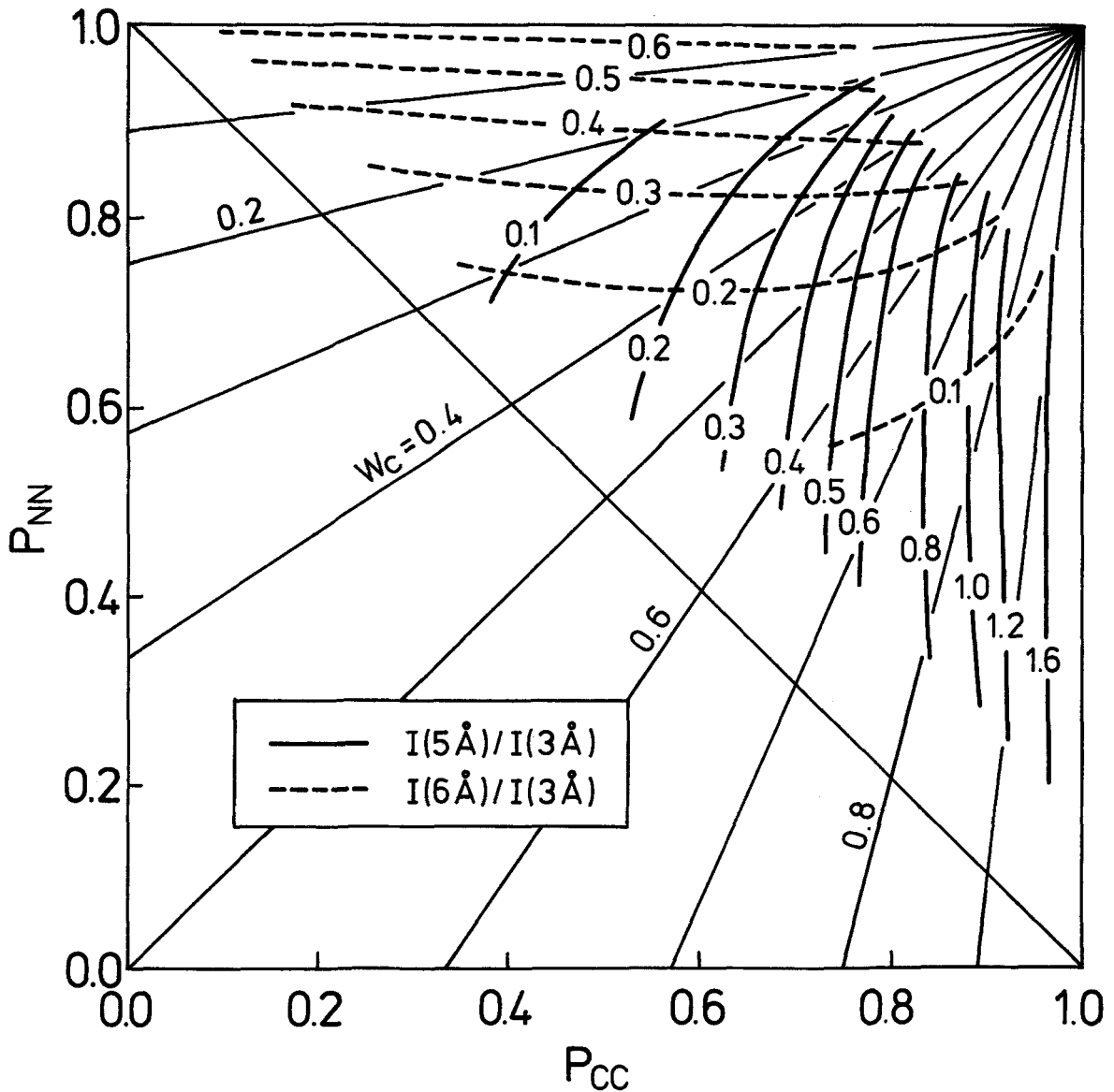


Figure 4. Calculated values for the intensity ratio of basal reflections for (Ca,Na)-smectites in relation to the interstratified structure of Ca-smectite layer (C) and Na-smectite layer (N). The numbers on each of the solid and broken curves represent the ratios $I(5 \text{ \AA})/I(3 \text{ \AA})$ and $I(6 \text{ \AA})/I(3 \text{ \AA})$, respectively.

referring to the diagram of Watanabe (1981). The transition probabilities are expressed by the following matrices:

$$I1; \begin{bmatrix} P_{MM} & P_{MS} \\ P_{SM} & P_{SS} \end{bmatrix} = \begin{bmatrix} 0.462 & 0.538 \\ 1.0 & 0.0 \end{bmatrix}$$

and

$$I2; \begin{bmatrix} P_{MM} & P_{MS} \\ P_{SM} & P_{SS} \end{bmatrix} = \begin{bmatrix} 0.182 & 0.818 \\ 1.0 & 0.0 \end{bmatrix},$$

where the symbols M and S stand for a mica layer and a smectite layer, respectively.

The XRD patterns of specimens I1 and I2 at 40% RH are shown in Figures 7 and 8. The long-spacing reflection at about 26 Å indicates a regular interstratification; however, the spacings and profiles of the higher-order basal reflections are quite different from each other. The basal reflections of specimen I1 are relatively sharp and symmetrical and occur at nearly submultiples of 25-Å. The basal reflections of specimen I2 are broad, and the 12-Å reflection is displaced compared with that of specimen I1. Reflections at about 7.4, 5.5, and 2.03 Å, which were not observed in the XRD pattern of specimen I1, were also noted.

Variation of the XRD patterns of the specimens at

Table 5. Probability parameters of interstratified structures of interstratified mica/smectites with component layers of 15.2-Å Ca-smectite layer (C), 12.4-Å Na-smectite layer (N), and 10.0-Å mica layer (M).

Specimen	W_C	W_N	W_M	P_{CMC}	P_{CMN}	P_{CMM}	P_{NMN}	P_{NMC}	P_{NMM}
I1	0.65	0.00	0.35	.14	.00	.86	—	—	—
I2	0.225	0.225	0.55	.58	.20	.22	.58	.20	.22

Transition probabilities were obtained assuming the sequence of MMM was not viable.

hedral mica and smectite layers; but, half of the inter-layer spaces of the smectite components are considered to be occupied mainly by Ca^{2+} , the rest mainly by Na^+ . From the value $P_{CMC}/(P_{CMC} + P_{CMN}) = P_{NMN}/(P_{NMN} + P_{NMC}) = .75$, the sequences CMC and NMN are found more often than those of CMN and NMC, respectively, in a one-dimensional row of the component layers. Therefore, the M/C/N model structure is proposed, the C/N sequence being obtained after eliminating the mica layer (M) from the M/C/N sequence (Figure 10). The C/N sequence shows that the interstratification of specimen I2 is a segregated structure of Ca- and Na-smectite layers. The calculated interstratification probability values of specimens I1 and I2 are listed in Table 5.

Distribution of Ca and Na ions

Regardless of the ratio of Ca-smectite layers to Na-smectite layers, the values of P_{CC} and P_{NN} of (Ca,Na)-smectites are intermediate between complete randomness ($P_{CC} + P_{NN} = 1$) and complete segregation ($P_{CC} = P_{NN} = 1$). Therefore, the particle consists of Ca-dominant domains and Na-dominant domains. From the observed XRD line profile, the number of the elementary layers in an X-ray-coherent domain is about 10, which is the number of layers (N) used in line profile calculations, and the distance in c^* direction is about 120–150 Å. The number of layers in each single domain may be less than 10, because domains coexist in an X-ray-coherent region. Figure 11 shows a model of these domains. Variation of the distribution in a and b directions, the scale of which in this figure is arbitrary,

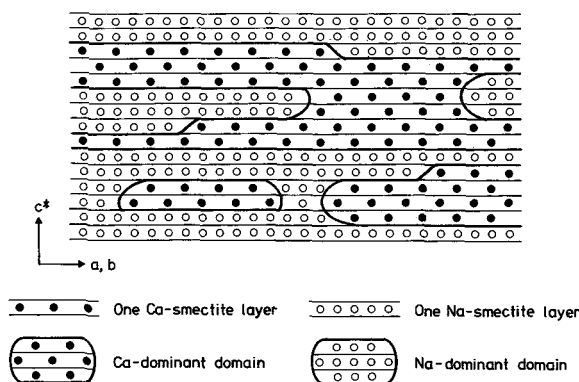


Figure 11. Schematic diagram for the distribution of Ca- and Na-smectite layers on the plane parallel to the c^* .

was estimated from the TEM photographs of organophilic montmorillonites (Yoshida and Suito, 1972).

For interstratified mica/smectite, the same result was obtained as was obtained for smectites. The Ca- and Na-smectite layers form segregated structures, despite sandwiching of the mica layer. Consequently, in both smectite and interstratified mica/smectite, Ca^{2+} and Na^+ were distributed in segregated structures. On the basis of calculated configuration entropies of Ca and Na ions in smectite, Yoshida (1979) concluded that Ca and Na ions are apt to be distributed in the segregated forms. Also, Gleaser and Méring (1954) reported 'demixing' of Ca and Na ions in smectite. These ideas support the results obtained in the present study.

ACKNOWLEDGMENTS

The writers are grateful to H. Shirozu of Kyushu University for constant guidance and instructive advice in the course of the work. Sincere thanks are also due to Emeritus Prof. T. Sudo of Tokyo University of Education and F. A. Mumpton of State University of New York for critical reading of the manuscript and helpful comments and to Hideo Akasako of West Japan Engineering Consultants, Inc. for the improvement of the computing program.

REFERENCES

- Fripiat, J. T., Jelli, A., Poncelet, G., and Andre, J. (1965) Thermodynamic properties and absorbed water molecules and electrical conduction in montmorillonite and silicates: *J. Phys. Chem.* **69**, 2185–2197.
- Glaeser, P. R. and Méring, J. (1954) Isotherms d'hydratation des montmorillonites bi-ioniques (Ca, Na): *Clay Miner. Bull.* **2**, 188–193.
- Hendricks, S. B., Nelson, R. A., and Alexander, L. T. (1940) Hydration mechanism of the clay mineral montmorillonite saturated with various cations: *J. Amer. Chem. Soc.* **62**, 1457–1464.
- Higashi, S. (1974) Sericite and interstratified sericite-montmorillonite associated with Kuroko deposits in the Hokuroku district, Japan: *Clay Sci.* **4**, 243–253.
- Jagodzinski, H. (1949) Eindimensionale Fehlordnung in Kristallen und ihr Einfluss auf die Röntgeninterferenzen. I. Berechnung des Fehlordnungsgrades aus den Röntgenintensitäten: *Acta Crystallogr.* **2**, 201–207.
- Kakinoki, J. and Komura, Y. (1952) Intensity of X-ray diffraction by a one-dimensionally disordered crystal. (I) General derivation in cases of the "Reichweite" $s=0$ and 1: *J. Phys. Soc. Japan* **7**, 30–35.
- Kakinoki, J. and Komura, Y. (1954) Intensity of X-ray diffraction by a one-dimensionally disordered crystal. (II)

- General derivation in the case of the correlation range $s \geq 2$: *J. Phys. Soc. Japan* **9**, 169–176.
- Keren, R. and Shainberg, I. (1975) Water vapor isotherms and heat of immersion of Na/Ca-montmorillonite system. I, homoionic clay: *Clays & Clay Minerals* **23**, 193–200.
- Klug, H. P. and Alexander, L. E. (1974) *X-ray Diffraction Procedures*: 2nd ed., Wiley, New York, 966 pp.
- Kodama, H., Shimoda, S., and Sudo, T. (1969) Hydrated mica complexes: Their structure and chemical composition: in *Proc. Int. Clay Conf., Tokyo, 1969, Vol. 1*, L. Heller, ed., Israel Univ. Press, Jerusalem, 186–196.
- Levy, R. and Francis, C. W. (1975) Demixing of sodium and calcium ions in montmorillonite crystallites: *Clays & Clay Minerals* **23**, 475–476.
- MacEwan, D. M. C., Ruiz Amil, A., and Brown, G. (1961) Interstratified clay minerals: in *The X-ray Identification and Crystal Structures of Clay Minerals*, G. Brown, ed., Mineralogical Society, London, 393–445.
- McAtee, J. L., Jr. (1956) Determination of random interstratification in montmorillonite: *Amer. Mineral.* **41**, 627–631.
- Mooney, R. W., Keenan, A. G., and Wood, L. A. (1952) Adsorption of water vapor by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by X-ray diffraction: *J. Amer. Chem. Soc.* **74**, 1371–1374.
- Ross, M. (1968) X-ray diffraction effects by non-ideal crystals of biotite, muscovite, montmorillonite, mixed-layer clays, graphite, and periclase: *Z. Kristallogr.* **126**, 80–97.
- Sato, M. (1965) Structure of interstratified (mixed-layer) minerals: *Nature* **208**, 70–71.
- Shimoda, S. (1972) An interstratified mineral of mica and montmorillonite from the mineralized district at Niida near the Shakanai mine, Akita prefecture, Japan: *Clay Sci.* **4**, 115–125.
- Watanabe, T. (1977) X-ray line profile of interstratified chlorite/saponite: *Sci. Rept. Fac. Sci., Kyushu Univ., Geology* **12**, 303–309 (in Japanese, with English abstract).
- Watanabe, T. (1981) Identification of illite/montmorillonite interstratifications by x-ray powder diffraction: *J. Miner. Soc. Japan* **15**, Spec. Issue, 32–41 (in Japanese, with English abstract).
- Yoshida, T. (1979) Approximate statistical thermodynamics of demixing of interlayer cations: *Nendo Kagaku* **19**, 1–9 (in Japanese, with English abstract).
- Yoshida, T. and Suito, E. (1972) Interstratified layer structure of the organo-montmorillonites as revealed by electron microscopy: *J. Appl. Crystallogr.* **5**, 119–124.
- Zettlemoyer, A. C., Young, E. J., and Chessick, J. J. (1955) Studies of the surface chemistry of silicate minerals—III. Heat of immersion of bentonite in water: *J. Phys. Chem.* **59**, 962–966.

(Received 15 February 1986; accepted 22 April 1987; Ms. 1560)