

DEHYDRATION AND REHYDRATION OF SAPONITE AND VERMICULITE

MOTOHARU KAWANO¹ AND KATSUTOSHI TOMITA

Institute of Earth Sciences, Faculty of Science, Kagoshima University
1-21-35 Korimoto, Kagoshima 890, Japan

Abstract—The rehydration properties and behavior of interlayer cations of Ca-, Mg-, Na-, and K-saturated homoionic saponite and vermiculite heated at various temperatures were examined and their rehydration mechanisms elucidated. The most notable features of saponite were (1) except for the Mg-saturated specimen, all saponite samples rehydrated until the crystal structure was destroyed by heating; (2) the rehydration rate in air after heating decreased in the order: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$; (3) the interlayer cations apparently migrated into hexagonal holes of the SiO_4 network on thermal dehydration; and (4) the b -parameter expanded on thermal dehydration. The rehydration properties and behavior of interlayer cations of vermiculite were: (1) except for the K-saturated specimen, all vermiculite samples rehydrated until the crystal structure was destroyed by heating; (2) the rehydration rate in air after heating decreased in the order: $Mg^{2+} > Ca^{2+} > Na^+ > K^+$; (3) the interlayer cations apparently did not migrate into the hexagonal holes, but remained at the center of the interlayer space, even after thermal dehydration; and (4) except for the K-saturated specimen, the b -parameters of the samples contracted on thermal dehydration. The different rehydration properties of saponite and vermiculite were apparently due to the behavior of the interlayer cations during thermal dehydration. For rehydration to occur, the interlayer cations of saponite had to migrate out of the hexagonal holes. Consequently, saponite saturated with a large cation rehydrated rapidly, whereas saponite saturated with a small cation rehydrated slowly. On the other hand, the interlayer cations of vermiculite remained in the interlayer space; therefore, the rehydration properties of vermiculite were strongly affected by the hydration energies of the interlayer cations. Furthermore, electron diffraction patterns suggested that the saponite and vermiculite consisted of random stacking and ordered stacking of adjacent 2:1 layers, respectively. The nature of the stacking of the minerals seemed to be the most important factor controlling the behavior of interlayer cations in the thermal dehydration process.

Key Words—Cation migration, Dehydration, Hydration energy, Interlayer cations, Rehydration, Saponite, Vermiculite.

要旨—Ca-, Mg-, Na- および K-飽和サポナイトとパーミキュライトの加熱後の復水性と層間陽イオンの挙動を検討し、これらの鉱物の復水機構を解明した。サポナイトの最も注目すべき特徴としては、(1) Mg-飽和試料を除くと加熱によって結晶構造が破壊するまで復水性を保持している。(2) 層間陽イオンの違いによる加熱後の復水速度は $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ の順に減少する。(3) 層間水の脱水によって層間陽イオンは SiO_4 ネットワークの六員環中に移動する。(4) 層間水の脱水によって b_0 は膨張する。パーミキュライトについては、(1) K-飽和試料を除くと加熱によって結晶構造が破壊するまで復水性を保持している。(2) 層間陽イオンの違いによる加熱後の復水速度は $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ の順に減少する。(3) 加熱による層間水の脱水後においても層間陽イオンは層間域の中央に位置し六員環中には移動しない。(4) K-飽和試料を除くと層間水の脱水によって b_0 は収縮する。サポナイトとパーミキュライトの復水性の違いは層間水の脱水過程における層間陽イオンの挙動に起因している。サポナイトが復水するためには層間陽イオンを六員環中から層間域に復帰させる必要があるために、サイズの大きい陽イオンの場合には復水速度が速くなるが、サイズの小さい陽イオンの場合には復水速度が遅くなる。一方、パーミキュライトは層間陽イオンの移動が生じないために、その復水性は層間陽イオンの水和エネルギーの大きさに依存する。さらに、電子線回折の結果は、サポナイトはランダム状態、パーミキュライトはオーダー状態の珪酸塩層の積層を示唆した。層間水の脱水過程における層間陽イオンの挙動をコントロールする最も重要な因子はこれらの鉱物の珪酸塩層の積層状態にあると思われる。

¹ Present address: Department of Environmental Sciences and Technology, Faculty of Agriculture, Kagoshima University, 1-21-24 Korimoto, Kagoshima 890, Japan.

INTRODUCTION

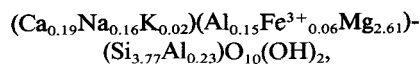
The rehydration properties of expandable phyllosilicates are considered to be strongly affected by their crystal chemistry, but few detailed investigations have been made. MacEwan and Wilson (1980) reported that, with the exception K- and NH_4 -saturated materials, saponite and vermiculite exhibited similar rehydration properties. They also stated that Li-, Na-, and K-saturated saponite heated at 700°C rehydrated readily in moist air, whereas saponite saturated with divalent cations failed to rehydrate after heating >450°C. These authors, however, did not mention a detailed rehydration mechanism for these minerals. Li-saturated montmorillonite collapses irreversibly if it is heated >200°C (Mering, 1946), because of the migration of Li^+ ions into the 2:1 layer (Hofmann and Klemen, 1950; Greene-Kelly, 1955; Glaeser and Mering, 1967; Calvet and Prost, 1971). Kawano and Tomita (1989a, 1989b, 1990a, 1990b) reported the rehydration properties of rectorite, beidellite, and montmorillonite heated at various temperatures. They pointed that: (1) rectorite and beidellite retained rehydration properties at higher temperatures compared with montmorillonite saturated with the same kind of interlayer cations; (2) K-saturated specimens rehydrated rapidly, but Mg-saturated specimens rehydrated slowly. These observations can be explained by: (1) differences in the electrostatic forces needed to extract the interlayer cations from the hexagonal holes of the SiO_4 network; and (2) on the basis of sizes of the interlayer cations. The attractive force between the octahedral sheet and interlayer cations within the hexagonal holes of montmorillonite is strong, but in rectorite and beidellite it is relatively weak. This difference is because the negative layer charge of montmorillonite originates mainly in the octahedral sheet, whereas the negative layer charges of the expandable layer of rectorite and beidellite originate mainly in the tetrahedral sheet. Therefore, rectorite and beidellite rehydrate after having been dehydrated at higher temperatures than montmorillonite. Small cations migrate easily into the hexagonal holes of the silicate sheet and become fixed, whereas large cations do not readily migrate into these holes. The rehydration of specimens saturated with small cations (e.g., Mg^{2+}) is therefore difficult compared with those saturated with large cations (e.g., K^+). If its interlayer cations migrate into hexagonal holes on thermal dehydration, saponite should readily rehydrate, because the protons of hydroxyl ions of trioctahedral phyllosilicates are directed toward the interlayer cations (Giese, 1975). Furthermore, K-saturated saponite should more readily rehydrate than Mg-saturated specimen, as mentioned above. On the other hand, K-saturated vermiculite dehydrates irreversibly without heating (Harward *et al.*, 1969); therefore, the rehydration mechanisms of saponite and vermiculite must be quite different.

The present paper reports the rehydration properties of saponite and vermiculite with reference to rehydration ability and rehydration rate. Rehydration ability refers to the retention of rehydration properties after heating at various temperatures, and rehydration rate refers to the rapidity of rehydration. The behavior of interlayer cations on thermal dehydration are also reported, and the rehydration mechanisms of the minerals are discussed.

MATERIALS AND EXPERIMENTAL METHODS

Materials

Saponite from Ballarat, California, and vermiculite from Llano County, Texas, obtained from the Source Clay Repository of The Clay Minerals Society, were used in this study. Chemical analyses of the specimens were reported by Post (1984) and Foster (1963), respectively. The structural formula of the saponite is as follows:



and that for the vermiculite is;



The iron in both materials is expressed as ferric ion.

Sample preparation

The <2- μm fraction of saponite and the <10- μm of vermiculite were collected by normal sedimentation methods and were saturated with Ca^{2+} , Mg^{2+} , Na^+ , and K^+ by treatment with 1 N chloride solutions. The excess salt was then removed by washing with 80% ethanol until the sample was Cl^- free. The homoionic specimens were then dried in air.

Rehydration ability

The powdered homoionic specimens were heated at temperatures between 100° to 900°C at intervals of 100°C for 1 hr and cooled in a desiccator of 0% relative humidity (RH) for 1 hr. The RH in the desiccator was controlled with di-phosphorus pentoxide. About 20 mg of the heated sample was oriented on glass slides using three or four drops of deionized water and then dried in air at 50% RH for 1 day. The $d(001)$ values were measured by X-ray powder diffraction (XRD) using a Rigaku diffractometer, Ni-filtered $\text{CuK}\alpha$ radiation, and a scanning speed of 0.5°/min. Specimens were maintained at 50% RH during analysis.

Rehydration rates in air

Homoionic specimens oriented on quartz glass slides were heated at 700°C for 1 hr and then cooled in a desiccator (0% RH) for 1 hr. XRD patterns were obtained from 14° to 2° 2θ at a scanning speed of 2°/min.

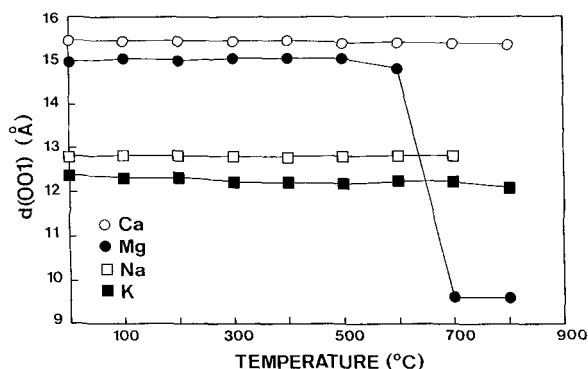


Figure 1. Variation of $d(001)$ values obtained at 50% RH for rehydrated homoionic (saturated with Ca, Mg, Na, or K) saponite samples after heating at various temperatures for 1 hr.

min during exposure to air at 50% RH for various periods of time (0, 60 min, and 1 day).

Position of interlayer cation

The positions of interlayer cations for dehydrated saponite and vermiculite were investigated by means of one-dimensional Fourier analysis. The XRD data for heated specimens oriented on quartz glass slides were obtained at a scanning speed of $0.5^\circ 2\theta/\text{min}$ from 90° to $2^\circ 2\theta$ at 0% RH. The Fourier synthesis was made using observed structure factors obtained from integrated intensities; their signs were derived from calculated structure factors. The atomic coordinates of initial Z-parameters for the trioctahedral silicate layer were taken from Reynolds (1980), and Z-parameters of interlayer cations and silicate layer along the c -axis were refined by the least squares method.

Changes of $d(060)$ after heating

The $d(060)$ values of homoionic specimens before and after heating at 400°C were measured by XRD. The XRD data were obtained at a scanning speed of $0.5^\circ 2\theta/\text{min}$ under 50% RH for the unheated specimens and 0% RH for the heated specimens. For saponite samples, thermal analysis was carried out with a Rigaku micro differential thermal-thermal gravimetric analysis (DTA-TGA) apparatus using about 25 mg of sample in the range from room temperature to 1100°C and using a heating rate of $10^\circ\text{C}/\text{min}$.

RESULTS

Rehydration abilities

Figure 1 shows variations of $d(001)$ values of heated homoionic saponite samples after water saturation. The Ca-, Na-, and K-saturated specimens retained the same values of $d(001)$ as those of the original hydrated forms until thermal decomposition took place. The Mg-saturated specimen, however, did not rehydrate after heating at 700°C , even after water saturation.

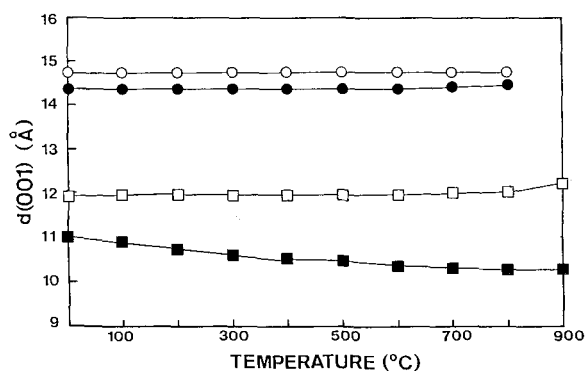


Figure 2. Variations of $d(001)$ values obtained at 50% RH for rehydrated homoionic (saturated with Ca, Mg, Na, or K) vermiculite samples after heating at various temperatures for 1 hr. Symbols as in Figure 1.

Figure 2 shows variations of $d(001)$ values of heated homoionic vermiculite samples after water saturation. The Ca-, Mg-, and Na-saturated specimens readily rehydrated until the crystal structure was destroyed by heating. The basal spacing of the K-saturated vermiculite contracted to about 11.0 \AA without heating and decreased gradually to 10.3 \AA at 900°C . These results suggest that the saponite and vermiculite readily rehydrated, although the detailed rehydration behaviors were slightly different.

Rehydration rates in air

Figure 3 shows XRD patterns of homoionic saponite samples heated at 700°C followed by exposure to air at 50% RH for various periods of time. The Mg-sat-

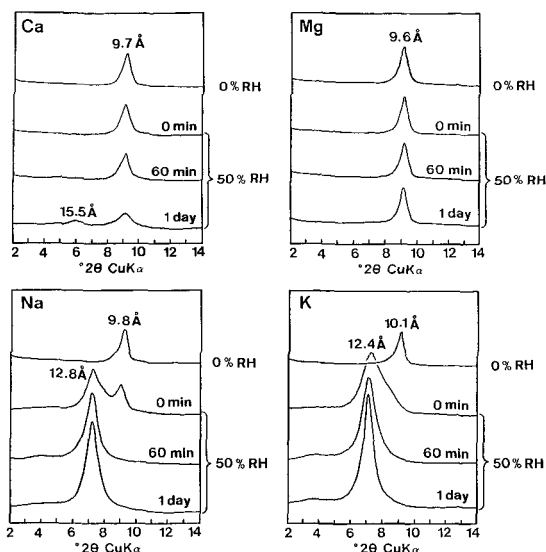


Figure 3. Changes in first-order reflections of homoionic (saturated with Ca, Mg, Na, or K) saponite samples on exposure to air at 50% RH for various periods of time after heating at 700°C for 1 hr. 0% = at 0% RH; 0 min, 60 min, and 1 day signify exposure time to air at 50% RH.

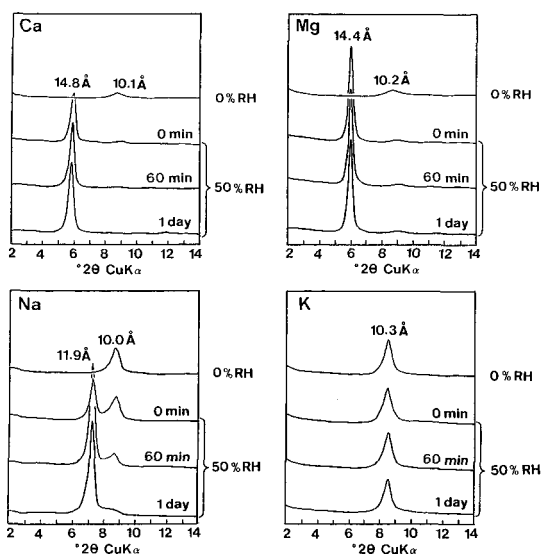


Figure 4. Changes in first-order reflections of homoionic (saturated with Ca, Mg, Na, or K) vermiculite samples on exposure to air at 50% RH for various periods of time after heating at 700°C for 1 hr. 0% = at 0% RH; 0 min, 60 min, and 1 day signify exposure time to air at 50% RH.

urated specimen remained dehydrated after exposure to air even for as long as 1 day. The Ca-saturated specimen showed a small peak of the two-layer hydrated form (15.5 Å), suggesting that the Ca-saturated specimen rehydrated to a greater extent than did the Mg-saturated specimen. The Na-saturated specimen partially rehydrated to a mixture of one-layer hydrated (12.8 Å) and dehydrated (9.8 Å) layers on exposure to air for a few minutes (0 min in Figure 3). The K-saturated specimen almost completely rehydrated, and the peak of the dehydrated form was absent from the XRD pattern at 0 min. This observation also suggests that the K-saturated specimen rehydrated more rapidly than the Na-saturated specimen. Consequently, the rehydration rates of these homoionic saponite samples ($K^+ > Na^+ > Ca^{2+} > Mg^{2+}$) were roughly compatible with the ionic radii ($K^+ > Na^+ > Ca^{2+} > Mg^{2+}$; Whittaker and Muntus, 1970) of saturating cations, rather than with their hydration energies.

Figure 4 shows XRD patterns of homoionic vermiculite samples heated at 700°C followed by exposure to air at 50% RH for various periods of time. These XRD patterns indicate that the first-order reflection of the Ca-saturated specimen shifted rapidly to 14.8 Å and was enhanced during exposure to air, suggesting that rehydration continued for at least 1 day. The Mg-saturated specimen rehydrated rapidly and completely within a few minutes. The Na-saturated specimen showed a segregated structure consisting of one-layer hydrated (11.9 Å) and dehydrated (10.0 Å) layers. A small peak of the dehydrated layer was noted even after exposure in air for 1 day. On the other hand, the

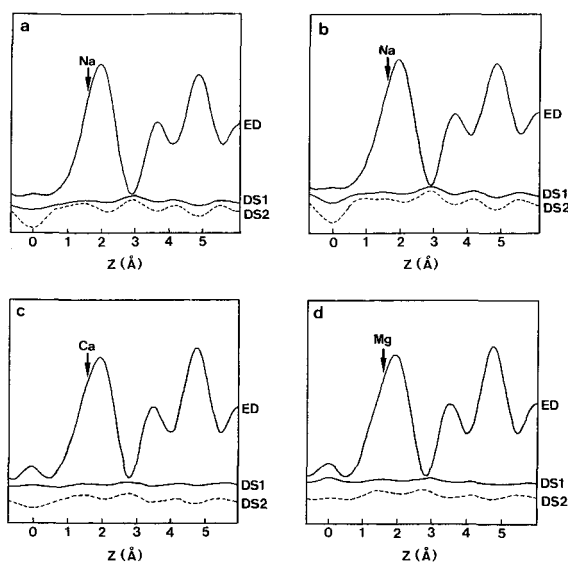


Figure 5. Electron density distribution and difference synthesis curves of Na-saturated saponite heated at (a) 400°C and (b) 700°C, and (c) Ca-saturated and (d) Mg-saturated saponite heated at 800°C. ED = electron density distribution; DS1 = difference synthesis calculated by using Z-parameters obtained by refinement; DS2 = difference synthesis calculated by assuming that interlayer cations are located at the center of interlayer space.

K-saturated vermiculite remained dehydrated. The rehydration rates of the homoionic vermiculite samples ($Mg^{2+} > Ca^{2+} > Na^+ > K^+$) were very much different from those of the saponite samples and were compatible with hydration energies of the saturating cations ($Mg^{2+} > Ca^{2+} > Na^+ > K^+$; Rosseinsky, 1965), instead of their ionic radii.

Position of interlayer cation after dehydration

The positions of interlayer cations for Na-saturated saponites heated at 400° and 700°C and Ca- and Mg-saturated saponites heated at 800°C were examined by means of one-dimensional Fourier analysis. The basal spacings and structure factors of the saponite samples are listed in Table 1. The electron density distribution (ED) and difference synthesis (DS) curves of the specimens are shown in Figures 5a–5d. The DS curves (DS2 in Figures 5a and 5b) of the Na-saturated specimens heated at 400° and 700°C, which were calculated assuming that the interlayer Na^+ ions were fixed at the center of the interlayer space ($Z = 0.000 \text{ Å}$), showed a negative peak in the interlayer region, suggesting that the interlayer Na^+ ions moved from the interlayer space to some other position. After refinement of the Z-parameters of the interlayer Na^+ ions and other elements in the silicate layer, the positions of interlayer Na^+ ions were determined around the basal oxygen plane as shown in Figures 5a and 5b. The DS curves (DS1 in Figures 5a and 5b) calculated by using the refined struc-

Table 1. Basal spacings and structure factors of Na-, Ca-, and Mg-saturated saponite heated at various temperatures.

00l	Na-saponite 400°C			Na-saponite 700°C		
	d (Å)	Fo	Fc	d (Å)	Fo	Fc
1	9.86	77.6	-69.5	9.91	78.3	-70.6
2	4.906	53.4	-41.3	4.920	53.9	-40.8
3	3.263	150.5	-150.8	3.269	150.3	-149.1
4	2.465	14.1	17.5	2.470	14.2	19.9
5	1.959	82.1	88.0	1.961	76.0	85.0
6	1.624	42.4	44.1	1.627	34.8	38.6
7	1.401	69.7	-76.5	1.399	68.8	-73.1
8	1.228	23.9	30.6	1.222	28.5	36.8

00l	Ca-saponite 800°C			Mg-saponite 800°C		
	d (Å)	Fo	Fc	d (Å)	Fo	Fc
1	9.62	70.7	-70.1	9.53	70.3	-69.4
2	4.783	44.0	-38.1	4.740	43.5	-38.1
3	3.178	146.3	-145.7	3.153	144.0	-144.7
4	2.383	23.3	22.3	2.356	26.9	22.2
5	1.908	69.5	69.8	1.896	69.2	67.3
6	1.589	41.3	38.0	1.575	53.2	47.3
7	1.363	61.9	-69.0	1.353	64.7	-76.2
8	1.194	44.5	46.2	1.185	39.2	39.8

|Fo| = observed structure factors; Fc = calculated structure factors.

ture suggested that the Na⁺ ions were apparently located at this position. These results imply that the interlayer Na⁺ ions migrated into the hexagonal holes of the SiO₄ network on thermal dehydration. For the Ca- and Mg-saturated specimens, similar results were obtained, as shown in Figures 5c and 5d. The positions of interlayer Ca²⁺ and Mg²⁺ ions, which were determined by least squares refinement, also indicate that these cations migrated into the hexagonal holes on thermal dehydration.

Figure 6 shows ED and DS curves of the Ca-, Na-, and K-saturated vermiculite samples heated at 800°C. The basal spacings and structure factors are listed in Table 2. The ED curves for these specimens show sharp peaks around the interlayer region, which were due to electron densities of the interlayer cations. After refinement of the atomic coordinates along the *c*-axis, the DS curves showed no significant residual electron densities. Consequently, these interlayer cations must

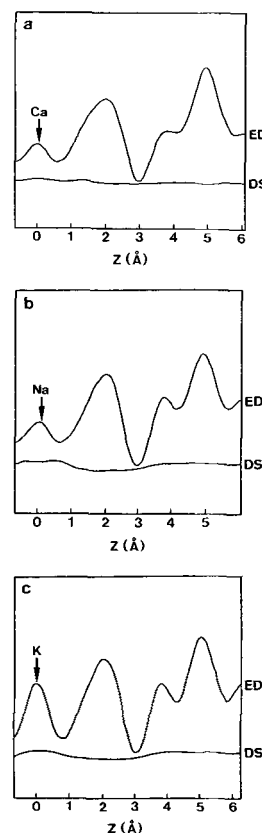


Figure 6. Electron density distribution and difference synthesis curves of (a) Ca-, (b) Na-, and (c) K-saturated vermiculite heated at 800°C. ED = electron density distribution; DS = difference synthesis calculated by using Z-parameters obtained by refinement.

have been located at the center of the interlayer space instead of within the hexagonal holes of the silicate network, even after thermal dehydration.

Changes of *d*(060) after heating

Figure 7 shows XRD patterns in the region of the (060) reflections of the homoionic saponite and vermiculite samples before and after heating at 400°C. The *d*(060) values of the unheated saponite samples were about 1.529–1.530 Å. The values increased slightly

Table 2. Basal spacings and structure factors of Ca-, Na-, and K-saturated vermiculite heated at 800°C.

00l	Ca			Na			K		
	d (Å)	Fo	Fc	d (Å)	Fo	Fc	d (Å)	Fo	Fc
1	9.63	54.4	-59.2	9.94	59.0	-54.7	10.35	49.6	-43.6
2	4.783	22.6	17.9	4.914	24.2	4.2	5.053	23.8	6.9
3	3.178	158.6	-159.3	3.267	132.0	-142.9	3.387	112.2	-124.3
4	2.106	35.4	35.9	2.478	21.1	19.8	2.536	47.7	45.5
5	1.910	63.0	61.0	1.959	84.8	80.7	2.024	105.5	102.5
6	1.590	33.9	35.1	1.631	36.6	36.9	1.684	59.1	56.8
7	1.363	41.0	-38.0	1.399	56.3	-48.4	1.443	52.1	-49.1
8	1.188	44.2	42.5	1.222	40.6	43.1	1.267	56.9	57.8

|Fo| = observed structure factors; Fc = calculated structure factors.

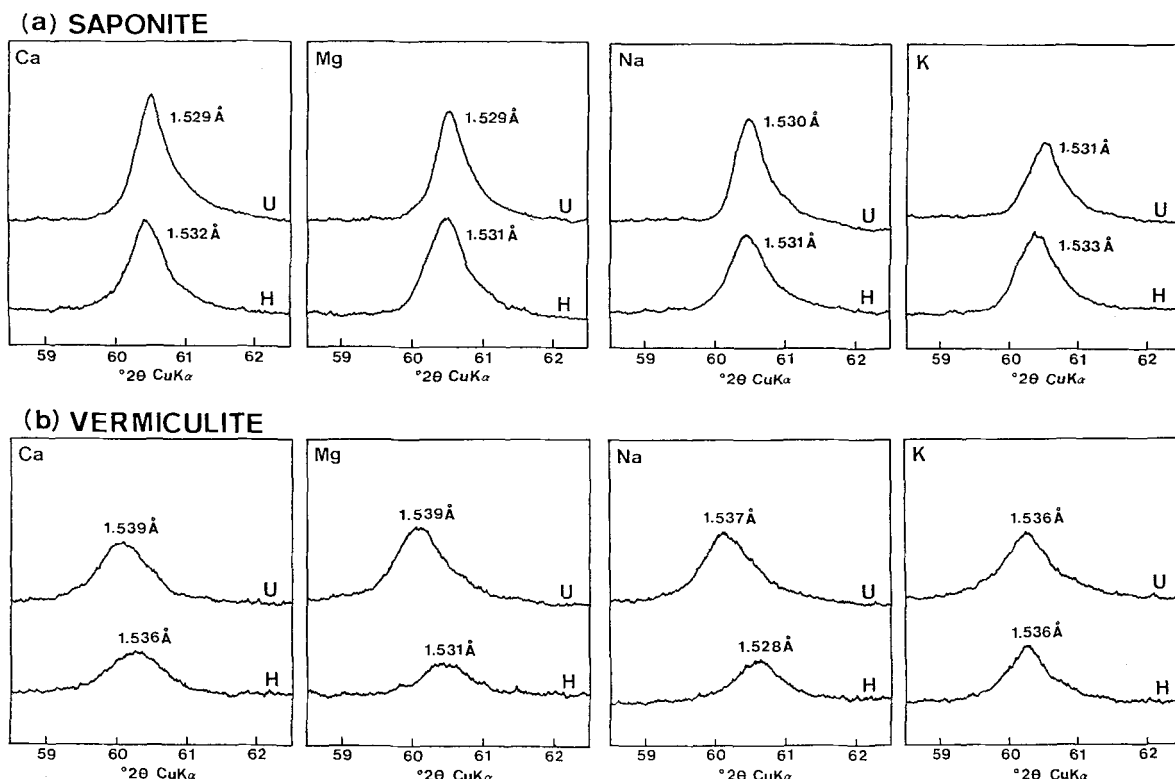


Figure 7. X-ray powder diffraction patterns of homoionic (saturated with Ca, Mg, Na, or K) (a) saponite and (b) vermiculite samples in the region of the (060) reflections (U) before and (H) after heating at 400°C.

after the sample was heated at 400°C for 1 hr, indicating that the b -parameter of the saponite samples expanded on thermal dehydration. The expansion of the b -parameter of other phyllosilicates by thermal treatment has also been reported (pyrophyllite, Brindley and Wardle, 1970; muscovite, Eberhart, 1963; Vedder and Wilkins, 1969; Udagawa *et al.*, 1974). Udagawa *et al.* (1974) concluded from a three-dimensional structural analysis of dehydroxylated muscovite that the expansion of the b -parameter was caused by atomic rearrangement of octahedral sheets. The DTA and TGA curves of the present saponite samples indicated that dehydroxylation took place at about 800°–840°C accompanying a rapid endothermic reaction and weight loss (Figure 8). Therefore, the expansion of the b -parameters of the saponite samples heated at 400°C could have been due to migration of interlayer cations from the interlayer space to hexagonal holes of the silicate network. The migrated cations probably caused adjustment of the deformed configuration of the tetrahedra. On the other hand, the $d(060)$ values of vermiculite samples, except for the K-saturated specimen, decreased slightly on heating at 400°C for 1 hr, indicating that the b -parameters of vermiculite samples, except for the K-saturated specimen, contracted on thermal dehydration. Leonard and Weed (1967) reported a similar behavior of the $d(060)$ value of ver-

miculite saturated with several different cations and heated to 350°C. The behavior of the $d(060)$ value of vermiculite during thermal dehydration was therefore completely different from that of the saponite mentioned above, suggesting that the interlayer cations of vermiculite did not migrate into the hexagonal holes of the silicate network.

DISCUSSION

Rehydration mechanism of saponite

The saponite samples rehydrated readily and rapidly, as mentioned above. The rehydration behavior of saponite is somewhat different from that of beidellite (Kawano and Tomita, 1990a) and is significantly different from that of montmorillonite (Kawano and Tomita, 1989b). The rehydration phenomenon can be interpreted as a restoration of the hydrated forms of interlayer cations in the interlayer space. The behavior of interlayer cations by thermal dehydration is therefore very important in understanding the rehydration mechanism of expandable phyllosilicates, including saponite and vermiculite. Interlayer cation migration into the hexagonal holes of silicate network on heating has been recognized in montmorillonite (Tettenhorst, 1962; McBride *et al.*, 1975; Luca and Cardile, 1989; Kawano and Tomita, 1989b), beidellite (Kawano and

Tomita, 1990a), and expandable layer of rectorite (Kawano and Tomita, 1989a, 1990b).

The present study has shown that saponite shows the same kind of interlayer cation migration. For rehydration to occur, the migrated cations must be extracted from the hexagonal holes. The forces affecting the extraction of the migrated interlayer cations are: (1) extractive force attributable to hydration of interlayer cations; (2) attractive electrostatic force of the octahedral sheet attributable to the negative charge of the octahedral sheet; and (3) repulsive electrostatic force of protons of the octahedral sheet hydroxyl ions against the migrated cations. The total extractive force is a composite of these electrostatic forces. The following factors also influence the strength of the forces: (1) hydration energy of the interlayer cations; (2) migrated position of the interlayer cations; (3) the negative charge density of octahedral sheet; and (4) the orientation of hydroxyl ions. The hydration energy of interlayer cations decreases in the order: $Mg^{2+} > Ca^{2+} > Na^+ > K^+$ (Rosseinsky, 1965). The strength of the extractive force attributed to the hydration energy seems to depend on the migrated position of the interlayer cations.

The attractive force caused by the negative charge of the octahedral sheet is also affected by the migrated position of the interlayer cations. If the cations migrate to a shallow extent into the hexagonal holes, they are readily extracted in moist air by the force of their hydration energy. The shorter distance from the migrated cations to water molecules increases the extractive force attributable to hydration energy, whereas the longer distance from the migrated cations to the octahedral sheet makes the attractive force to that sheet weaker. If the interlayer cations migrate deep into the holes, the extractive force due to hydration energy of the migrated cations is weaker, and the attractive force to the octahedral negative charge is relatively stronger. A large octahedral negative-charge density increases the attractive force between the migrated interlayer cations and the octahedral sheet. With reference to the orientation of hydroxyl ions, the protons of the hydroxyl ions of trioctahedral smectite, e.g., saponite, are directed toward the migrated interlayer cations, and the distance from the protons to the migrated cations is at a minimum; therefore, the repulsive force of saponite is relatively stronger. The hydroxyl ions of dioctahedral smectite orient slightly toward the empty octahedral site, and the repulsive force of montmorillonite and beidellite is relatively weaker. The influence of hydroxyl ions on the fixation of interlayer cations in the silicate network has been reported for micas (Bassett, 1960; Newman, 1969; Hoda and Hood, 1972). The negative charge distribution of the present saponite is $-0.13/O_{10}(OH)_2$ in the octahedral sheet and $-0.23/O_{10}(OH)_2$ in the tetrahedral sheets. The negative charge of the octahedral sheet increased the attractive force between migrated interlayer cations and the octahedral

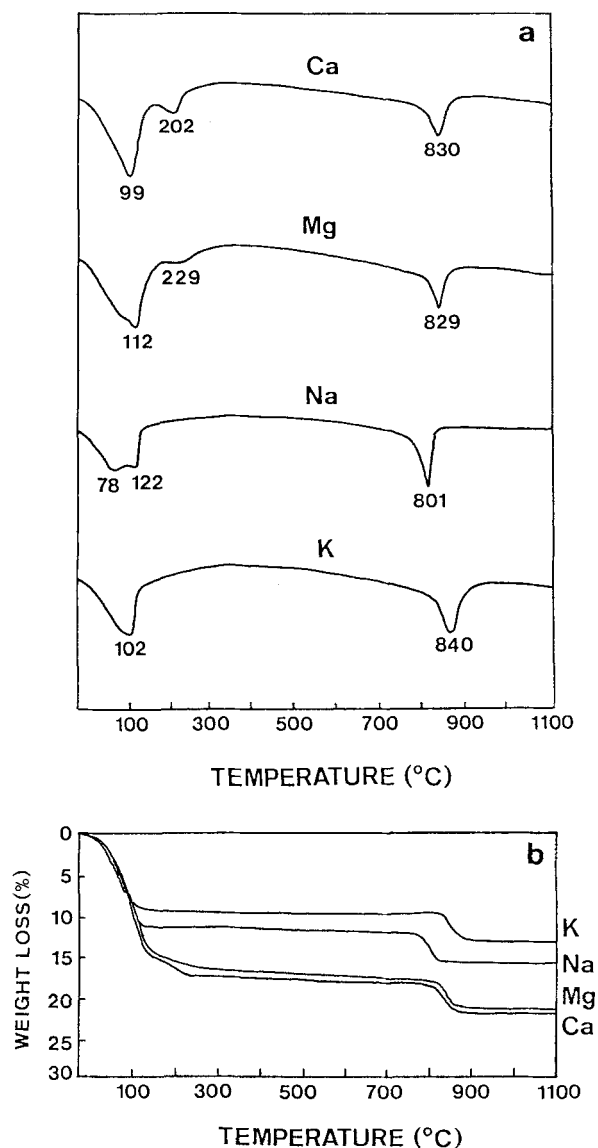


Figure 8. (a) Differential thermal analysis and (b) thermogravimetric analysis curves of homoionic (saturated with Ca, Mg, Na, or K) saponite samples.

sheet of the saponite compared with that of the beidellite; however, protons directed toward the migrated interlayer cations apparently repelled the interlayer cations toward the interlayer space. Consequently, saponite had strong rehydration ability.

Rehydration mechanism of vermiculite

The rehydration properties and behaviors of interlayer cations of vermiculite are completely different from those of saponite, as described above. Figure 9 shows electron micrographs and electron diffraction patterns of unheated Mg-saturated saponite and vermiculite. The electron micrograph of saponite clearly show particles having euhedral lath-like habits. The

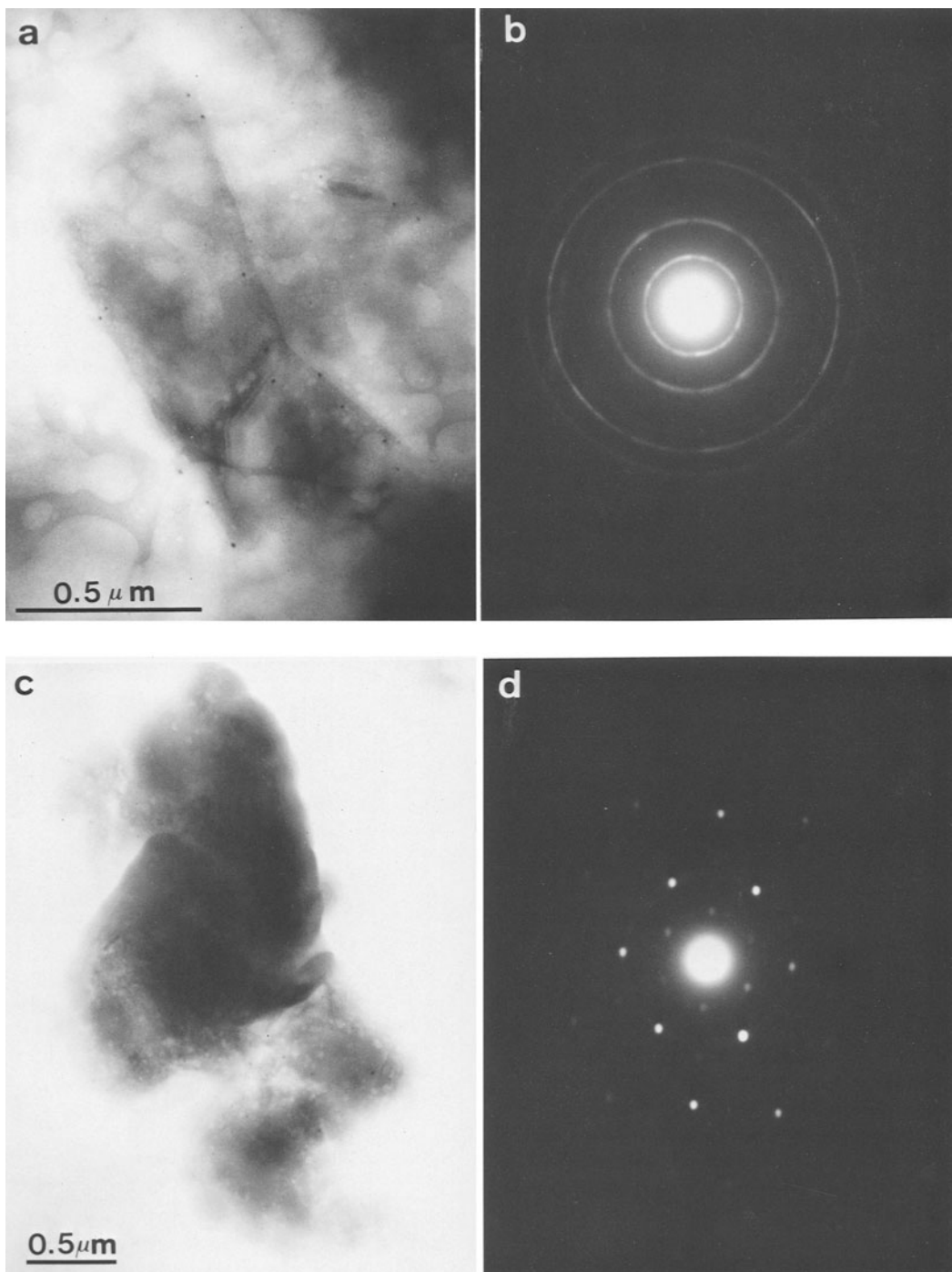


Figure 9. Transmission electron micrographs and electron diffraction patterns of (a, b) Mg-saturated saponite and (c, d) vermiculite.

reflections of the specimen were distributed uniformly in circles, suggesting a turbostratic stacking of adjacent 2:1 layers or simply a large number of randomly oriented thin particles.

On the other hand, the electron diffraction pattern

of vermiculite shows spot reflections having approximately hexagonal symmetry, implying that the vermiculite consists of ordered stacking of adjacent 2:1 layers. The differences in the rehydration properties of saponite and vermiculite are probably due to the nature

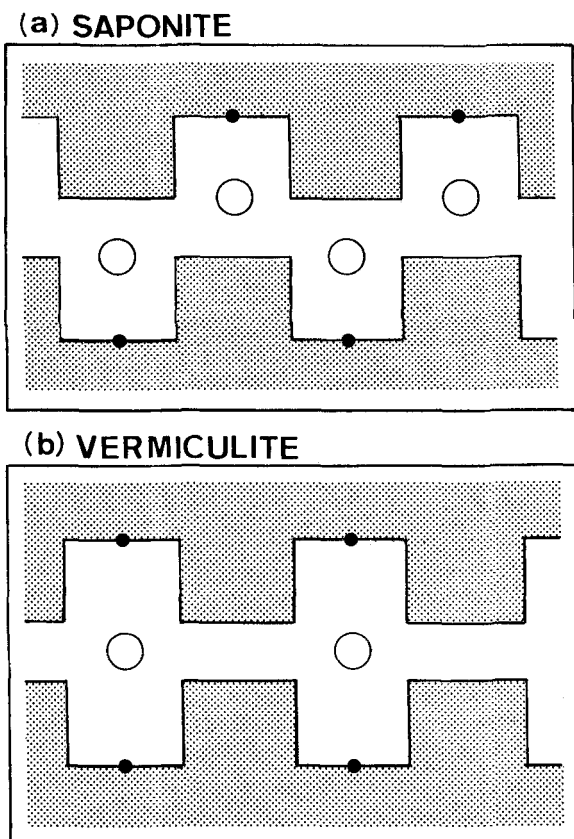


Figure 10. Schematic diagram showing the nature of stacking of adjacent silicate layers of dehydrated (a) saponite and (b) vermiculite, and the positions of interlayer cations (O). Shadow parts represent silicate layers.

of stacking of adjacent 2:1 layers of the minerals. The turbostratic stacking of saponite probably enhanced migration of interlayer cations into the hexagonal holes, as shown schematically in Figure 10a, whereas the ordered stacking of vermiculite inhibited such cation migration (Figure 10b). Therefore, the interlayer cations of vermiculite remained at the center of the adjacent 2:1 layers facing each other even after thermal dehydration and rehydrated easily in moist air or on water saturation.

The dehydration of K-saturated vermiculite in moist air without heating was apparently related to the size of the hexagonal holes in the basal oxygen plane and of the interlayer cations. If the interlayer cations were about the same size as the hexagonal holes, the cations were close packed with the basal oxygens of adjacent 2:1 layers, similar to the interlayer configuration of mica. For smaller cations (e.g., Mg^{2+}), however, this packing was incomplete, and the cations did not contact the surrounding oxygens. Therefore, the adsorption of water molecules, which are mainly affected by hydration energies of the interlayer cations, was rapid.

Mamy and Gaultier (1976) reported the modifica-

tion of turbostratic stacking to an ordered stacking by subjecting K-saturated montmorillonite to 100 cycles of alternate wetting and drying at 80°C. They showed a reduction of cation-exchange capacity and a contraction of the basal spacing to about 10 Å, indicating that smectites having ordered stacking exhibited vermiculite-like hydration properties (Barshad, 1948, 1950). Thus, the collapse of the interlayer space on K-saturation appears to be restricted to the expandable phyllosilicates consisting of ordered stacking of adjacent 2:1 layers, rather than those having greater negative charge density of the 2:1 layers. Consequently, the most important factor controlling the rehydration properties of saponite or vermiculite appears to be the nature of stacking of adjacent 2:1 layers.

ACKNOWLEDGMENTS

The authors thank the staff of the Institute of Earth Sciences, Faculty of Science, Kagoshima University for their many generousities. We also thank F. A. Mumpton and the reviewers for their critical reading of the manuscript, useful suggestions, and many recommendations.

REFERENCES

- Barshad, I. (1948) Vermiculite and its relation to biotite as revealed by base-exchange reactions, X-ray analysis, differential thermal curves and water content: *Amer. Mineral.* **33**, 655–678.
- Barshad, I. (1950) The effect of interlayer cations on the expansion of mica-type crystal lattice: *Amer. Mineral.* **35**, 225–238.
- Bassett, W. A. (1960) Role of hydroxyl orientation in mica alteration: *Bull. Geol. Soc. Amer.* **71**, 449–456.
- Brindley, G. W. and Wardle, R. (1970) Monoclinic and triclinic forms of pyrophyllite and pyrophyllite anhydride: *Amer. Mineral.* **55**, 1259–1272.
- Calvet, R. and Prost, R. (1971) Cation migration into empty octahedral sites and surface properties of clays: *Clays & Clay Minerals* **19**, 175–186.
- Eberhart, J. T. (1963) Transformation du mica en muscovite par chauffage entre 700 et 1200°C: *Bull. Soc. Franc. Miner. Cristallogr.* **86**, 213–251.
- Foster, M. D. (1963) Interpretation of the composition of vermiculites and hydrobiotite: in *Clays and Clay Minerals, Proc. 10th Natl. Conf., Austin, Texas, 1961*, Ada Swineford and P. C. Franks, eds., Pergamon Press, New York, 70–89.
- Giese, R. F. (1975) The effect of F/OH substitution on some layer silicate minerals: *Z. Kristallogr.* **141**, 138–144.
- Glaeser, R. and Méring, J. (1967) Effect du chauffage sur les montmorillonites saturées de cations de petit rayon: *C.R. Hebd. Séanc. Acad. Sci. Paris* **265**, 833–835.
- Greene-Kelly, R. (1955) Dehydration of the montmorillonite minerals: *Mineral. Mag.* **30**, 604–615.
- Harward, M. E., Carstea, D. D., and Sayegh, A. H. (1969) Properties of vermiculite and smectite: Expansion and collapse: *Clays & Clay Minerals* **16**, 437–447.
- Hoda, S. N. and Hood, W. C. (1972) Laboratory alteration of trioctahedral micas: *Clays & Clay Minerals* **20**, 343–358.
- Hofmann, U. and Klemen, R. (1950) Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung: *Z. Anorg. Allg. Chem.* **262**, 95–99.
- Kawano, M. and Tomita, K. (1989a) Rehydration properties of Na-rectorite from Makurazaki, Kagoshima Prefecture, Japan: *Mineral. J. (Tokyo)* **14**, 351–372.

- Kawano, M. and Tomita, K. (1989b) X-ray studies of rehydration behaviors for montmorillonite: *Clay Sci.* **7**, 277–287.
- Kawano, M. and Tomita, K. (1990a) X-ray powder diffraction studies on the rehydration properties of beidellite: *Clays & Clay Minerals* (in press).
- Kawano, M. and Tomita, K. (1990b) Rehydration mechanism of rectorite: *Mineral. J.* (submitted).
- Leonard, R. A. and Weed, S. B. (1967) Influence of exchange ions on the b-dimensions of dioctahedral vermiculite: *Clays & Clay Minerals* **15**, 149–161.
- Luca, V. and Cardile, M. C. (1989) Cation migration in smectite minerals: Electron spin resonance of exchanged Fe³⁺ probes: *Clays & Clay Minerals* **37**, 325–332.
- MacEwan, D. M. C. and Wilson, M. J. (1980) Interlayer and intercalation complexes of clay minerals: in *Crystal Structures of Clay Minerals and their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 249–303.
- Mamy, J. and Gaultier, J. P. (1976) Evolution de l'ordre cristalline dans la montmorillonite en relation avec la diminution d'échangeabilité du potassium: in *Proc. Int. Clay Conf., Mexico City, 1975*, S. W. Bailey, eds., Applied Publishing, Wilmette, Illinois, 149–155.
- McBride, M. B., Mortland, M. M., and Pinnavaia, T. J. (1975) Exchange ion positions in smectite: Effects on electron spin resonance of structural iron: *Clays & Clay Minerals* **23**, 162–164.
- Méring, J. (1946) On the hydration of montmorillonite: *Trans. Faraday Soc.* **42B**, 205–219.
- Newman, A. C. D. (1969) Cation exchange properties of micas. I. The relation between mica composition and potassium exchange in solutions of different pH: *J. Soil Sci.* **20**, 357–373.
- Post, J. L. (1984) Saponite from near Ballarat, California: *Clays & Clay Minerals* **32**, 147–153.
- Reynolds, R. C. (1980) Interstratified clay minerals: in *Crystal Structures of Clay Minerals and their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 249–303.
- Rosseinsky, D. R. (1965) Electron potentials and hydration energies. Theories and correlations: *Chemical Reviews* **65**, 467–490.
- Tettenhorst, R. (1962) Cation migration in montmorillonites: *Amer. Mineral.* **47**, 769–773.
- Udagawa, S., Urabe, K., and Hasu, H. (1974) The crystal structure of muscovite dehydroxylate: *J. Japan. Assoc. Min. Petr. Econ. Geol.* **69**, 381–389 (in Japanese).
- Vedder, W. and Wilkins, R. W. T. (1969) Dehydroxylation and rehydroxylation, oxidation and reduction of micas: *Amer. Mineral.* **54**, 482–509.
- Whittaker, E. J. W. and Muntus, R. (1970) Ionic radii for use in geochemistry: *Geochim. Cosmochim. Acta* **34**, 945–956.

(Received 31 July 1990; accepted 27 September 1990; Ms. 2026)