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AN EXPANSIBLE MINERAL HAVING HIGH REHYDRATION ABILITY

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Abstract—An interstratified mineral (mica–montmorillonite) from a hydrothermally altered andesite in the southern part of Satsuma Peninsula, Japan fully rehydrates after having been heated to 800°C.

INTRODUCTION

MONTMORILLONITES and vermiculites usually show an irreversible collapse when heated to temperatures ranging from 600 to 700°C (Greene-Kelly, 1953; Walker, 1951). We have found an interstratified mineral which has high rehydration ability and a reversible basal spacing collapse even after heating to 800°C.

MODE OF OCCURRENCE

In the southern part of the Satsuma Peninsula, Kagoshima Prefecture, Japan, fine-grained sandstone and shale are widely distributed. These rocks are covered by a lava flow consisting of pyroxene andesite, thought to be Tertiary in age. Some hydrothermally altered zones, distributed near the Iwato mine in the southern part of the andesite, contain pyrite, sericite and chlorite. The hydrothermally argillized zone which contains the interstratified mineral is developed along a fault about 2 m wide in the altered andesite.

MINERALOGICAL DATA

Fractions less than 2 μm were obtained by combined sedimentation and centrifugal separation in distilled water, and were dried in air. They were examined by X-ray diffraction, thermal analysis, infrared absorption, chemical analysis and electron microscopy.

X-ray diffraction analysis

Specimens were oriented on glass slides and basal spacings of the regular, ethylene glycolated, and heated samples were determined by X-ray diffraction, (see Fig. 1). The regular pattern shows a clear 27·2 Å reflection (Fig. 1a), which moves to 29·4 Å by treatment with ethylene glycol (Fig. 1b); heated to 800°C for 1 hr, the specimen shows a 10·1 Å reflection (Fig. 1c). These data indicate that the 27·2 Å spacing is a combination of a 10 Å mica spacing and an expansible spacing.

A 14·7 Å reflection in the powder pattern of the regular specimen (marked as *C* in the Fig. 1a) moved to a 15·5 Å by treatment with ethylene glycol, and to a 12·3 Å by heat treatment. The 14·7 Å mineral was confirmed as a random mixed-layer chlorite–montmorillonite. It was impossible to separate this mixed-layer chlorite–montmorillonite from the interstratified mineral of mica and montmorillonite.

After heating to 800°C, the specimen, cooled in air and dried in air after saturating with water, gave the X-ray pattern shown in Fig. 1d. The spacing moved to a 29·4 Å by treatment with ethylene glycol (Fig. 1e) and contracted to 10·16 Å by heat treatment at 800°C (Fig. 1f). The specimen heated to 900°C could no longer be expanded (Fig. 1g). It is obvious that rehydration and rehydroxylation occurred in the sample heated to 800°C. It has been said that hydrous forms of layer silicates, e.g. montmorillonite, hydrated halloysite and vermiculite never rehydrate after heating to 800°C (Greene-Kelly, 1953; Walker, 1951).

Fourier transform

A Fourier transform method after MacEwan (1956) was used to deduce the nature of the interstratification. The equation employed in this calculation was formulated by MacEwan (1956) and can be written as

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

where the geometric factor, E, and the square of the structure factor, $|F_l|^2$, are evaluated at the position of the intensity maximum, and I is the integrated intensity. μ_l is the reciprocal spacing.

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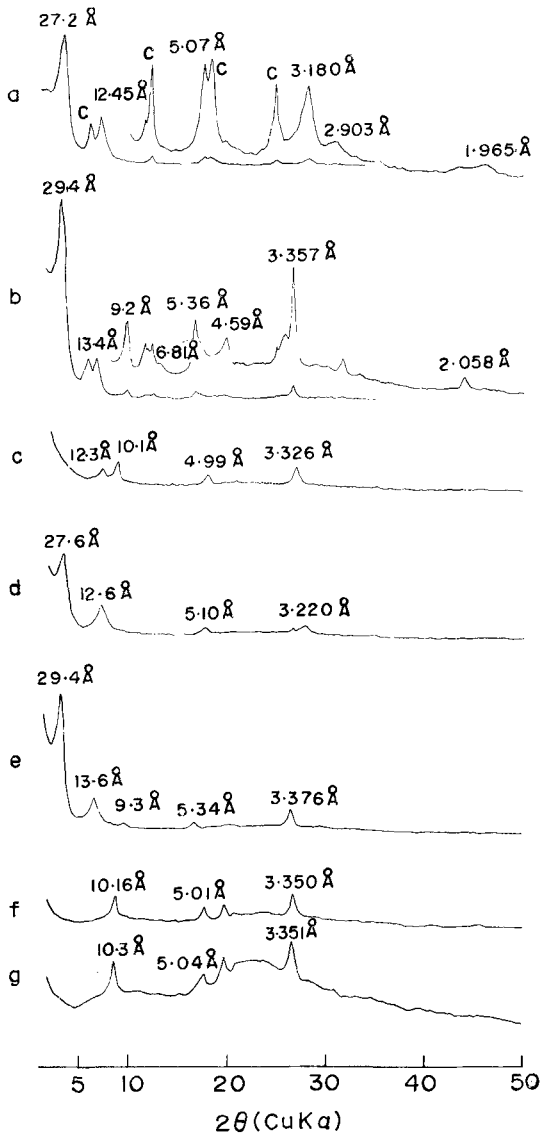


Fig. 1. X-ray diffraction patterns of the interstratified mineral after various treatments. (a) The untreated specimen; (b) sample treated with ethylene glycol; (c) sample heated to 800°C for 1 hr; (d) sample saturated with water after heating to 800°C; (e) sample treated with ethylene glycol after saturating with water; (f) sample heated to 800°C; (g) sample saturated with water after heating to 900°C for 1 hr.

$(1+\cos^2 2\theta/\sin 2\theta)$ was used for E. The function $W(R)$ is defined as the probability of finding another layer at a distance R (measured perpendicularly) from any layer.

Figure 2 shows the result of the Fourier transform of basal reflections of the specimen. In the figure, A represents a mica layer and B represents a montmorillonite (hydrous mica) layer having two layers of water molecules between silicate layers; i.e. a spacing of about 15·5 Å. The outstanding peaks of type AB and $ABAB$, indicate a marked tendency for alternation of two different layers. Numerals given above the curve are calculated peak heights for $P_A = 0{\cdot}55$, $P_B = 0{\cdot}45$, $P_{AA} = 0{\cdot}18$, $P_{AB} = 0{\cdot}82$, $P_{BA} = 1{\cdot}0$, $P_{BB} = 0$. 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.

Differential thermal analysis

The results of differential thermal analyses are shown in Fig. 3. The curves include the untreated specimen, the specimen heated to 800°C (Fig. 3b) and 900°C (Fig. 3d) and a specimen which was dried in air following saturation with water after heating to 800°C (Fig. 3c). The first endothermic peak at about 50°C in the interstratified mineral (Fig. 3a) is attributable to sorbed water; the second, at 145°C, is due to removal of interlayer water. The third endotherm is attributable to removal of water associated with the exchangeable cations. The fourth endothermic reaction, with a peak at 613°C, is dehydroxylation. The exotherm at 1010°C is due to formation of mullite. The endothermic peaks below 200°C are observed in the heated sample (Fig. 3b), but the dehydroxylation endotherm shifted from 613°C to about 550°C and the intensity decreased. Thus, the interlayer water driven off by heating is regained instantly on cooling to room temperature; however, expansion of the lattice to its original dimension was not observed in the X-ray powder pattern (Fig. 1c). The intensity of the dehydroxylation endotherm increased for the sample, which had been heated, dried in air after saturating with water (Fig. 3c). In this case, interlayer water is almost fully regained and expansion of the basal spacing to its original dimension was observed in the X-ray diffraction pattern (Fig. 1d). The endothermic peaks disappeared for the sample heated at 900°C for 1 hr (Fig. 3d).

I.R. absorption spectra

I.R. absorption spectra of the interstratified mineral are shown in Fig. 4a, together with those of the sample heated to 800°C for 1 hr (Fig. 4b) and the sample, which had been heated, dried in air after saturating with water (Fig. 4c). The interstratified mineral showed absorption bands at

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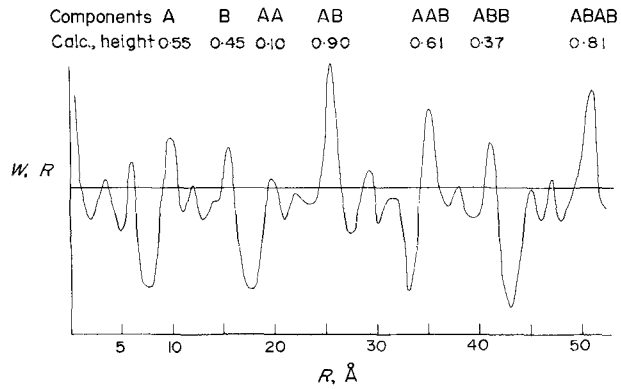


Fig. 2. Fourier transform of basal reflections (six reflections) of the interstratified mineral.

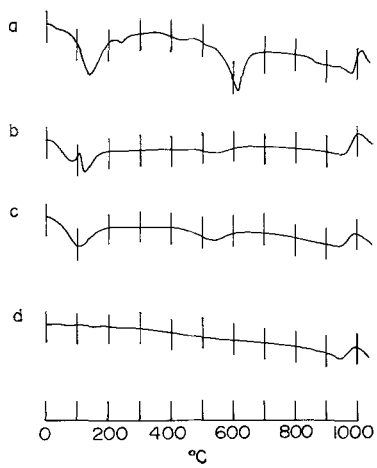


Fig. 3. Differential thermal analysis curves of (a) the untreated specimen; (b) sample heated to 800°C for 1 hr; (c) sample saturated with water after heating to 800°C; (d) sample heated to 900°C.

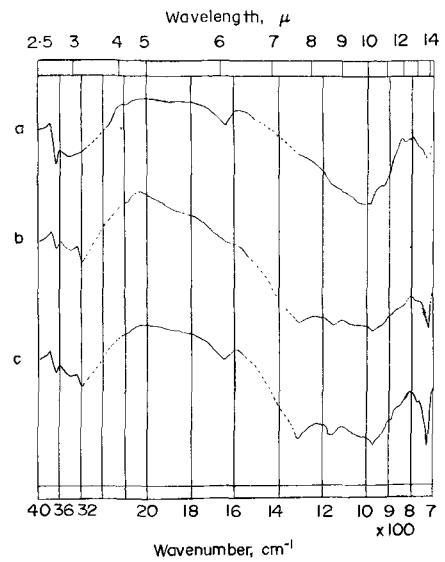


Fig. 4. I.R. absorption spectra of (a) the untreated specimen; (b) sample heated to 800°C for 1 hr; (c) sample saturated with water after heating to 800°C.

about 3640 cm^{-1}, 3400 cm^{-1}, 1640 cm^{-1}, 1010 cm^{-1} and 920 cm^{-1}. The band at 3640 cm^{-1} is due to the O–H stretching vibration and the band at 920 cm^{-1} is assigned to the O–H–Al^{3+} vibration (Stubičan and Roy, 1961a, b). The bands at 3400 and 1640 cm^{-1} are attributable to interlayer water and sorbed water respectively. The band at 1640 cm^{-1} almost disappeared after heating to 800°C, but could still be recognized. Rehydration of the heated sample restores the 1640 cm^{-1} band. The bands at 3400 and 3640 cm^{-1} are observed in the heated specimen, but are small compared with those of the unheated sample. These facts, which agree with the results of differential thermal analysis, mean that interlayer and OH water driven off at 800°C were regained almost instantly on cooling to room temperature, or that OH water could not be expelled completely and interlayer water was regained immediately on cooling.

Chemical analysis

The chemical analysis for the interstratified mineral is listed in Table 2. As it was impossible to separate the rehydratable interstratified mineral from the random mixed-layer chlorite–montmorillonite and to estimate the amount of the interstratified mineral, calculation of the structure formula could not be made. The specimen has a higher content of $H_2O(+)$ and lower content of K_2O than ordinary mica mineral. As $H_2O(-)$ was obtained below 110°C, it is considered that the sorbed water in interlayers could not be completely expelled at

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this temperature, because this specimen has high rehydration ability. Thus, some of the $H_2O(+)$ should have been counted as $H_2O(-)$.

Electron microscopy

An electron micrograph of the interstratified mineral, Fig. 5, shows thin hexagonal plates as does mica.

DISCUSSION

Most montmorillonites heated to 640°C lose interlayer water irreversibly (Greene-Kelly, 1953). Vermiculites heated to 700°C do not expand again (Walker, 1951). However, this mixed-layer mineral from Iwato after heating to 800°C was again expanded by water and ethylene glycol. That is, this mixed-layer mineral resaturated with water after



Fig. 5. Electron micrograph of the interstratified mineral.

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Table 1. X-ray powder data for the interstratified mineral after various treatments: λ(CuKα) = 1·5418 Å

(a)		(b)		(c)		(d)		(e)	
d(Å)	*I*	d(Å)	1498	d(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
27·2		29·4	842·7	10·1	11	27·6	63	29·4	96
12·45	518	13·4	118·4	4·99	7	12·6	30	13·6	22
5·07	65	9·2	32·0	3·326	11	5·10	4	9·3	3
3·180	76	6·81	7·5			3·220	5	5·34	5
2·903	14	5·36	47·0					3·376	11
1·965	11	3·357	49·0						

(a)—Untreated interstratified mineral.
(b)—Treated with ethylene glycol.
(c)—Heated to 800°C for 1 hr.
(d)—Saturated with water after heating.
(e)—Treated with ethylene glycol after water saturation.

Table 2. Chemical composition of the interstratified mineral

SiO_2	45·82%
TiO_2	0·49
Al_2O_3	29·83
Fe_2O_3 } FeO }	4·98
MnO	0·02
MgO	3·94
CaO	tr
K_2O	1·40
Na_2O	0·80
$H_2O(+)$	8·32
$H_2O(-)$	5·04
Total	100·64%

heating to 800°C showed the same behavior as did the original sample. Thus, rehydration and rehydroxylation of the heated sample occurred. A mineral with such high rehydration ability has not previously been reported.

Natural montmorillonites treated the same way do not expand again. Expansible minerals synthesized from sericite by White's method (White, 1956 and 1958) using $LiNO_3$, Scott's method (Scott, Hunziker and Hanway, 1960; Scott and Reed, 1962a and b) using sodium tetraphenylboron (Na-TPB), and a mixed-layer mineral formed from sericite by Tomita and Dozono's method (1972) were all irreversibly dehydrated by heating to 800°C. However, the Tomita–Dozono sample, if boiled in acid (0·8 N H_2SO_4) after heating to 800°C, was expanded again by treatment with ethylene glycol. A mixed-layer mineral synthesized from sericite by $LiNO_3$ treatment (Tomita and Sudo, 1971) and a mixed-layer mineral formed from pre-heated sericite by acid treatment after Tomita and Sudo's method (1968a, b) were also irreversible after heating to 800°C, but again boiling the heated specimens in acid (0·8 N H_2SO_4) restored their ability to be expanded by treatment with ethylene glycol.

After completion of this manuscript, we found that another interstratified mineral (mica–montmorillonite) reported by Tomita *et al.* (1969) also had high rehydration ability, and that this property was present in mixed-layer minerals from different places in Japan. Thus, some mixed-layer minerals have high rehydration ability, which in our opinion is due to their structures. Unfortunately we could not obtain a single mixed-layer mineral, so it was impossible to investigate the structure in detail.

Granquist and Kennedy (1967) have discussed the high temperature (500°C) sorption of water by a synthetic ammonium dioctahedral clay. The dehydroxylation is partially reversible and the presence of fluoride in hydroxyl sites enhances the water sorption capacity. Wright *et al.* (1972) concluded that the thermally activated substance had protons in the tetrahedral vacancies of the octahedral layer. We think that it is necessary to establish the mechanism of dehydration and dehydroxylation of mixed-layer mineral on heating, and of rehydration of the heated mineral.

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Résumé—Un minéral interstratifié (mica–montmorillonite) provenant d'une andésite altérée par voie hydrothermale dans la partie sud de la péninsule de Satsuma, Japon, se réhydrate entièrement après avoir été chauffée à 800°C.

Kurzreferat—Ein Wechsellagerungsmineral (Glimmer–Montmorillonit) aus einem hydrothermal umgewandelten Andesit im südlichen Teil der Satsuma-Halbinsel, Japan, zeigt nach Erhitzung auf 800°C vollständige Rehydratisierung.

Резюме — Минерал с перемежающимся напластованием (слюда-монтмориллонит) от гидротермически измененного андезина из южной части Сатсумского полуострова (Япония) после нагрева до 800°C полностью вновь гидратируется.

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