

CLAY MINERALS IN THE KOBADA DISTRICT, EBINO CITY, MIYAZAKI PREFECTURE

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Abstract

In the Kobada district, Einbo city, Miyazaki Prefecture, altered andesites are distributed. Fractions less than $2\ \mu\text{m}$ of the altered andesites were studied by X-ray diffraction method, and mixed-layer minerals of mica/smectite were found besides smectite and kaolinite in the fractions. The mixed-layer minerals consist of a regular type and a random type. The probability parameters defining the structure of the regularly interstratified mineral can be shown as: P_A (mica layer existing probability)=0.51, P_B (smectite layer existing porability)=0.49, P_{AA} (probability that A succeeds A)=0.02, P_{AB} =0.98, P_{BA} =1 and P_{BB} =0.

Introduction

In the Kobada district, andesites of Miocene~Quaternary age are widely distributed, and propylitic alteration is observed in the andesites. The authors collected some samples of the altered andesites, and the fractions less than $2\ \mu\text{m}$ of the samples were investigated. The writers found that a regular type of mixed-layer mineral of mica/smectite exists in the altered andesites besides smectite and kaolinite. The mineralogical properties of the regularly interstratified mineral are described in detail in this paper.

Geology and occurrence

In the Kobada district, Ebino city, various volcanic rocks of the Miocene~Quaternary age are widely distributed. The oldest andesite in this district is altered, and it is called the Masaki propylites. The Nagasaka lava, Yahazu lava, Chayahira lava and Takishita lava are overlying the andesite. The Takishita lava is covered by the Kakuto andesites.

Sampling points are shown in Fig. 1. The distance between point A_0 and point A_1 is 1.5 m. Specimens D_0 - D_{19} were collected at intervals of 70 cm, and specimens G_0 - G_{10} were at intervals of 6 m. Specimens H_0 - H_{55} were collected at intervals of 70 cm.

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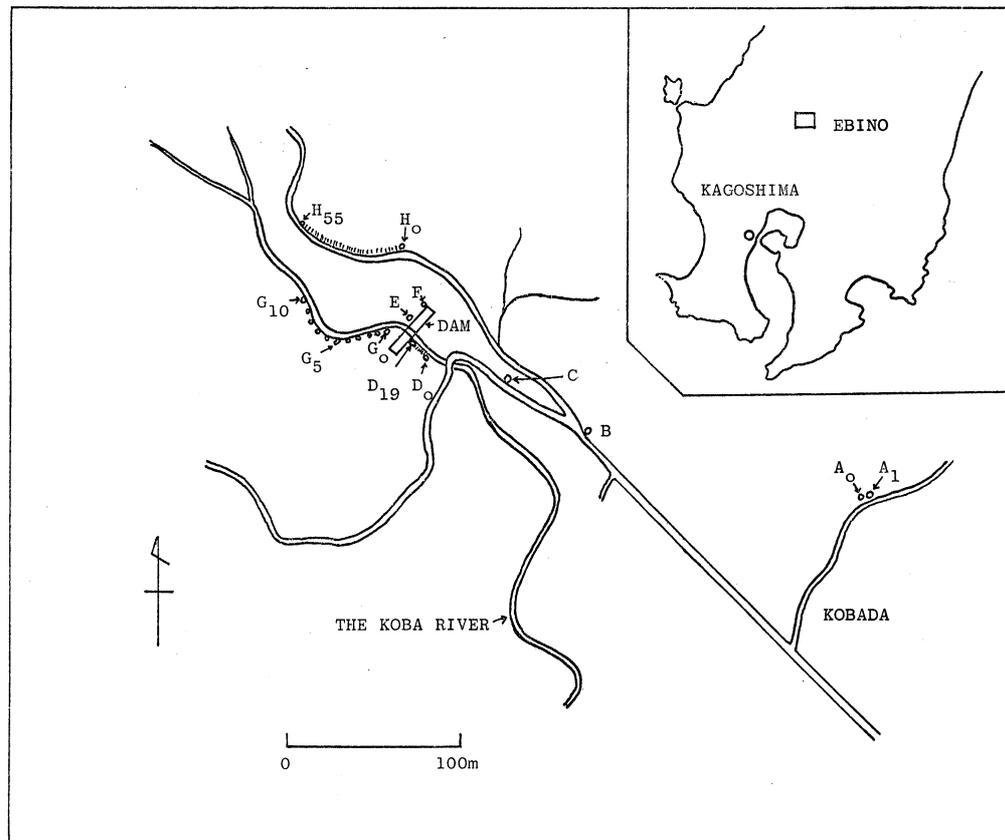


Fig. 1. Sampling points.

Mineralogical data

The fractions less than $2\ \mu\text{m}$ were obtained from the altered andesites by a crusher, an agate mortar and combined sedimentation and centrifugal separation. After drying, X-ray diffraction patterns were obtained from the materials preferred in orientation. Samples collected in this area could be classified into 4 groups by differences of including clay minerals. They are 1. specimens containing only a regularly interstratified mineral of mica/smectite (Type I); 2. specimens containing a regularly interstratified mineral of mica/smectite, smectite and kaolinite (Type II); 3. specimens containing a random mixed-layer mineral of mica/smectite, smectite and kaolinite (Type III), and 4. specimens containing kaolinite and smectite (Type IV). Types of the collected samples are listed in Table 1.

A. *Specimens containing only a regularly interstratified mineral of mica/smectite (Type I).*

As specimen A_0 was almost pure sample, the specimen was selected and investigated mineralogically.

X-ray analysis

X-ray powder patterns of the specimen A_0 after various treatments are shown in Fig. 2. $D(001)$ for the specimen shows $26\ \text{\AA}$, and it moved to $27.6\ \text{\AA}$ by treatment with

Table 1. Types of collected specimens.

Sample No.	Type	Sample No.	Type	Sample No.	Type
A0	I	G0	II	H21	II
A1	II	G1	II	H22	II
B	II	G2	II	H23	II
C	II	G3	II	H25	II
D0	II	G4	II	H27	II
D1	II	G5	II	H28	II
D3	II	G6	II	H29	II
D4	III	G7	III	H30	II
D5	II	G8	III	H31	IV
D6	II	G9	III	H33	III
D7	II	G10	III	H35	IV
D8	II	H0	III	H37	II
D9	II	H1	III	H39	II
D10	II	H3	II	H40	II
D11	II	H5	II	H41	II
D12	II	H7	III	H43	III
D13	II	H8	III	H45	II
D14	I	H9	III	H47	II
D15	II	H10	III	H48	II
D16	II	H11	III	H49	II
D17	II	H12	III	H50	II
D18	II	H13	III	H52	II
D19	II	H16	III	H53	II
E	II	H17	III	H54	II
F	II	H19	II	H55	II
		H20	II		

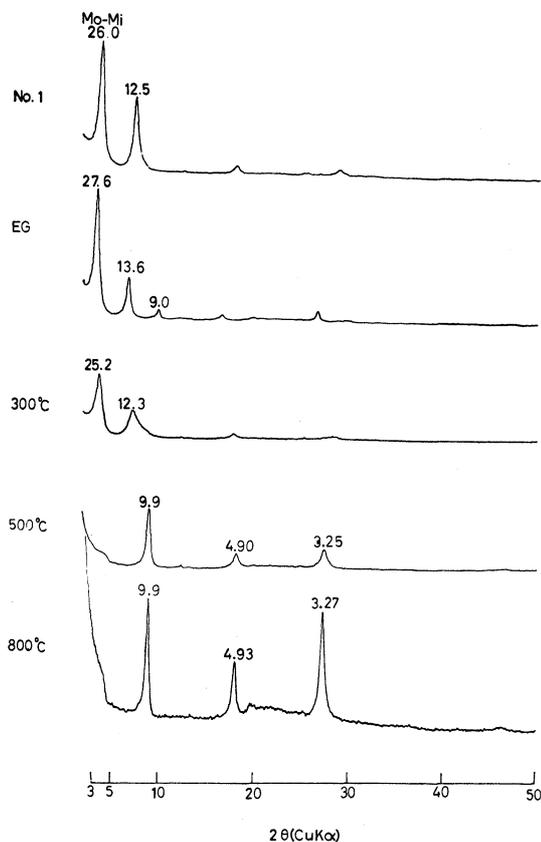


Fig. 2. X-ray powder diffraction patterns for the specimen A₀ after various treatments. No. 1. untreated sample A₀; EG. treated with ethylene glycol; 300 °C. heated to 300°C for 1 hr.

ethylene glycol. It contracted to 25.2 Å by heating to 300°C for one hour. The peak disappeared and shifted to 9.9 Å by heating to 800°C for one hour. Fourier transform method after MacEwan (1956) was used to deduce the nature of the interstratification of the interstratified mineral. The equation employed in this calculation was formulated by MacEwan and can be written as

$$W(R) = \sum_R \frac{I}{E|F_l|^2} \cos 2\pi\mu_R R$$

where $E, |F_l|^2, \mu_R$ are values at the position of the intensity maximum, and I is the integrated intensity. μ_R is the reciprocal spacing. $(1 + \cos^2 2\theta) / \sin 2\theta$ was used for the angular factor, E . The function $W(R)$ is defined as the probability of finding another layer at a distance R (measured perpendicularly) from any layer. Figure 3 shows the result of the Fourier transform of basal reflections of the specimen A_0 . In the figure, A represents mica layer and B represents smectite layer having two layers of water molecules between silicate layers. The outstanding peaks of type AB and $ABAB$ indicate a marked tendency for alternation of two different layers. Numerals given above the curve of the specimen A_0 are calculated peak heights for $P_A=0.51, P_B=0.49, P_{AA}=0.02, P_{AB}=0.98, P_{BA}=1, P_{BB}=0$, where A : mica layer, B : smectite layer. P_A represents the frequency of occurrence of A , and P_B that of B . P_{AB} is the probability that B succeeds A , assuming that the first layer is A ; P_{AA}, P_{BA} are similarly defined. Result of Fourier transform for the interstratified mineral is plotted as A in Fig. 4. The figure is based on a graph proposed by Sato (1965). In the figure, $P_{AA}=\alpha, P_{AB}=1-\alpha, P_{BB}=\beta, P_{BA}=1-\beta, \beta=K\alpha+(1-K), K=P_A/P_B$ were used. Using this equation all the

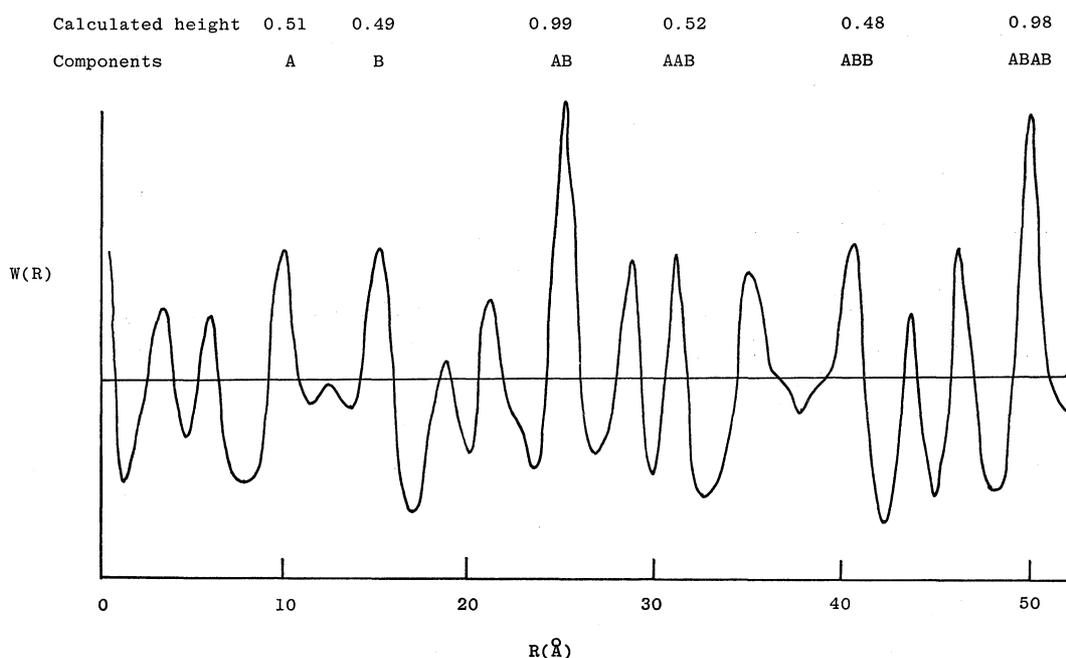


Fig. 3. Fourier transform of basal reflections of the specimen A_0 .

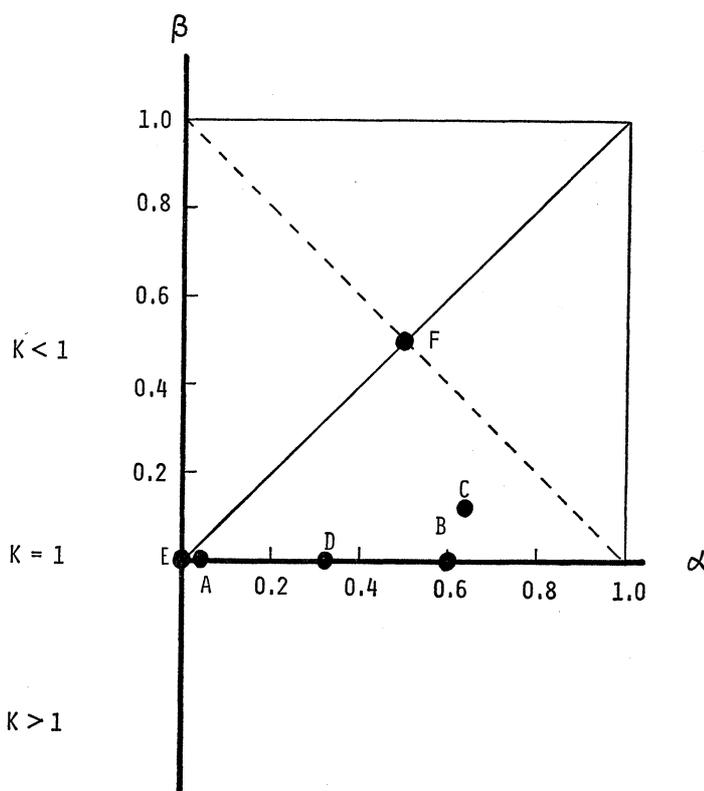


Fig. 4. Results of Fourier transform for the specimen $A_0(A)$, and some examples of mixed-layer minerals of mica/smectite. B and C are the specimens from Kamisunagawa in Hokkaido, which were reported by Kobayashi and Oinuma (1960), and D is from Honami mine reported by Sudo *et al.* (1962). E is the 1:1 regular structures reported by Brindley (1956), Sudo *et al.* (1962) and Tomita and Sudo (1968b). F is 1:1 random mixed-layer structure.

interstratified structures consisting of two kinds of layers can be plotted on the graph shown in Fig. 4. The random structures are plotted on the diagonal dotted line and regular type of mixed-layer minerals are distributed along the axes of coordinates. In the figure, B and C are the specimens from Kamisunagawa in Hokkaido, Japan, which were investigated by Kobayashi and Oinuma (1960), and D is from Honami mine in Nagano Prefecture reported by Sudo *et al.* (1962). E is the 1:1 regular structures reported by Brindley (1956), Sudo *et al.* (1962) and Tomita and Sudo (1968b). F is 1:1 random mixed-layer structure.

Differential thermal analysis

Differential thermal analysis curve was taken with an automatic thermal analyser at a heating rate of 10°C per one minute. A differential thermal analysis curve of the specimen A_0 is shown in Fig. 5. A double endothermic peaks at about 150°C are attributable to dehydration of adsorbed water and interlayer water. An endothermic peak at 240°C is due to dehydration of adsorbed water accompanied with exchangeable cations in expansible interlayers. An endothermic peak at 585°C is attributable to dehydroxylation of structure water.

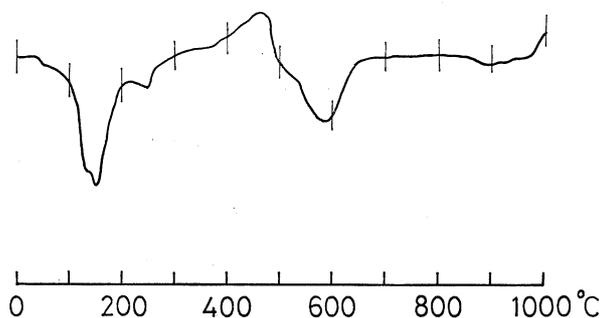


Fig. 5. Differential thermal analysis curve of the specimen A_0 .

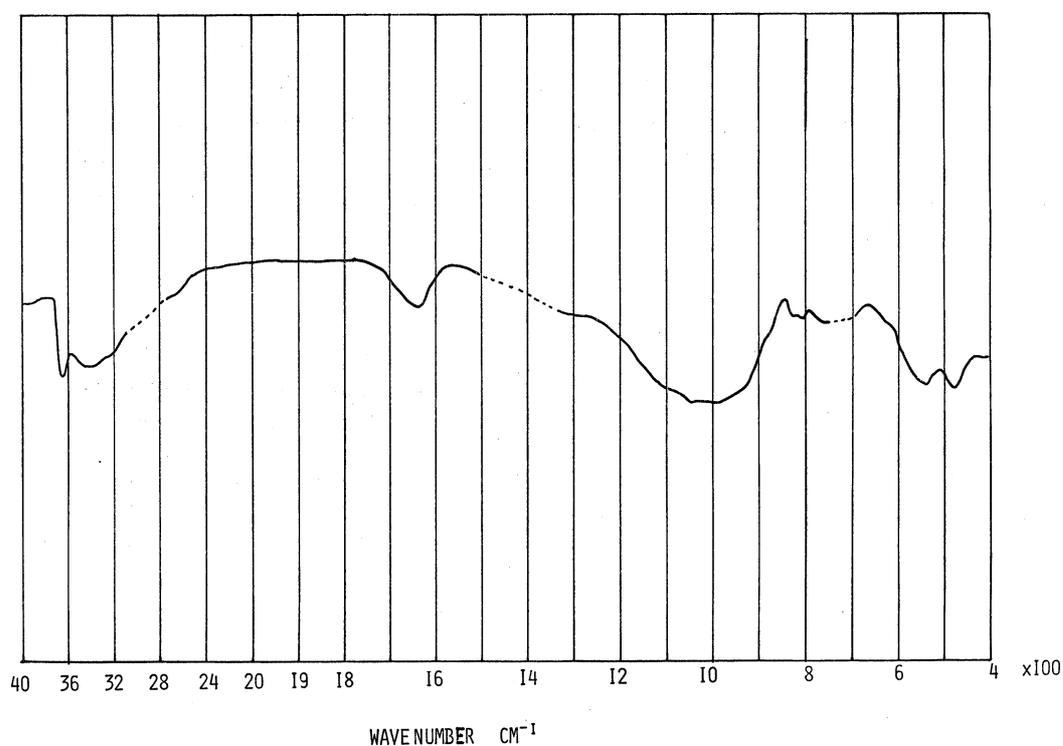


Fig. 6. Infrared absorption spectra of the specimen A_0 .

Infrared absorption spectra

Infrared absorption spectra of the interstratified mineral were obtained by the Nujol paste method. Figure 6 shows the infrared absorption spectra of the specimen A_0 . A band at 3650 cm^{-1} in the specimen is caused by the O-H stretching vibration. A band at 1640 cm^{-1} is due to adsorbed water vibration. In addition to these bands, a broad absorption band at 3400 cm^{-1} is observed, which is due to the adsorbed water in interlayers and is considered to be the same kind as that observed in absorption spectra of smectite. Double absorption bands in the range of $800\text{--}830\text{ cm}^{-1}$ which are characteristic to regularly interstratified mica/smectite minerals as reported by Oinuma and HAYASHI (1965) are observed.

Scanning electron microscopy

Figure 7 shows a scanning electron micrograph of the interstratified mineral. It shows flaky particles with irregular outlines.

Chemical analysis

Chemical analysis data for the interstratified mineral are listed in Table 2 together with those of allevardite (HÉNIN et al., 1954) and mixed-layer minerals (TOMITA and

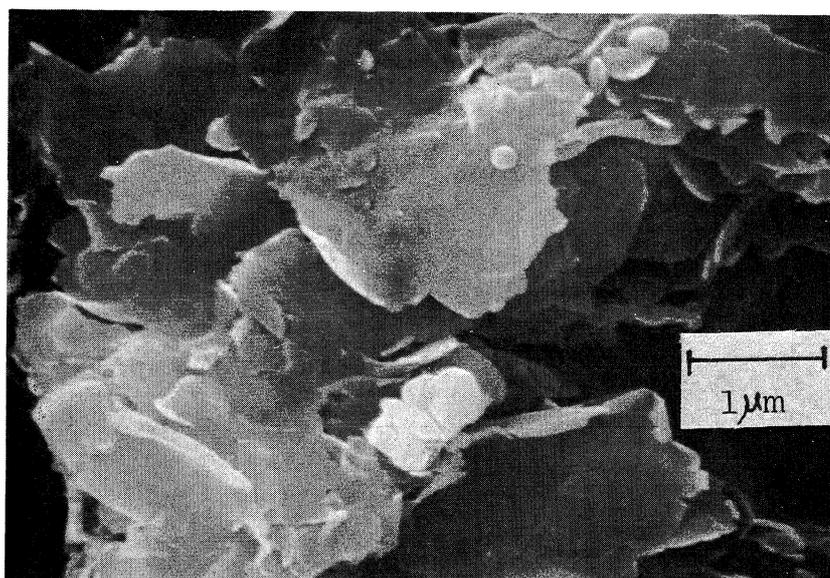


Fig. 7. Scanning electron micrograph of the specimen A_0 .

Table 2. Chemical compositions of some mixed-layer minerals of mica/smectite.

	1	2	3
SiO ₂	46.12%	45.20%	45.82%
TiO ₂	0.75	0.30	0.49
Al ₂ O ₃	30.15	32.15	29.83
Fe ₂ O ₃	} 1.93	0.65	} 4.98
FeO		0.55	
MnO	tr.		0.02
MgO	0.64	0.35	3.94
CaO	0.85	1.00	tr.
K ₂ O	1.45	1.10	1.40
Na ₂ O	1.73	2.25	0.80
H ₂ O(+)	9.90	6.04	8.32
H ₂ O(-)	6.47	9.72	5.04
P ₂ O ₅	tr.	0.15	tr.
Total	99.99%	99.46%	100.64%

1. specimen A_0 .
2. allevardite (After Hénin, Esquevin and Caillère, 1954).
3. specimen from Iwato (After Tomita and Dozono, 1973).

DOZONO, 1973). Allevardite is identical with rectorite (BROWN and WEIR, 1963a, b). The chemical composition of the specimen A_0 is similar to that of rectorite.

B. *Specimens containing a regularly interstratified minerals of mica/smectite, smectite and kaolinite (Type II).*

A specimen H_{27} was selected as a representative of this type. X-ray powder patterns of the specimen H_{27} after various treatments are shown in Fig. 8. A 26 Å reflection of a regularly interstratified mineral of mica/smectite moved to a 28.5 Å by treatment with ethylene glycol. A 15.2 Å peak of a smectite expanded to a 17.3 Å by treatment with ethylene glycol. These peaks moved to 9.9 Å after heating to 800°C for one hour. A 7.2 Å reflection of a kaolinite disappeared by heating at 800°C.

C. *Specimens containing a random interstratified mineral of mica/smectite, smectite and kaolinite (Type III).*

A specimen G_8 was selected as one of the type III specimens. X-ray powder

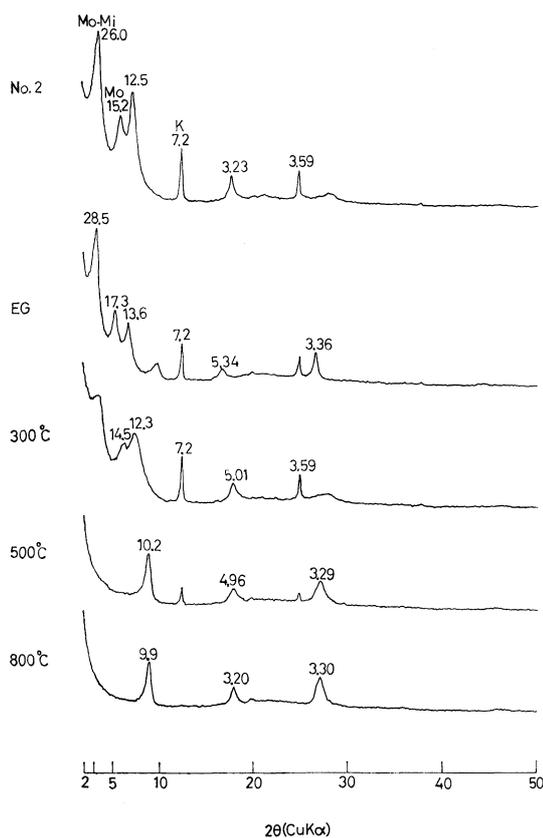


Fig. 8.

Fig. 8. X-ray powder diffraction patterns for the specimen H_{27} after various treatments.

No. 2. untreated sample H_{27} ; EG. treated with ethylene glycol; 300°C. heated at 300°C for 1 hr.

Fig. 9. X-ray powder diffraction patterns for the specimen G_8 after various treatments.

No. 3. untreated specimen G_8 ; EG. treated with ethylene glycol; 300°C. heated to 300°C for 1 hr.

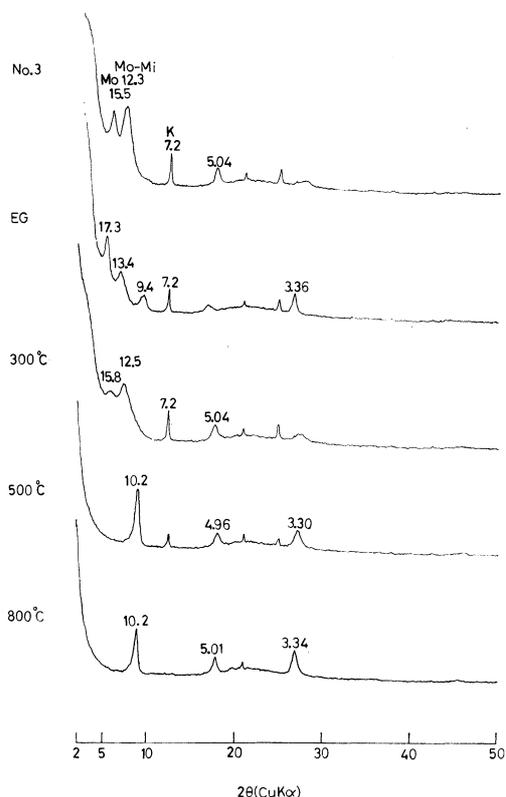


Fig. 9.

patterns of the specimen after various treatments are shown in Fig. 9. A 12.3 Å reflection of the random mixed-layer mineral moved to a 13.4 Å by treatment with ethylene glycol, and it moved to a 10.2 Å by heating at 800°C. A 15.5 Å peak of a smectite

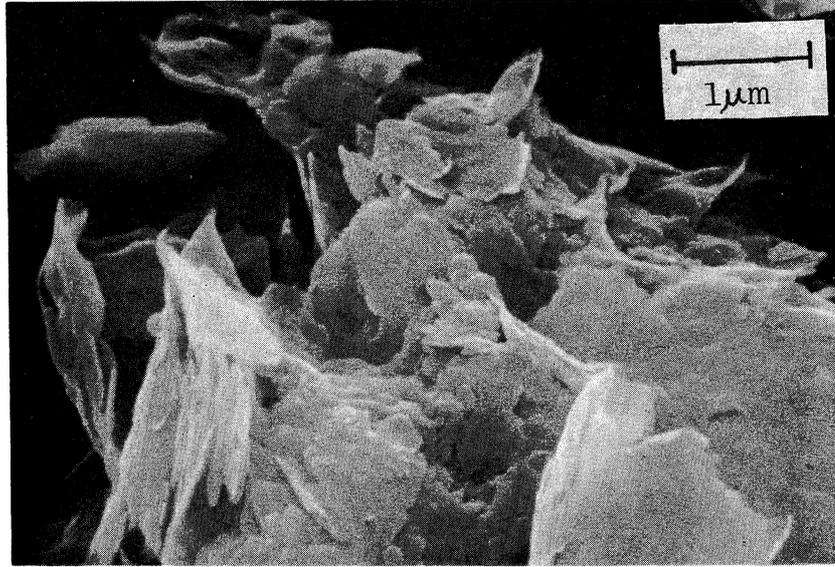


Fig. 10. Scanning electron micrograph of the specimen G₈.

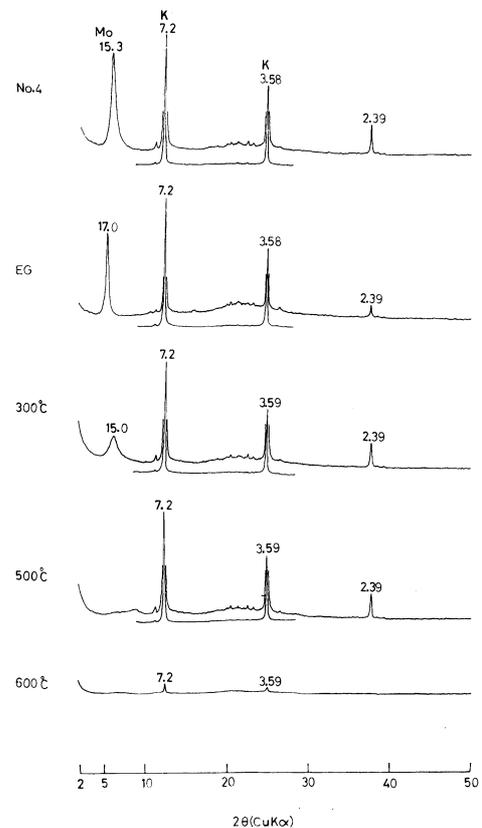


Fig. 11. X-ray powder diffraction patterns for the specimen H₃₅ after various treatments. No. 4. untreated specimen H₃₅; EG, treated with ethylene glycol; 300°C, heated to 300°C for 1 hr.

expanded to a 17.3 Å by treatment with ethylene glycol, and moved to 10.2 Å after heating to 800°C.

A scanning electron micrograph of the specimen G₈ is shown in Fig. 10. It shows flaky shapes with irregular outlines.

D. *Specimens containing kaolinite and smectite* (Type IV).

A specimen H₃₅ was selected as a representative of this group. X-ray powder patterns of the specimen after various treatments are shown in Fig. 11. A 15.3 Å peak of the smectite expanded to a 17 Å by ethylene glycol treatment, and it moved to a 15 Å after heating to 300°C for one hour. The smectite did not show any clear diffraction pattern after heating to 500°C. A 7.2 Å peak of kaolinite persisted up to 600°C by heating. These phenomena are uncommon for ordinary smectites and kaolinites found in Japan.

Discussion

Concerning the origin of the interstratified mineral of mica/smectite, three mechanisms are considered. They are classified into two groups. One is primary origin. It is defined as the crystallization of interstratified mineral from amorphous materials, natural minerals except mica minerals and smectite, or natural rocks (IYAMA and ROY, 1963; MATSUDA and HENMI, 1974; EBERL and HOWER, 1977). The other one is secondary origin. It is defined as alteration products formed in intermediate stages in the transformation of mica to smectite (UEDA and SUDO, 1966; TOMITA and SUDO, 1968a, b, 1971; TOMITA and DOZONO, 1972; TOMITA, 1974, 1977, 1978, 1979a, b), or smectite to mica (MÉRING and GLAESER, 1954; BRINDLEY and SANDALAKI, 1963; SHUTOV *et al.*, 1969; EBERL and HOWER, 1977; EBERL, 1978).

Judging from the mineralogical properties and occurrence of the mixed-layer mineral found in this district, it is difficult to conclude how the interstratified mineral was formed, but judging from a fact that any mica minerals are not found in this area, it is difficult to consider that the mixed-layer mineral was formed from mica. The authors think that the mixed-layer mineral was probably formed directly from andesites under hydrothermal condition.

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References

- BRINDLEY, G.W. (1956), Allevardite, a swelling double-layer mica mineral. *Amer. Mineral.*, **35**, 590-559.

- BRINDLEY, G.W. and SANDALAKI, Z. (1963), Structure, composition and genesis of some long-spacing mica-like minerals. *Amer. Mineral.*, **48**, 138-148.
- BROWN, G. and WEIR, A.H. (1963a). The identity of rectorite and allevardite. *Proc. International Clay Conf.*, **1963**, Vol. 1. Stockholm, Sweden, 27-35, Pergamon Press.
- BROWN, G. and WEIR, A.H. (1963b), An addition to the paper "the identity of rectorite and allevardite" in Vol. 1, Page 27, *Proc. International Clay Conf.*, 1963, Vol. 2, Stockholm, Sweden, 87-90, Pergamon Press.
- EBERL, D. (1978), Reaction series for dioctahedral smectites. *Clays and Clay Minerals*, **26**, 327-340, Pergamon Press.
- EBERL, D. and HOWER, J. (1977). The hydrothermal transformation of sodium and potassium smectite into mixed-layer clay. *Clays and Clay Minerals*, **25**, 215-227, Pergamon Press.
- HENIN, S, ESQUEVIN, J. and CAILLIERE, S. (1954), Sur la fibrosite de certains mineraux de nature montmorillonitique. *Bull. Soc. Franç. Miner. Crist.*, **77**, 491-499.
- IYAMA, J.T. and ROY, R. (1963), Controlled synthesis of heteropolytypic (mixed-layer) clay minerals. *Clays and Clay minerals*, **10**, 4-22, Pergamon Press.
- KOBAYASHI, K. and OINUMA, K. (1960), Clay mineralogical study on sedimentary rocks of Kamisunagawa district, Ishikari coal-field, Hokkaido. *J. Geol. Soc. Japan*, **779**, 506-516.
- MACEWAN, D.M.C. (1946), Fourier transform methods for studying scattering from lamellar systems — I. A direct method for analysing interstratified mixtures. *Kolloid Z.*, **149**, 96-108.
- MATSUDA, T. and HENMI, K. (1974), Syntheses of interstratified minerals from kaolin with addition of various cations. *Kobutsugaku Zasshi*, **11**, 152-161.
- MERING, J. and GLAESER, R. (1954), Sur le role de la valences cations échangeables dans la montmorillonite. *Bull. Soc. Franç. Miner. Crist.*, **77**, 519-530.
- OINUMA, K. and HAYASHI, H. (1965), Infrared study of mixed-layer clay minerals. *Amer. Mineral.*, **50**, 1213-1227.
- SATO, M. (1965), Structure of interstratified (mixed-layer) minerals. *Nature*, **208**, 70-71.
- SHUTOV, V.D., DRITS, V.A. and SAKHAROV, B.A. (1969), On the mechanism of a postsedimentary transformation of montmorillonite into hydro-mica. *Proc. International Clay Conf.*, 1969, Vol. 1, 523-531.
- SUDO, T., HAYASHI, H. and SHIMODA, S. (1962), Mineralogical problems of intermediate clay minerals. *Clays and Clay Minerals*, 9th Nat. Conf., 378-392, Pergamon Press, Oxford.
- TOMITA, K. (1974), Similarities of rehydration and rehydroxylation properties of rectorite and 2M clay micas. *Clays and Clay Minerals*, **22**, 79-85, Pergamon Press.
- TOMITA, K. (1977), Experimental transformation of 2M sericite into a rectorite-type mixed-layer mineral by treatment with various salts. *Clays and Clay Minerals*, **25**, 302-308, Pergamon Press.
- TOMITA, K. (1978), Experimental transformation of 2M sericite into a rectorite-type mixed-layer mineral by treatment with various salts. II. Experiments using a magnetic stirrer and a centrifuge. *Clays and Clay Minerals*, **26**, 209-216, Pergamon Press.
- TOMITA, K. (1979a), Synthesis of a regularly interstratified mineral of mica/montmorillonite and its formation mechanism. *Kobutsugaku Zasshi*, **14**, 105-129. (in Japanese with English abstract).
- TOMITA, K. (1979b). Experimental formation of a regular mixed-layer mineral of mica and montmorillonite from 2M₁ sericite by treatment with solution containing sodium cobaltinitrite. *Jour. Japan. Assoc. Min. Petr. Econ. Geol.*, **74**, 265-273.
- TOMITA, K. and DOZONO, M. (1972), Formation of an interstratified mineral by extraction of potassium from mica with sodium tetraphenylboron. *Clays and Clay Minerals*, **20**, 225-231, Pergamon Press.
- TOMITA, K. and DOZONO, M. (1973), An expansible mineral having high rehydration ability. *Clays and Clay Minerals*, **21**, 185-190, Pergamon Press.
- TOMITA, K. and SUDO, T. (1968a), Interstratified structure formed from a pre-heated mica by acid treatments. *Nature*, **217**, 1043-1044.

- TOMITA, K. and SUDO, T. (1968b), Conversion of mica into an interstratified mineral. *Rept. Faculty of Sci., Kagoshima Univ.*, **1**, 89-119.
- TOMITA, K. and SUDO, T. (1971), Transformation of sericite into an interstratified mineral. *Clays and Clay Minerals*, **19**, 263-270. Pergamon Press.
- UEDA, S. and SUDO, T. (1966), Synthesis of an interstratified mineral from mica. *Nature*, **211**, 1393-1394.