FURTHER INVESTIGATIONS ON THE REHYDRATION CHARACTERISTICS OF RECTORITE

Motoharu Kawano[1] and Katsutoshi Tomita[2]

[1] Department of Environmental Sciences and Technology, Faculty of Agriculture
Kagoshima University, 1-21-24 Korimoto, Kagoshima 890, Japan

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

Abstract—The rehydration and rehydroxylation properties of homoionic rectorites (saturated with Ca^{2+}, Mg^{2+}, Na^+, or K^+) were further investigated. The rehydration properties of the rectorite were characterized as follows: (1) basal spacings of rehydrated materials after heating above 500°C changed to 22.5 Å for H_2O-complexes, 26.85 Å for ethylene glycol-complexes, and 27.65 Å for glycerol-complexes; (2) rehydrated Ca- and Mg-materials exhibited single layer hydrates at <50% RH, and rehydrated K-material showed double layer hydrates at 80% RH; (3) IR absorption spectra due to rehydrated H_2O and OH exhibited the same or very close absorption intensities and frequencies to each other; (4) DTA-TGA curves of rehydrated materials indicated that the amount of rehydrated H_2O approached about 4.2 wt. %, and about one-half of OH was rehydroxylated after heating at 800°C; and (5) interlayer cations of expandable layer components became non-exchangeable after heating above 500°C. These results suggest the following rehydration mechanism of rectorite: the interlayer cations migrate into the hexagonal holes of the SiO_4 network by thermal dehydration. The cations migrated below 400°C easily return to the interlayer space and their original hydrated configurations have been recovered completely on rehydration. However, those migrated above 500°C are fixed to the hexagonal holes but water molecules are regained in the interlayer space. Consequently, electrostatic effects of interlayer cations on formation of water molecule layers are considerably reduced.

Key Words—Electrostatic effects, Hexagonal holes, Interlayer cation, Rectorite, Rehydration mechanism, Thermal dehydration.

INTRODUCTION

The expandable phyllosilicates exhibit various rehydration and rehydroxylation behaviors which are strongly dependent on the kind of interlayer cation and also on the crystallochemical characteristics (MacEwan and Wilson, 1980). Méring (1946) reported that Ca-smectite dehydrates irreversibly at a considerably lower temperature than Na-smectite, because Ca-smectite forms oxide linkages O-Ca-O in the space between the adjacent silicate layers, but Na-smectite does not. Greene-Kelly (1952) suggested that irreversible collapse is caused by reduction of the net charge on the exchangeable cation due to a strong interaction between the cation and the silicate layer. Recently, Kawano and Tomita (1991a, 1991b) investigated the behavior of interlayer cations in the dehydration and rehydration processes of some expandable phyllosilicates and their rehydration characteristics. They reported that the important factors affecting the dehydration and rehydration of the minerals are: (1) ionic size of the interlayer cations; (2) electrostatic force between the interlayer cation and the octahedral sheet; and (3) nature of stacking of the adjacent silicate layers.

For the rehydration properties of rectorite, Shimoda *et al.* (1969) noted that rectorite from Takatama mine, Fukushima Prefecture, Japan retains its rehydration ability up to 700°C. A rectorite having similar strong rehydration ability has been discovered in Makurazaki area, Kagoshima Prefecture, Japan (Tomita and Dozono, 1973). Kawano and Tomita (1989b) described the mineralogy and general rehydration properties of rectorite and pointed out that: (1) rectorite would rehydrate until the crystal structure was destroyed by heating; (2) Mg- and K-saturated rectorite heated at 400°C exhibited the slowest and the fastest rehydration rates, respectively; and (3) different hydration states appeared on rehydration after heating at >500°C. This last rehydration property is the most important characteristic. It has not been observed in any other expandable phyllosilicates.

The present paper reports the results of detailed investigations on the following problems concerning the rehydration of rectorite: (1) basal spacings of rehydrated (H_2O-complex), ethylene glycol-solvated (EG-complex), and glycerol-solvated (GL-complex) materials; (2) expansion characteristics of H_2O-complexes under various relative humidity conditions; (3) IR absorption spectra of H_2O-complexes; (4) amounts of rehydrated interlayer H_2O and OH; and (5) exchangeabilities of interlayer cations after heating.

MATERIAL AND EXPERIMENTAL METHODS

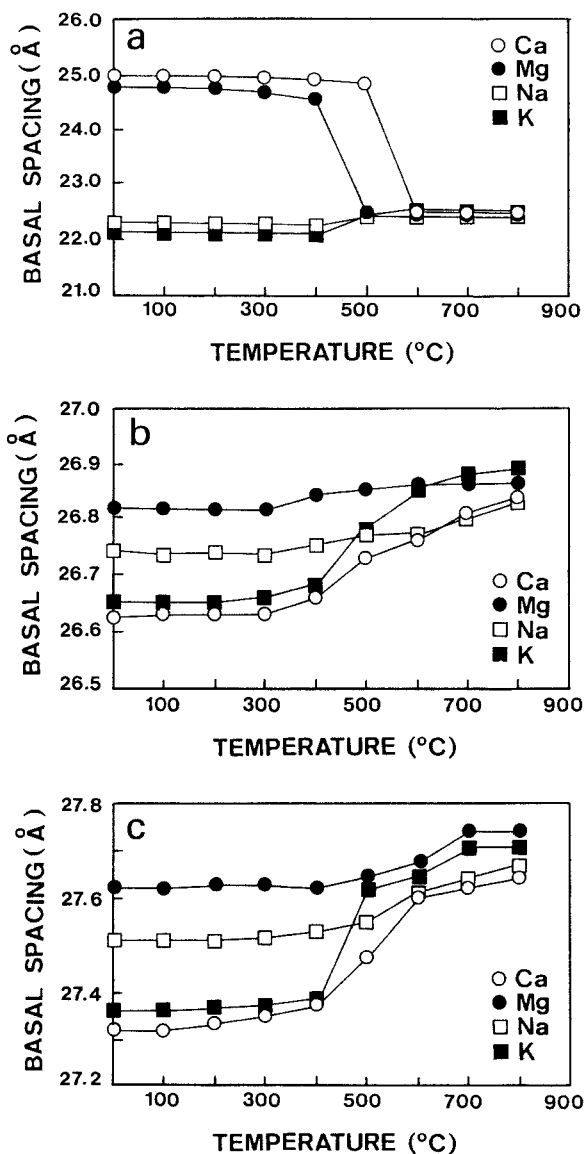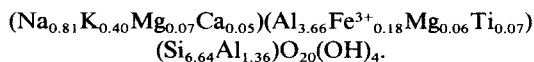The rectorite samples used in this study were from Makurazaki volcanic area, Kagoshima Prefecture, Ja-

Figure 1. Variations of basal spacings of (a) homoionic (Ca²⁺, Mg²⁺, Na⁺, or K⁺) rehydrated rectorites, and (b) ethylene glycol- and (c) glycerol-complexes of the rehydrated materials after heating at various temperatures for 1 hr. Relative humidity was held at 50% during measurement.

pan. The detailed mineralogical properties have been reported by Kawano and Tomita (1989b). The chemical composition of the material is:

$$(Na_{0.81}K_{0.40}Mg_{0.07}Ca_{0.05})(Al_{3.66}Fe^{3+}_{0.18}Mg_{0.06}Ti_{0.07})$$
$$(Si_{6.64}Al_{1.36})O_{20}(OH)_4.$$

The cation-exchange capacity is 53.1 meq/100 g on the ignited weight basis. The d(060) value is 1.492 Å.

The homoionic (Ca²⁺, Mg²⁺, Na⁺ or K⁺) materials

prepared by the same procedure as Kawano and Tomita (1991b) were heated in air at temperatures between 100° to 900°C at intervals of 100°C for 1 hr. After cooling in a desiccator at 0% RH, the heated materials were re-wet by adding several drops of deionized water for 1 day and dried in air at 50% RH.

These materials were oriented on glass slides by resuspension in deionized water and allowed to dry again at 50% RH. They were used for XRD analysis. The basal spacings of H₂O-, EG-, and GL-complexes were obtained by averaging the d-values of basal reflections, excluding the first-order peak, in the <40° 2θ interval. The XRD analysis was made with a RIGAKU diffractometer (CuKα radiation, 30 kV, 100 mA) equipped with a graphite monochromator, ½° divergence and scattering slits, using a scanning speed of 0.5° 2θ/min. All materials were kept at 50% RH during X-ray examination.

The basal spacings of materials rehydrated after heating at 800°C were examined by XRD under 20%, 30%, 40%, 50%, 60%, 70%, and 80% RH. The materials were kept in the atmosphere at least 5 hr before X-ray examination. The basal spacings were determined by the same procedure as described above.

IR absorption spectra of OH and H₂O vibrations were made from original unheated materials and from materials rehydrated after heating at 800°C for 1 hr. Materials were kept at 50% RH during measurement. The spectra were made with a NIHONBUNKO infrared absorption spectrophotometer using oriented materials on a KBr window.

The H₂O wt. % and OH wt. % of rehydrated materials was measured with a RIGAKU differential thermal and thermogravimetric analysis (DTA-TGA) apparatus. Measurement was made from room temperature to 1100°C with a heating rate of 10°C/min using powdered samples of about 25 mg. Materials were kept at 50% RH before analysis. Weight losses at temperatures below and above 400°C were assigned to H₂O wt. % and OH wt. %, respectively.

About 0.5 g of unheated homoionic materials were heated in air at temperatures between 100° to 900°C at intervals of 100°C for 1 hr, and were washed with 0.1 N SrCl₂ solution more than five times. The extracted cations (Ca²⁺, Mg²⁺, Na⁺, or K⁺) were measured with an atomic absorption spectrometer (AAS). To make sure that no interlayer cations were lost during heating, heated materials prepared by the same procedure were dissolved in HF-HClO₄. We then measured interlayer cations (Ca²⁺, Mg²⁺, Na⁺, or K⁺) by AAS.

The humidity of the atmosphere was controlled by an ordinary dehumidifier and humidifier equipped with a SHINYEI RHI-600 humidity auto-controller system. The measurement of humidity was made with a SHINYEI THP-B3T semiconductor humidity sensor. The accuracy was estimated as ±3% RH.
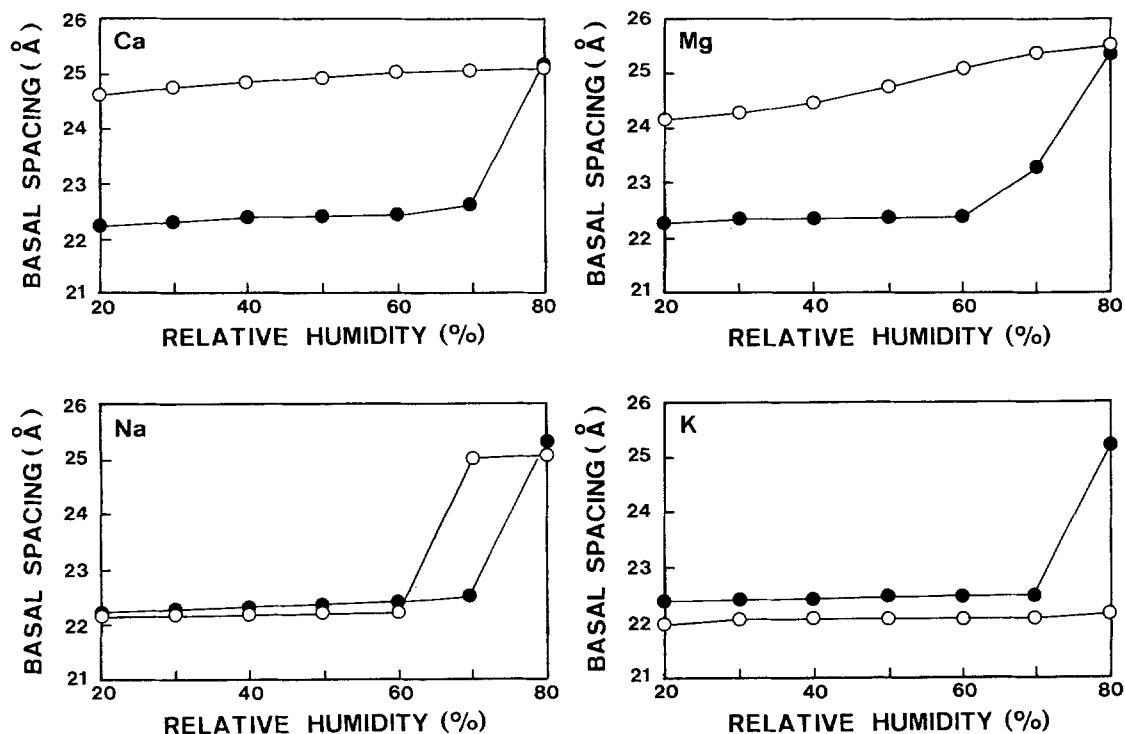
Figure 2.   Variations of basal spacings of (O) homoionic (Ca^{2+}, Mg^{2+}, Na^+, or K^+) original rectorites and (●) their rehydrated forms after heating at 800°C for 1 hr with various relative humidity conditions.

RESULTS

Basal spacings of H_2O-, EG-, and GL-complexes

Figure 1a shows variations of basal spacings of rehydrated homoionic materials (H_2O-complexes) after heating at various temperatures. The d-values of these materials, previously heated up to 400°C, did not show significant changes. The Ca- and Mg-materials changed to single layer hydrates after heating above 500°–600°C, whereas the Na- and K-materials expanded slightly. The transition phases of Ca-material at 500°C and Mg-material at 400°C exhibited two hydration states with approximately 24.7 Å layers and small amounts of 22.5 Å layers. The basal spacings of all materials became very close to 22.5 Å, regardless of saturating cation above 500°C. The XRD profiles of the materials rehydrated after heating at 800°C also exhibited similar patterns to each other, all which are single layer hydrates.

Figures 1b and 1c show variations of basal spacings of EG- and GL-complexes, respectively. The d-values of EG-complexes of unheated materials are slightly different from each other ($Mg^{2+} > Na^+ > K^+ > Ca^{2+}$), suggesting that the kind of interlayer cation also affects the expansion property on EG-solvation. The basal spacings of the materials almost remained constant below 400°C but increased with increasing tempera-

tures between 400° and 800°C to about 26.8–26.9 Å at 800°C, independent of the saturating cation. The GL-complexes exhibited similar behavior with the d-values increasing to about 27.7 Å (Figure 1c).

Expansion characteristics of H_2O-complexes under various relative humidity conditions

Figure 2 shows a comparison of basal spacings of unheated materials at various RH conditions with those of materials rehydrated after heating at 800°C. The basal spacings of unheated Ca- and Mg-materials increased slightly and continuously with the relative humidity. However, the rehydrated Ca- and Mg-materials exhibited single layer hydrates between 20% and 70% RH and double layer hydrates at 80% RH. For the Na-materials, transition of single-double layer hydrate occurred at 70% RH for unheated material and at 80% RH for rehydrated material. The unheated K-material showed a single layer hydrate with basal spacing of approximately 22 Å between 20% and 80% RH. Whereas, the K-saturated rehydrated material expanded slightly to 22.5 Å between 20% and 70% RH and changed to a double layer hydrate with a basal spacing of 25.2 Å at 80% RH. The expansion characteristics of these unheated materials are very similar to those of homoionic rectorites reported by Matsuda
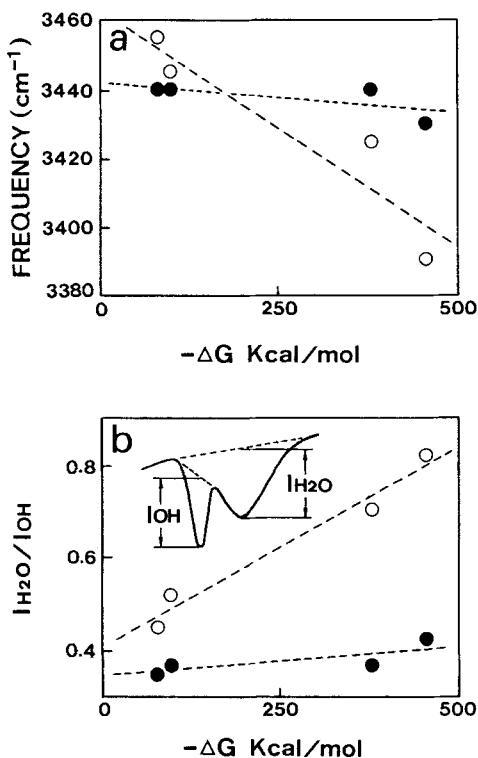
Figure 3. Relationship (a) between H_2O absorption frequencies and hydration energies of interlayer cations, and (b) between absorption intensity ratios of I_{H_2O}/I_{OH} and hydration energy. The samples plotted in this figure are (○) homoionic (Ca^{2+}, Mg^{2+}, Na^+, or K^+) unheated rectorites and (●) homoionic materials rehydrated after heating at 800°C for 1 hr. Relative humidity was held at 50% during measurement.
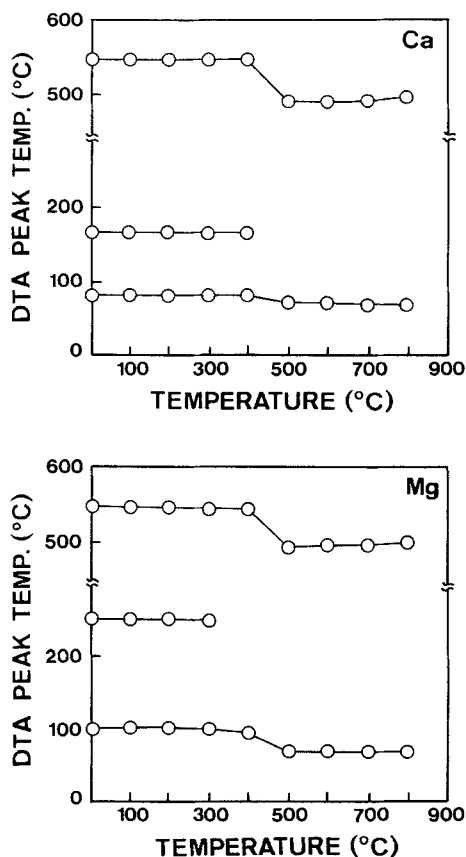

Figure 4. Endothermic peak temperatures from differential thermal analysis curves of Ca- and Mg-saturated rectorites rehydrated after heating at various temperatures for 1 hr. Relative humidity was held at 50% during measurement.

(1984, 1989). However, the expandabilities of rehydrated materials are quite different.

IR absorption spectra of interlayer H_2O and OH

The IR spectra of unheated materials exhibited strong absorptions due to OH vibration at 3645–3637 cm^{-1} and broad absorptions due to H_2O stretching vibration at 3455–3390 cm^{-1}. The materials rehydrated after heating below 400°C showed the same spectra as those of unheated materials. The materials rehydrated after heating above 500°C also exhibited pronounced absorption bands due to OH and H_2O, although the absorption frequencies and intensities were slightly different from those of unheated materials. Figure 3a shows the relationship between absorption frequencies of H_2O and hydration energies (Rosseinsky, 1965) of interlayer cations. The samples plotted on this Figure are homoionic (Ca^{2+}, Mg^{2+}, Na^+, or K^+) unheated materials and homoionic materials rehydrated after heating at 800°C. The absorptions of unheated materials shifted to lower frequency with increasing hydration energy. On the other hand, the absorption frequencies of rehydrated materials were nearly constant at 3440 cm^{-1}. Figure

3b shows the relationship between absorption intensity ratios of I_{H_2O}/I_{OH} and hydration energies. The same materials as Figure 3a were plotted on this figure. The amounts of rehydroxylated OH were estimated to be approximately one-half of the original OH (Figure 5b). Therefore, the I_{OH} of rehydrated materials were normalized to completely rehydroxylated state with the values of OH wt. % obtained by TGA. The I_{H_2O}/I_{OH} ratios of unheated materials shifted to larger values with increasing hydration energy. Whereas, the rehydrated materials gave nearly constant values.

Rehydration of interlayer H_2O and rehydroxylated OH

Figure 4 shows the variation of DTA endothermic peak temperatures of unheated and rehydrated Ca- and Mg-materials. For the Ca-material, the endothermic peak temperatures of materials rehydrated after heating below 400°C were unchanged. Whereas, the first dehydration peak (82°C) shifted to a slightly lower temperature, the secondary dehydration peak (168°C) disappeared, and the dehydroxylation peak (547°C) shifted to a considerably lower temperature after heating
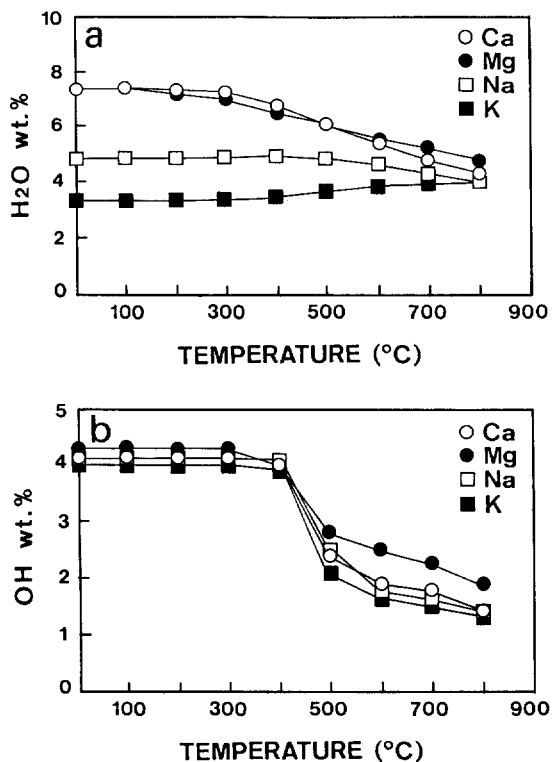
Figure 5. Variations of (a) H_2O wt. % and (b) OH wt. % of homoionic (Ca^{2+}, Mg^{2+}, Na^+, or K^+) rectorites rehydrated after heating at various temperatures for 1 hr. The values of wt. % were obtained from TGA curves, in which weight losses below and above 400°C were assigned to H_2O wt. % and OH wt. %, respectively.

Figure 6. Variations of oxide wt. % of CaO, MgO, Na_2O, and K_2O of (a) representative homoionic rectorites after heating at various temperatures for 1 hr, and (b) variations of exchangeable cations of homoionic (Ca^{2+}, Mg^{2+}, Na^+, or K^+) rectorites after heating at various temperatures for 1 hr.

above 500°C. Similar phenomena were also recognized in the Mg-material (Figure 4b).

The variations of H_2O wt. % and OH wt. % of rehydrated materials are presented in Figures 5a and 5b, respectively. The H_2O wt. % of rehydrated Ca- and Mg-materials decreased continuously, whereas that of rehydrated Na- and K-materials remained almost unchanged. All materials rehydrated after heating at 800°C averaged 4–5 wt. % H_2O, regardless of saturating cation. The OH wt. % of all rehydrated materials decreased rapidly at 500°C, and continued to decrease slightly when they were heated at higher temperatures. At 500°C and above, about one-half of original OH appeared to be regained in the dehydroxylated structure after leaving in the wet state for 1 day. No significant change of rehydroxylated OH wt. % was observed after leaving it wet for 2 months.

Changes of exchangeability of interlayer cations

Figure 6a shows oxide wt. % of CaO, MgO, Na_2O, and K_2O of representative homoionic materials after heating at various temperatures. The values of all elements remained constant, suggesting that no interlayer cations were lost during heating up to 900°C. The
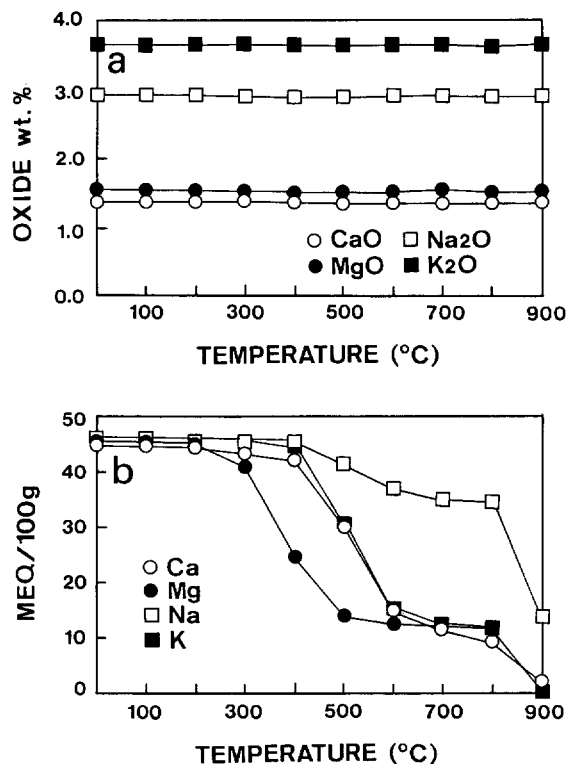
exchangeable cations extracted with 0.1 N $SrCl_2$ solution after heating at various temperatures are given in Figure 6b. The exchangeability of Ca^{2+}, Mg^{2+}, and K^+ ions decreased rapidly at temperatures about 400°–600°C. The magnitude of decrease for the Na^+ ion was less than for the other cations. Figure 7 shows exchangeable cations of Ca-saturated material after heating at various temperatures. The exchangeable Ca^{2+} ion decreased rapidly between 500° and 600°C; exchangeable Na^+ and K^+ ions increased between 500° and 800°C. A similar phenomenon could also be observed in the K-saturated material (Figure 7): exchangeable K decreased and exchangeable Na increased.

DISCUSSION

The rehydration properties of rectorite after heating below and above dehydroxylation temperatures are distinctly different from each other. For the materials rehydrated after heating below dehydroxylation temperatures, there were no significant changes in the basal spacings, endothermic peaks due to removal of interlayer water, and IR absorption frequencies of interlayer water compared with those of original unheated ma-
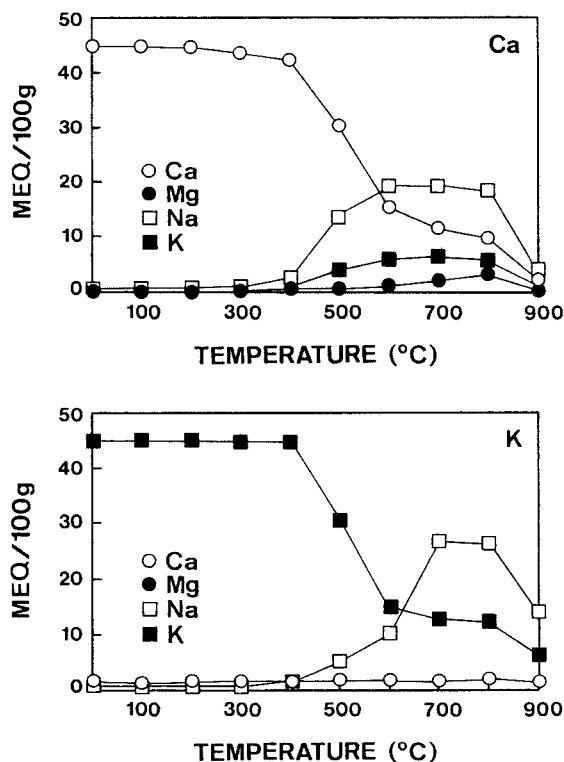
Figure 7. Variations of exchangeable cations of Ca- and K-saturated rectorites after heating at various temperatures for 1 hr.

ings may be observed. On the contrary, if the above properties decrease, some expansion can be expected (Suquet *et al.*, 1975). According to Figure 1, the basal spacings of Ca- and Mg-materials contracted drastically, whereas those of Na- and K-materials expanded slightly. These results suggest that factors other than those mentioned above can be considered to explain the particular behavior of basal spacings. Furthermore, the EG- and GL-complexes expanded after heating above 500°C. The greater negative layer charge of 2:1 layer and larger ionic radii of interlayer cations inhibit the expansion of EG- and GL-complexes (MacEwan and Wilson, 1980). Based on this fact, these expansion characteristics suggest that the negative layer charge decreased by heating above 400°C.

However, the H_2O-complexes of Ca- and Mg-materials contracted rapidly at 500°C which can not be explained by reduction of the layer charge. This behavior may be due to reduction of electrostatic effects of interlayer cations rather than structural changes of the 2:1 layer. The correlation relationship observed in the IR spectra of unheated materials disappeared in those of rehydrated materials, which also suggests that electrostatic effects of interlayer cations have been reduced on rehydration. It is also well known that the adsorption of water, ethylene glycol, and glycerol molecules are due to dipole attractions to the interlayer cations and also to hydrogen bonding to the oxygen surfaces (Emerson, 1957; Brindley and Roy, 1964; Bissada *et al.*, 1967; Dowdy and Mortland, 1967, 1968). Therefore, reduction of electrostatic effects can be attributed to a decrease in dipole attraction by migration of the interlayer cations into the hexagonal holes.

A decrease in exchangeable Ca^{2+} ion of Ca-material at temperatures between 500° and 600°C (Figure 7) is due to fixation to interlayer of smectite layer components, because no removal of interlayer cations took place up to 900°C (Figure 6a). An increase in exchangeable Na^+ and K^+ ions between 500° and 800°C is due to extraction of the ions from the interlayer sites of mica layer components (Tomita and Sudo, 1968; Scott *et al.*, 1972; Smith and Scott, 1974), because interlayer cations of smectite layers have been completely exchanged by Ca^{2+} ion. The amounts of extracted Na^+ ions are considerably larger than those of K^+ ions compared with their atomic abundance ratio (Na/K = 2.0). This is probably due to larger hydration energy of Na^+ ion. Therefore, the small decreasing value of exchangeable Na^+ ion (Figure 6b) was compensated by Na^+ ion extracted from the mica layers. Consequently, the interlayer cations of expandable layers of rectorite were fixed by heating at 400°–600°C, regardless of which cation was present. This phenomenon is apparently different from that of the smectite group, for which fixation temperatures became higher with increasing ionic radii of interlayer cations (MacEwan and Wilson, 1980). The results of exchange-

terials. The rehydrated H_2O wt. % and amounts of exchangeable cations also remained unchanged. It is well known that interlayer cations of smectites and rectorites migrate into the hexagonal holes of the SiO_4 network during thermal dehydration (Tettenhorst, 1962; Pezerat and Méring, 1967; McBride *et al.*, 1974; Luca and Cardile, 1988, 1989; Kawano and Tomita, 1989b, 1991a, 1991b). Therefore, these results suggest that the migrated cations return to the interlayer space, and original hydrated configurations are restored on rehydration. This rehydration process appears to be the same as reported by Kawano and Tomita (1989a, 1991a, 1991b) for the smectite group.

For the rehydration properties after heating above dehydroxylation temperature, the basal spacings did not collapse up to 800°C and unique expansion characteristics were observed (Figure 1). The basal spacings of expandable phyllosilicates are mainly influenced by the following factors; (1) the nature of interlayer cations (e.g., hydration energy and ionic radius); (2) negative layer charge of 2:1 layer; (3) orientation of OH; and (4) relative humidity of atmosphere. If negative layer charge and/or orientation angle of OH change, the basal spacings should behave similarly to each other. Namely, if the negative layer charge and/or the orientation angle increase, some contraction of basal spac-

ability of interlayer cations strongly suggest that the cations migrated into the hexagonal holes and are fixed there by heating above 500°C. However, water molecules are regained in the interlayer space with the cations remaining in the hexagonal holes. This relocation of interlayer cations perhaps reduced the dipole attractions between interlayer cations and water molecules. The rehydration mechanism of rectorite is completely different from vermiculite and smectite (Kawano and Tomita, 1991a, 1991b).

After leaving in the wet state for 1 day under room temperature, about one-half of the original OH was immediately regained in dehydroxylated rectorite structure. Further rehydroxylation could not be recognized after leaving in a wet state for 2 months. The removal of rehydroxylated OH took place at slightly lower temperature than original OH as reported by many investigators (e.g., Grim and Brindley, 1948; Jonas, 1955; Heller et al., 1962). Illite and montmorillonite regain very small amounts of OH on exposure to moist air for long periods of time after complete dehydroxylation at 800°C (Grim and Brindley, 1948). Larger amounts of OH can be regained in the dehydroxylated structure under a high temperature water vapor condition (Jonas, 1955; Heller et al., 1962; Vedder and Wilkins, 1969). A 2M mica exhibits rehydration and rehydroxylation behaviors similar to those of rectorite after boiling in an acid solution (Tomita, 1974). For rectorite, however, remarkable rehydroxylation occurred simply by leaving in a wet state at room temperature for at least 1 day. No clay minerals having such a strong rehydroxylation property have been reported yet.

ACKNOWLEDGMENTS

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