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著者	TOMITA Katsutoshi, KOISO Masato, YAMAMOTO Masahiko, OBA Noboru
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CLAY MINERALS IN THE ALTERED ANDESITES IN YOKOGAWA-CHO, KAGOSHIMA PREFECTURE

By

Katsutoshi TOMITA*, Masato KOISO**, Masahiko YAMAMOTO* and Noboru ÔBA

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Abstract

In the Yamagano area, Yokogawa-cho, Kagoshima 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 chlorite-montmorillonite, and mica-montmorillonite were found besides montmorillonite and chlorite in the fractions. The mixed-layer mineral of chlorite-montmorillonite was probably formed from a chlorite formed in the altered andesites by subsequent attacks of hydrothermal action or weathering.

Introduction

In the northern part of Kagoshima Prefecture, andesites of Miocene~Pliocene age are widely distributed, and propylitic alteration is observed in the andesites. The authors collected three samples of the altered andesites, and fractions less than $2\ \mu\text{m}$ of the samples were investigated. The writers found that mixed-layer minerals of chlorite-montmorillonite and mica-montmorillonite exist in the altered andesites besides chlorite and montmorillonite. The mineralogical properties of the mixed-layer mineral of mica-montmorillonite is described in detail in this paper.

Outline of Geology

In Yokogawa-cho, Kagoshima Prefecture, two pyroxene andesites of Miocene~Pliocene age are widely distributed. The Nagano formation overlies the andesites and are covered by andesites of Pliocene~Pleistocene age. Pyroclastic flow deposits are distributed on the younger andesites. The andesites of Miocene~Pliocene age are altered. In Yokogawa-cho, propylitic alteration is observed in the Ohra andesites and the Nakadake andesites. Chlorite is the dominant phase of alteration. Some samples were collected from the Ohra andesites. Sampling points are shown in Fig. 1. Calcite and laumontite are present in some fractures in the Ohra andesites (TOMITA *et al.*, 1979).

* Institute of Earth Sciences, Faculty of Science, Kagoshima University, Kagoshima, Japan.

** Daiei Development Company, Sasebo City, Nagasaki Prefecture.

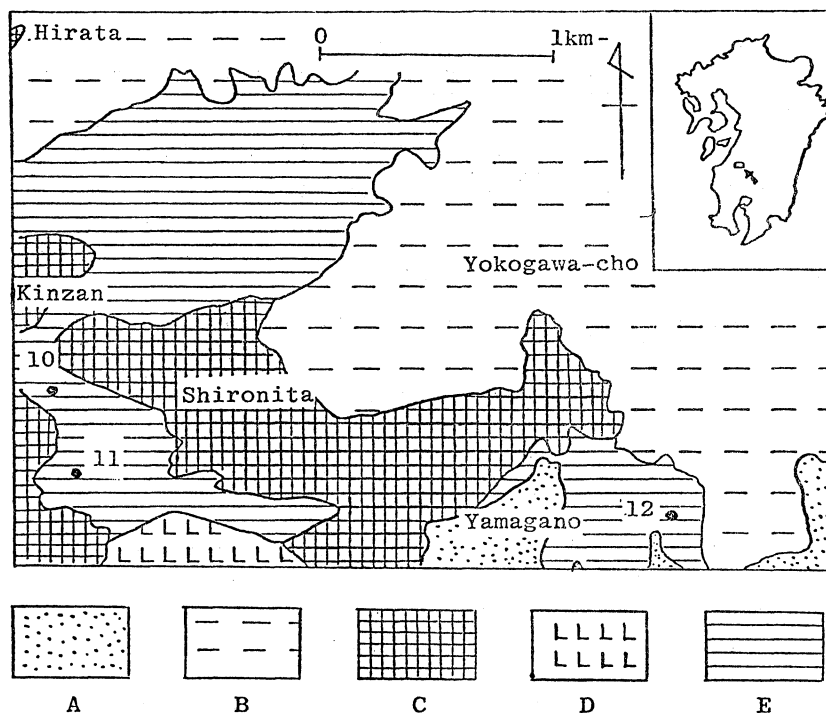


Fig. 1. Geological map of the surveyed area and the sampling points. A: Ito pyroclastic flow deposits. B: Kunimidake andesites. C: Nagano Formation. D: Nakadake andesites. E: Ohra andesites.

Mineralogical Data

The collected altered andesites were crushed with a crusher, and they were grounded in an agate mortar and fractions less than $2\ \mu\text{m}$ were obtained by combined sedimentation and centrifugal separation, and were dried in air. The dried samples were examined. Preferred particle orientation was used for X-ray diffraction analysis.

The X-ray powder patterns of the specimens No. 10, 11 and 12 are shown in Fig. 2, and the X-ray powder patterns of the specimens after treatment with ethylene glycol are shown in Fig. 3. The X-ray powder patterns of the specimen No. 10 after heating at various temperatures are shown in Fig. 4. Judging from those patterns, the specimen No. 10 contains chlorite and an interstratified mineral of mica and montmorillonite. The specimen No. 11 contains montmorillonite, chlorite and a mixed-layer mineral of chlorite and montmorillonite. The specimen No. 12 contains chlorite, a mixed-layer mineral of mica and montmorillonite, and a mixed-layer mineral of chlorite and montmorillonite.

Mineralogical properties of the interstratified mineral of mica and montmorillonite

As the specimens No. 11 and No. 12 are complex mixtures of some minerals, it was impossible to deduce the nature of layer stacking of the mixed-layer minerals. The specimen No. 10 is a mixed-layer mineral of mica and montmorillonite and contains

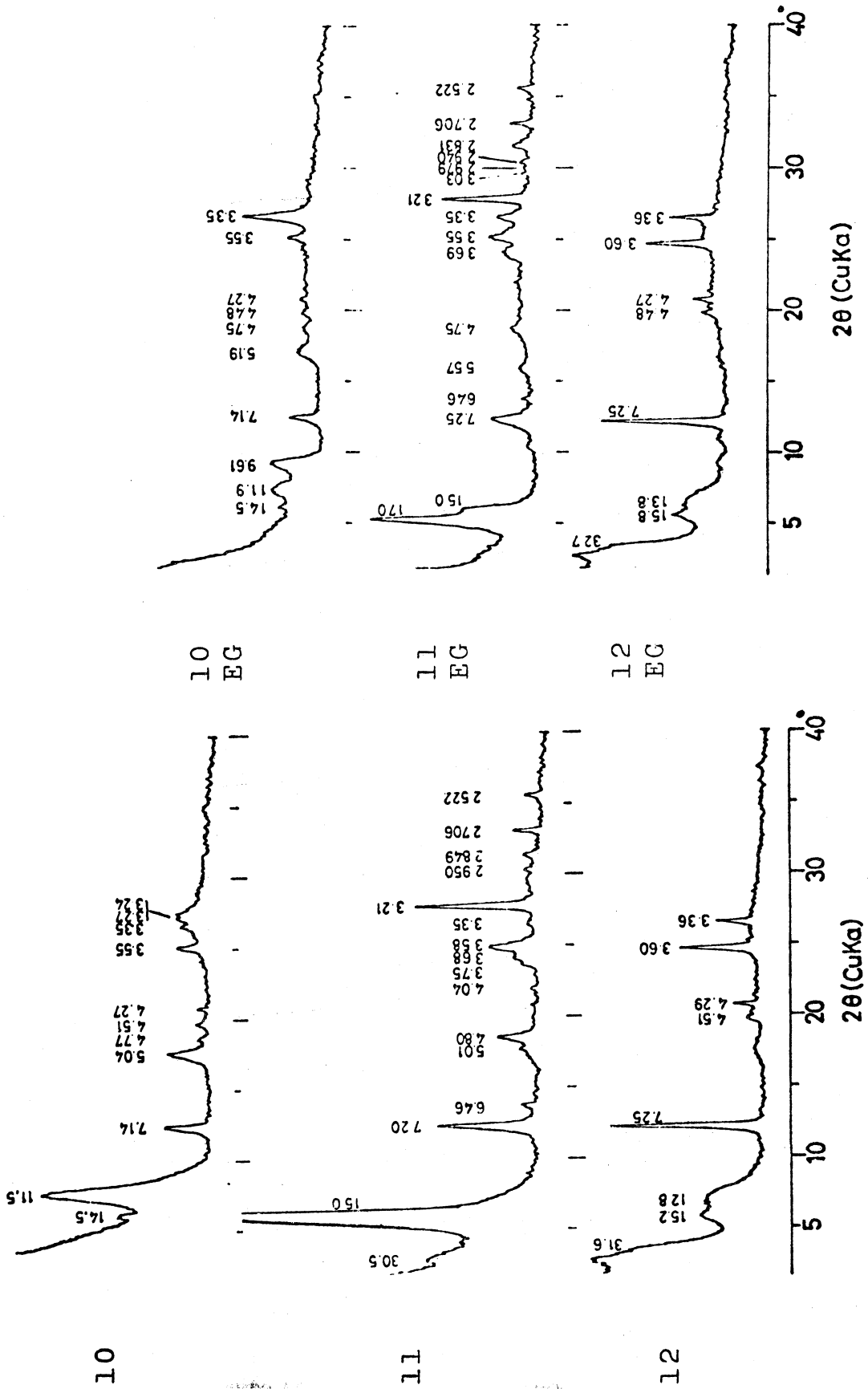


Fig. 3. X-ray powder diffraction patterns for the specimens No. 10, 11 and 12 after treatment with ethylene glycol.

Fig. 2. X-ray powder diffraction patterns for the specimens No. 10, 11 and 12.

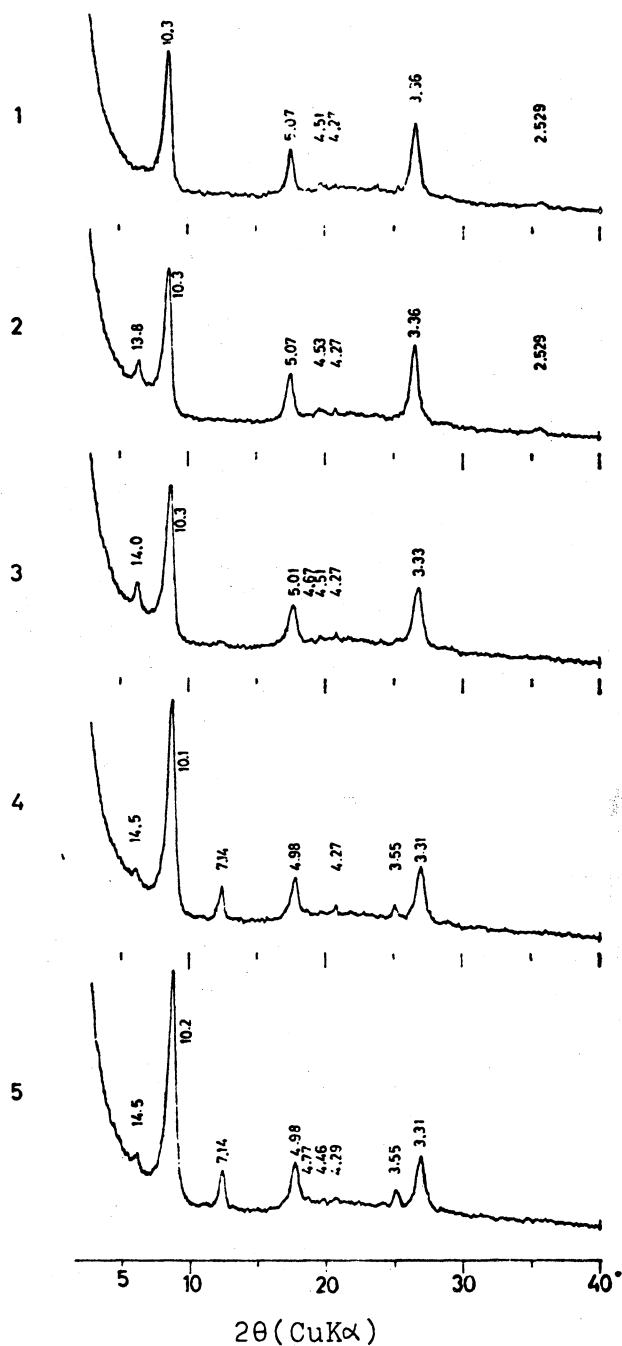


Fig. 4. X-ray powder diffraction patterns for the specimen No. 10 after heating at various temperatures for one hour. 1. 800°C; 2. 700°C; 3. 600°C; 4. 500°C; 5. 400°C.

only chlorite besides the mixed-layer mineral. The specimen No. 10 was selected and investigated in detail.

X-ray analysis

The specimen was studied using MacEwan's Fourier transform method to deduce the nature of the interstratification of the specimen. The equation employed in this

calculation was formulated by MACÉWAN (1956a) and can be written as

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

where $E, |F|^2, \mu_R$ are values at the position of the intensity maximum and I is the integrated intensity. μ_R is the reciprocal spacing. The $|F|^2$ values of dioctahedral mica-type layer with $1K^+, 1H_2O$ in interlayers were used for the Fourier transform. The values for $|F|^2$ were estimated from the tabulated data of COLE and LANCUCKI (1966). $(1 + \cos^2 2\theta / \sin 2\theta)$ was used for the combined Lorentz-polarization factor function. The function $W(R)$ is defined as the probability of finding another layer at a distance R (measured perpendicularly) from any layer. Figure 5 shows the result of the Fourier transform of basal reflections of the specimen No. 10 treated with ethylene glycol, where

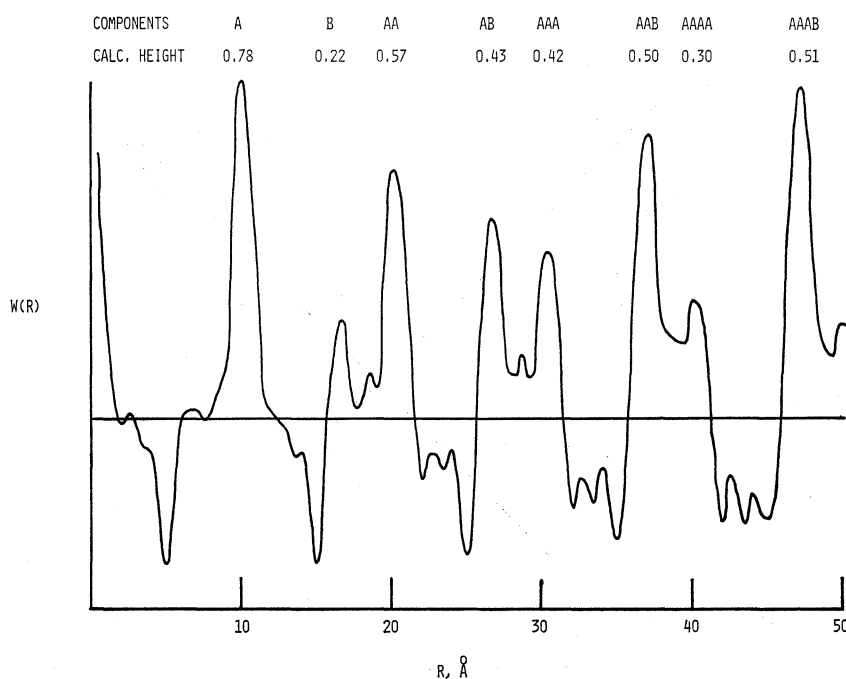


Fig. 5. Fourier transform of basal reflections of the ethylene glycol-treated specimen No. 10.

Table 1. Observed and calculated heights of peaks from Fourier transform of the specimen No. 10.

Peak	Calc. heights	Observed heights
A	0.78	0.78
B	0.22	0.22
AA	0.57	0.57
AB	0.43	0.46
AAA	0.42	0.38
AAB	0.50	0.66
AAAA	0.30	0.28
AAAB	0.51	0.76

A represents a mica layer and B an expandable layer. The outstanding peaks A and AA indicate that mica layers are dominant in the specimen, and expandable layers are a little. Numerals given above the curve are calculated peak heights for $P_A=0.78$, $P_B=0.22$, $P_{AA}=0.73$, $P_{AB}=0.27$, $P_{BA}=0.94$, $P_{BB}=0.06$, where A: mica layer, B: expandable layer. Calculated and observed peak heights on the Fourier transform from the specimen are listed in Table 1. 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_{BB} , P_{BA} are similarly defined. Calculated relative peak heights agree with the observed peak heights. Result of Fourier transform for the interstratified mineral is plotted as (F) in Fig. 6. The figure is based on a graph proposed by SATO (1965). In the figure, $P_{AA}=a$, $P_{AB}=1-a$, $P_{BB}=\beta$, $P_{BA}=1-\beta$, $\beta=K\alpha+(1-K)$, $K=P_A/P_B$, were used.

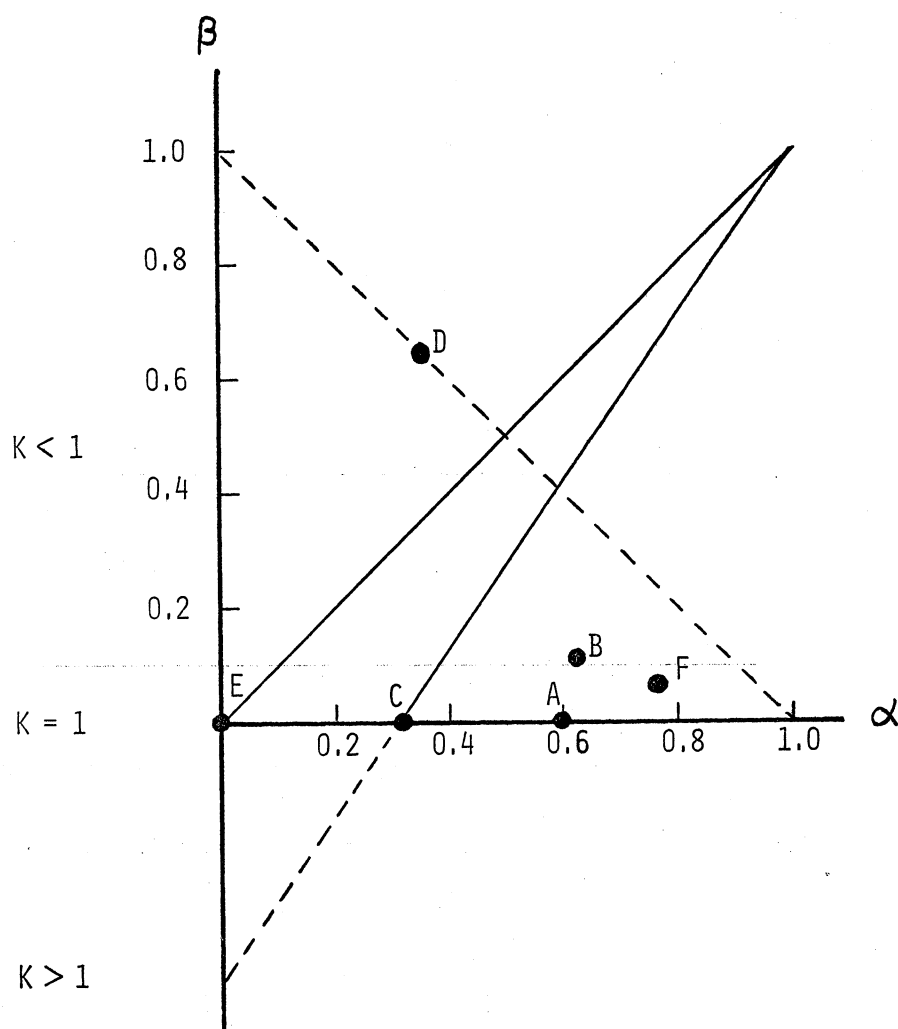


Fig. 6. Result of Fourier transform for the specimen No. 10 (F) and some examples of mica-montmorillonite interstratified minerals examined. (A) and (B) are the specimens from Kamisunagawa, and (C) is from Honami mine. (D) is the specimen investigated by MAC EWAN (1956b). (E) is the 1:1 regular structures reported by SUDO *et al.* (1962), BRINDLEY (1956), and TOMITA and SUDO (1968b), where $P_{AA}=a$, $P_{BB}=\beta$, and $K=P_A/P_B$.

Using this equation all the interstratified structures consisting of two kinds of layers can be plotted on the graph shown in Fig. 6. The random structures are plotted on the diagonal dotted line and regular type of mixed-layer minerals are distributed along the axes of coordinates. (A) and (B) are the specimen from Kamisunagawa in Hokkaido, Japan, which were investigated by KOBAYASHI and OINUMA (1960), and (C) is from Honami mine, in Nagano Prefecture, Japan, reported by SUDO *et al.* (1962). (D) is the specimen investigated by MACEWAN (1956b) using the Fourier transform method. (E) is the 1:1 regular structures reported by some investigators (SUDO *et al.*, 1962; BRINDLEY, 1956; TOMITA and SUDO, 1968b).

Table 2. Chemical composition of the specimen No. 10.

SiO ₂	48.71%
TiO ₂	1.13
Al ₂ O ₃	24.52
Fe ₂ O ₃)	
FeO	5.30
MnO	0.05
MgO	2.75
CaO	0.69
Na ₂ O	0.76
K ₂ O	5.05
H ₂ O(+)	
H ₂ O(-)	11.28
P ₂ O ₅	0.12
Total	100.36%

(Analyst: M. Koiso)

Chemical analysis

Chemical composition of the specimen is listed in Table 2. The specimen has a lower content of K₂O and a higher content of H₂O as compared with those of ordinary micas.

Differential thermal analysis

Differential thermal analysis curve was taken at a heating rate of 10°C per a minute for the specimen, and the curve is shown in Fig. 7. An endothermic peak with a shoulder between 100°C and 170°C is due to the dehydration of adsorbed water and interlayer water in the mixed-layer mineral. A broad endothermic peak at 580°C is due to dehydroxylation of the mixed-layer mineral, and a broad endothermic peak

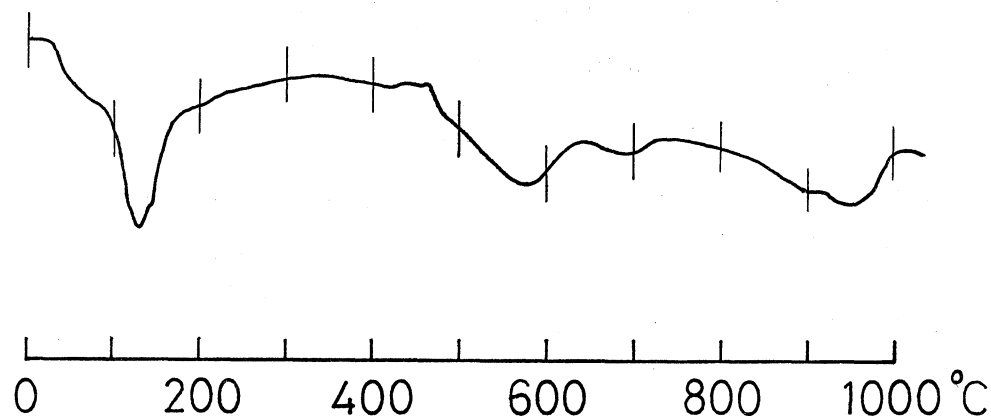


Fig. 7. Differential thermal analysis curve of the specimen No. 10.

between 650°C and 720°C is due to dehydroxylation of brucite layer of the chlorite. An endothermic peak, which is followed by an exothermic peak at about 1010°C, is due to dehydroxylation of silicate layer of the chlorite. A small double exothermic peaks between 420°C and 480°C are due to existence of a small amount of pyrite.

Infrared absorption spectra

Infrared absorption spectra was obtained with the Nujol paste method. Figure 8 shows spectra of the specimen. A broad absorption near 3400 cm^{-1} is due to the absorption of interlayer water contained in expandable layers in the mixed-layer mineral. A band at 1640 cm^{-1} is due to adsorbed water. A band at 3620 cm^{-1} is due to the OH stretching vibration of the mixed-layer mineral and chlorite.

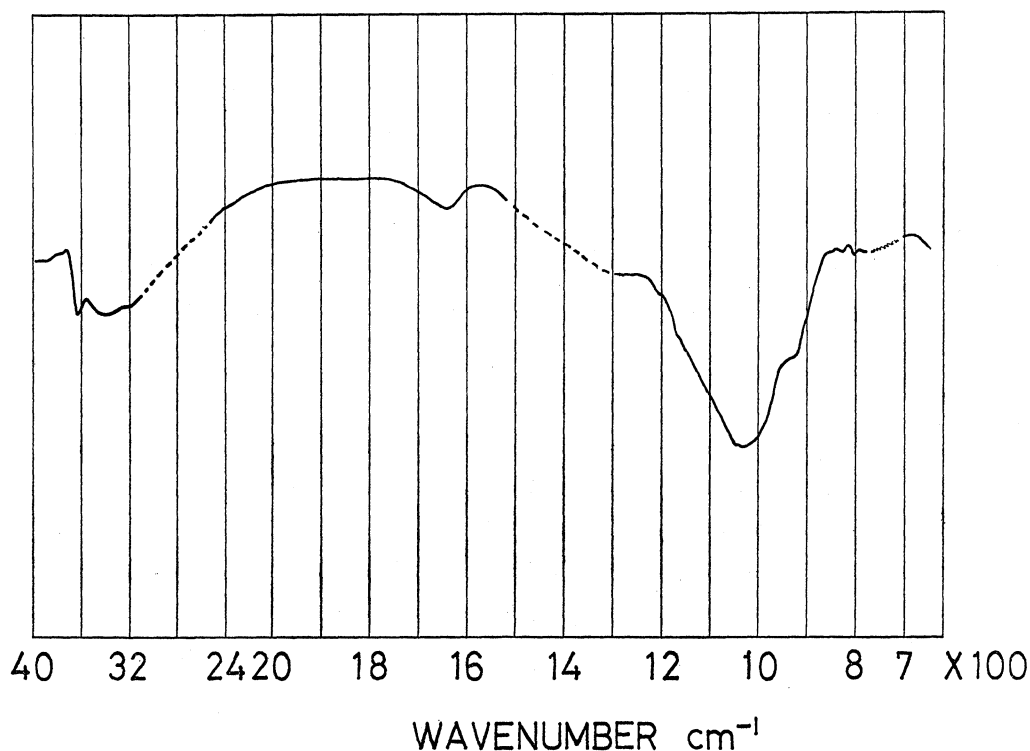


Fig. 8. I.R. absorption spectra of the specimen No. 10.

Discussion

Interstratified minerals of chlorite and montmorillonite or chlorite and vermiculite occur in sedimentary rocks, particularly in carbonate sediments (LIPPMANN, 1954; EARLEY *et al.*, 1956; BRADLEY and WEAVER, 1956), and in the altered zone of hydrothermal ore deposits (SUDO, 1954; SUDO and HAYASHI, 1955; TAKAHASHI, 1959). They also occur in basic pyroclastic sediments (YOSHIMURA, 1971) and in "Green Tuff" (KIMBARA and SUDO, 1973). They also occur as weathering products of altered basic rocks (TOMITA *et al.*, 1978). Interstratified mineral of mica and montmorillonite was

reported by many investigators. Such mineral is often found in the hydrothermal alteration zone (SHIMODA and SUDO, 1960; STEINER, 1953), and it was also found in the hydrothermal alteration zone in Kagoshima Prefecture (TATEYAMA *et al.*, 1970; TOMITA *et al.*, 1969; TOMITA and DOZONO, 1973; 1974; TOMITA and ITO, 1975; TOMITA *et al.*, 1975). Concerning the origin of mixed-layer mineral of mica and montmorillonite, three hypothetical mechanisms are considered, and they are classified into two groups. One is primary origin. It is defined as the crystallization of mixed-layer mineral from amorphous materials or natural minerals except micas and smectites (IIYAMA 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, 1979b), or smectite to mica (MERING 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 minerals found in this area, it is difficult to conclude the formation mechanism. Concerning the formation of the mixed-layer mineral of mica and montmorillonite (specimen No. 10) found in this area, two hypotheses are considered. One is that it was formed from a 1M sericite formed in the altered andesite by subsequent weak attacks of hydrothermal action or weathering, and the other one is that it was formed directly from the andesite by hydrothermal action. The mixed-layer mineral of chlorite and montmorillonite (specimens No. 11 and No. 12) was probably formed from a chlorite formed in the altered andesites by subsequent attacks of hydrothermal action or weathering.

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