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X-RAY POWDER DIFFRACTION STUDIES ON THE REHYDRATION PROPERTIES OF BEIDELLITE

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Abstract—The rehydration properties of Ca-, Mg-, Na-, and K-saturated homoionic beidellites after heating at various temperatures were compared with those of montmorillonites. The behavior of interlayer Na^+ during dehydration and rehydration was also investigated by means of one-dimensional Fourier analysis. The K- and Mg-saturated specimens exhibited fast and slow rehydration rates, respectively, during exposure to air of 50% RH after heating at 800°C. These homoionic specimens showed strong rehydration properties on saturation with deionized water after heating <900°C for 1 hr. On the basis of Fourier analysis, the interlayer cations appeared to have migrated into the hexagonal holes of SiO_4 network on thermal dehydration, and the migrated cations returned to the interlayer space on rehydration. This behavior of the interlayer cations appears to have been strongly dependent on value of the octahedral negative charge and on the sizes of interlayer cations. The small octahedral negative charge of beidellite produced a weaker attractive electrostatic force between the octahedral sheets and the migrated interlayer cations. Therefore, the migrated interlayer cations in beidellite were easily extracted from the hexagonal holes, and rehydration was rapid. The small cation migrated easily into hexagonal holes and was fixed to the holes. On the contrary, large cations were probably difficult to fix and were easily extracted from the hexagonal holes. Consequently, the rehydration rate of K-saturated beidellite was fast, and that of Mg-saturated beidellite was slow.

Key Words—Beidellite, Cation migration, Dehydration, Fourier analysis, Interlayer ration, Rehydration, X-ray powder diffraction.

要旨－Ｃａ，Ｍｇ，Ｎａ および Ｋの単一陽イオンで飽和したバイデライトの加熱後の復水性をモンモリロナイトの復水性と比較検討した．層間水の脱水および復水に伴う層間Ｎａイオンの挙動についても一次元フーリエ解析から検討を加えた．

８００℃で加熱したバイデライトを５０％ＲＨの空気中に放置した場合，Ｋ－飽和試料の復水速度は速く，Ｍｇ－飽和試料の復水速度は遅い結果を示した．９００℃で１時間加熱したバイデライトを脱イオン水で湿した場合，４種類すべての試料が強い復水性を示した．フーリエ解析によると，層間陽イオンは層間水の脱水によってSiO_4ネットワークの六員環中に移動するが，復水によって層間域に戻ることが明らかとなった．これらの層間陽イオンの挙動は八面体シートの負電荷と層間陽イオンのサイズに依存する．バイデライトは八面体シートの負電荷が小さいために八面体シートと層間陽イオンとの間に働く静電気力は小さい．従って層間陽イオンは容易に六員環中から層間域へ復帰し，復水性が強くなる．またサイズの小さい層間陽イオンは六員環中への固定が容易であるが，サイズが大きい場合は固定が困難であるために層間域へ復帰しやすくなるものと思われる．そのためにＫ－飽和試料の復水速度は速くなり，Ｍｇ－飽和試料の復水速度は遅くなる．

INTRODUCTION

A notable crystal chemical feature of beidellite is the negative charge arising principally from the cation substitution of Al^{3+} for Si^{4+} in tetrahedral sheets. Montmorillonite, on the other hand, is characterized by the predominant substitution of Mg^{2+} for Al^{3+} in octahedral sheets. The different charge localization affects the expansion properties of Li-saturated specimens of both materials on heating. Hofmann and Klemen (1950) and Greene-Kelly (1953, 1955) attributed the phenomenon to the migration of small cations into empty octahedral sites of montmorillonite. Glaeser and Méring (1967) agreed with this hypothesis. Calvet and Prost (1971) suggested that some Li^+ ions move toward octahedral cavities and that the rest remain in the bottom of the hexagonal holes. Ben Hadj-Amara *et al.* (1987) examined the migrated position of interlayer Ni^{2+} ions of beidellite by X-ray modeling techniques and showed that all Ni^{2+} ions, having an ionic radius as small as Li^+, move into empty octahedral sites after 24 hr of heating at 240°C. On the other hand, Komarov *et al.* (1977) and Luca and Cardile (1988, 1989) suggested that interlayer Li^+ and Fe^{3+} ions in montmorillonite do not migrate into the octahedral sheets, but remain in hexagonal holes even after heating. From infrared

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(IR) spectra and electron spin resonance (ESR) signals, Tettenhorst (1962) and McBride *et al.* (1974), respectively, suggested that medium- and large-size cations (e.g., Na^+, Ca^{2+}, and K^+) move into hexagonal holes of the SiO_4 network instead of into empty octahedral sites. Pezerat and Méring (1967) examined the position of interlayer Na^+ ions of dehydrated montmorillonite by means of one-dimensional Fourier analysis; they claimed that the ions are located at surface on hexagonal holes of silicate layers. Kawano and Tomita (1989b) reported that interlayer Na^+ ions of montmorillonite move into the hexagonal holes of the SiO_4 network on thermal dehydration. They also pointed out that migrated Na^+ ions of the specimen heated at 400°C easily returned to the interlayer space after water saturation, but if the specimen had been heated at 800°C, they relocated near the basal oxygen plane and remained at the migrated position, even after water saturation, keeping the dehydrated structure. Therefore, the rehydration ability of smectite on thermal dehydration seems to be affected by the behavior of interlayer Na^+ ions during dehydration and rehydration.

The present paper reports rehydration properties of beidellite after thermal dehydration. The behavior of interlayer cations during dehydration and rehydration is also examined by means of one-dimensional Fourier analysis, and the rehydration mechanism of beidellite is clarified.

EXPERIMENTAL

Material

Beidellite from Sano mine, Nagano Prefecture, Japan, and montmorillonite from Cheto, Arizona, were used in this study. The detailed mineralogical properties of the beidellite were reported by Matsuda (1988). The structural formula of the specimen is:

$$(Na_{0.09}K_{0.05}Mg_{0.06}Ca_{0.15})(Al_{1.92}Mg_{0.07}Ti_{0.01})(Si_{3.50}Al_{0.50})O_{10}(OH)_2.$$

The chemical composition of the montmorillonite from Cheto was reported by Uno *et al.* (1986) as follows:

$$(Mg_{0.02}Ca_{0.49}Na_{0.02}K_{0.01}H_{0.03})(Al_{2.99}Fe^{3+}{}_{0.10}Fe^{2+}{}_{0.02}Mg_{0.95})(Si_{7.76}Al_{0.24})O_{20}(OH)_4.$$

The <2-μm fractions of both minerals were collected by normal sedimentation methods and were saturated with Ca^{2+}, Mg^{2+}, Na^+, or K^+ ions by treatment with 1 N chloride solutions. The excess salt was then removed by washing five times with 80% ethanol until the complete absence of Cl^- ions.

Methods

To study rehydration properties of beidellite, the following experiments were carried out: (1) The variation of d(001) values after heating at various temperatures was determined. (2) The variation of d(001) values of rehydrated specimens was measured. (3) The rehydration rates in air were measured after heating at 800°C. (4) The behavior of interlayer cations during dehydration and rehydration was determined.

The variation of d(001) values after heating was examined by the following procedures. The homoionic specimens oriented on quartz glass slides were heated for 1 hr between 100° and 900°C at intervals of 100°C and then cooled in a desiccator for 1 hr. The relative humidity (RH) in the desiccator was controlled at 0% with di-phosphorus pentanoxide. The d(001) values of the heated specimens were immediately measured by X-ray powder diffraction (XRD) analysis using Ni-filtered CuKα radiation under the condition of 50% RH, after taking the sample out of the desiccator. The XRD patterns were obtained from 14° to 2°2θ at a scanning speed of 0.5°2θ/min.

The variations of d(001) values of rehydrated specimens were examined as follows. The homoionic powdered specimens were heated for 1 hr between 100° and 900°C at 100°C intervals and then cooled in a desiccator at 0% RH for 1 hr. The heated specimens were re-solvated with deionized water at room temperature and then immediately oriented on glass slides. The wet samples were dried in air at 50% RH for 1 day. The d(001) values of the rehydrated specimens were measured by XRD at a scanning speed of 0.5°2θ/min at 50% RH.

The rehydration rates in air were investigated as follows. The homoionic specimens oriented on quartz glass slides were heated at 800°C for 1 hr and then cooled in a desiccator at 0% RH for 1 hr. XRD patterns were obtained from 14° to 2°2θ at a scanning speed of 2°2θ/min at 0% and 50% RH. For the 50% RH experiments, changes in the first-order reflection on exposure to air for various periods of time were investigated.

The behavior of interlayer cation in the Na-saturated beidellite, unheated, heated at 400° and 800°C for 1 hr, and rehydrated after heating at 800°C, prepared by the same procedures as mentioned above, was investigated by means of one-dimensional Fourier analysis. The initial structural model used was from Reynolds (1980), and the Z-parameters along the *c*-axis were refined by the least squares method. The XRD data were obtained with a Rigaku diffractometer using a 1/6° divergence slit and a 1/6° scatter slit. Matsuda (1989) reported that Na-saturated beidellite exhibits a homogeneous one-layer hydration state between 30% and 60% RH. The present unheated and rehydrated specimens also showed a homogeneous one-layer hydration state at 50% RH, but showed no interstratification of the one- and two-layer hydration states (see below). The DTA curve of the present specimen (Matsuda, 1988) indicated that the dehydroxylation reaction took place between 500° and 700°C; hence, the heating temperature of 800°C was apparently sufficient for complete dehydroxylation.

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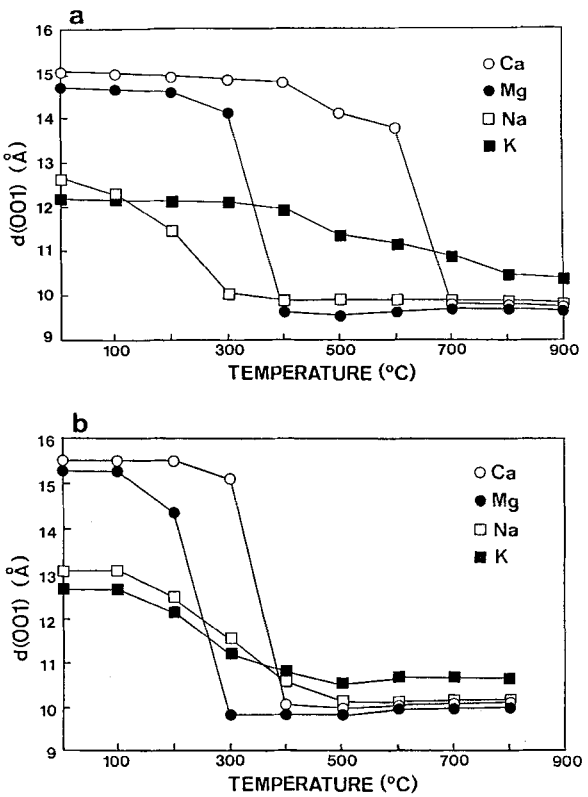


Figure 1. Variation of d(001) obtained at 50% RH for homoionic (saturated with Ca, Mg, Na, or K) (a) beidellite and (b) montmorillonite heated at various temperatures for 1 hr.

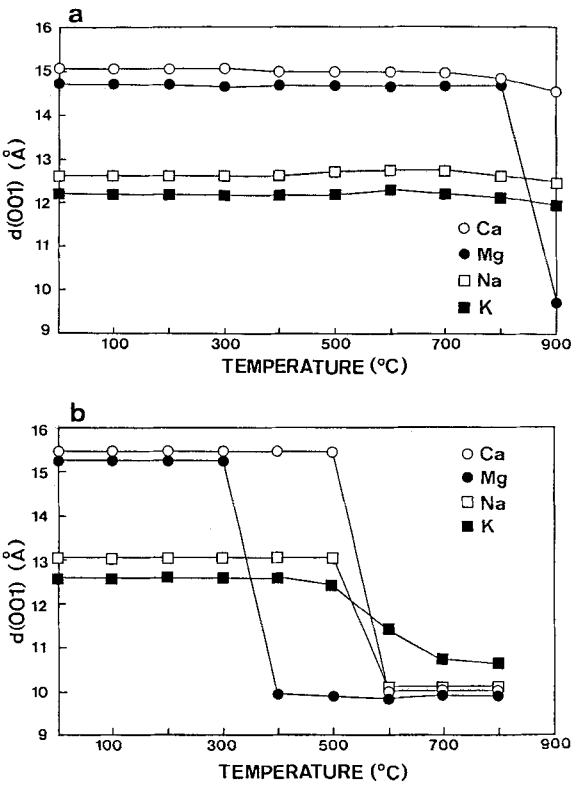


Figure 2. Variation of d(001) obtained at 50% RH for rehydrated homoionic (saturated with Ca, Mg, Na, or K) (a) beidellites and (b) montmorillonite after heating at various temperatures for 1 hr.

RESULTS

Variations of d(001) after heating

Figure 1a shows d(001) values of homoionic beidellites obtained at 50% RH after heating at various temperatures for 1 hr. The unheated Ca- and Mg-saturated specimens exhibited two-layer hydration having d(001) values of about 15.1 and 14.7 Å, respectively. On the other hand, the Na- and K-saturated specimens showed one-layer hydration having d(001) values of about 12.6 and 12.2 Å, respectively. These results generally agree with the hydration states of beidellite as reported by Suquet *et al.* (1975). After the sample had been heated at various temperatures, the d(001) value of the Ca-saturated specimen, previously heated at temperatures <400°C, did not change; however, it decreased to about 9.9 Å at 700°C. The d(001) value of the Mg-saturated specimen exhibited a similar decrease as that of the Ca-saturated specimen at 400°C. The d(001) value of the Na-saturated specimen gradually decreased <300°C and remained the same above the temperatures. On the other hand, the d(001) value of the K-saturated specimen did not change at temperatures <400°C, but decreased at temperatures between 400° and 900°C. Figure 1b shows the d(001) of homoionic montmorillonites from Cheto after heating at various temperatures for 1 hr. The d(001) values of the montmorillonites decreased at apparently lower temperatures than those of the beidellites. After the samples had been heated at 900°C for 1 hr, the d(001) values of the homoionic dehydrated specimens ($K^+ > Na^+ > Ca^{2+} > Mg^{2+}$) decreased as the ionic radii of saturating cations ($K^+ > Na^+ > Ca^{2+} > Mg^{2+}$; Whittaker and Muntus, 1970). The removal of interlayer water from smectites takes place <300°C (Midgley and Gross, 1956; Greene-Kelly, 1957), suggesting that the present beidellite had a strong rehydration ability. Namely, the heated specimens seem to have rehydrated rapidly on exposure to air at 50% RH (see below).

Variations of d(001) after water saturation

Figure 2a shows variations of d(001) of rehydrated homoionic beidellites obtained at 50% RH after heating at various temperatures for 1 hr. These homoionic specimens rehydrated completely on water saturation, even after heating at 800°C. Similar values of d(001) to those of unheated specimens and a rational series of higher order reflections were clearly observed. These results suggest that the homogenous hydration state in the interlayer space of the rehydrated specimens was

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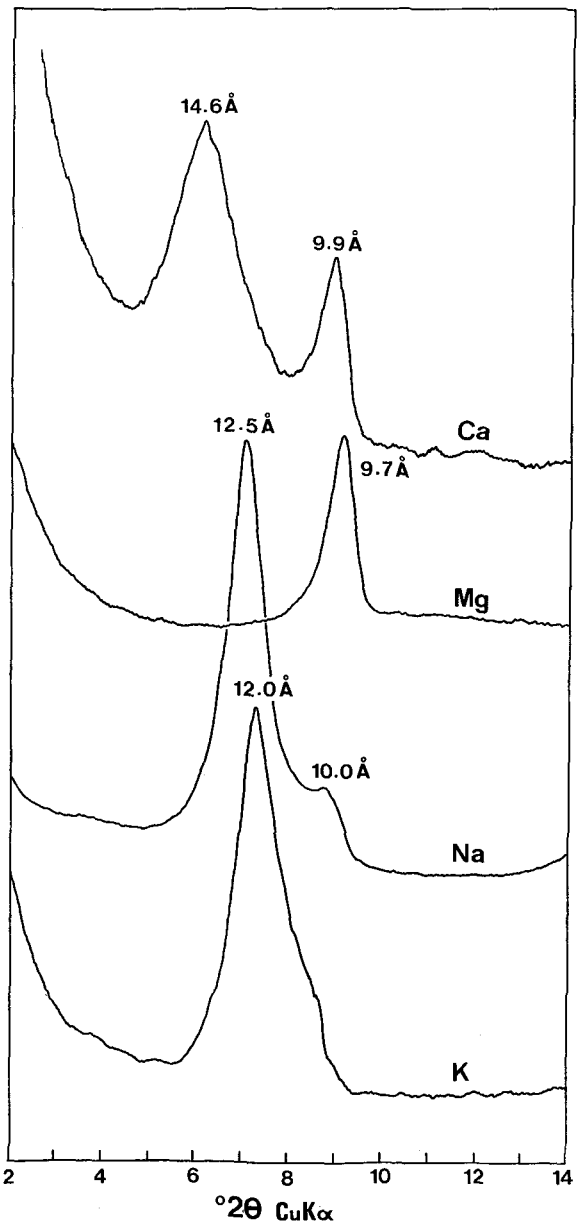


Figure 3. X-ray diffraction patterns obtained at 50% RH for homoionic (saturated with Ca, Mg, Na, or K) beidellite saturated with deionized water after heating at 900°C for 1 hr.

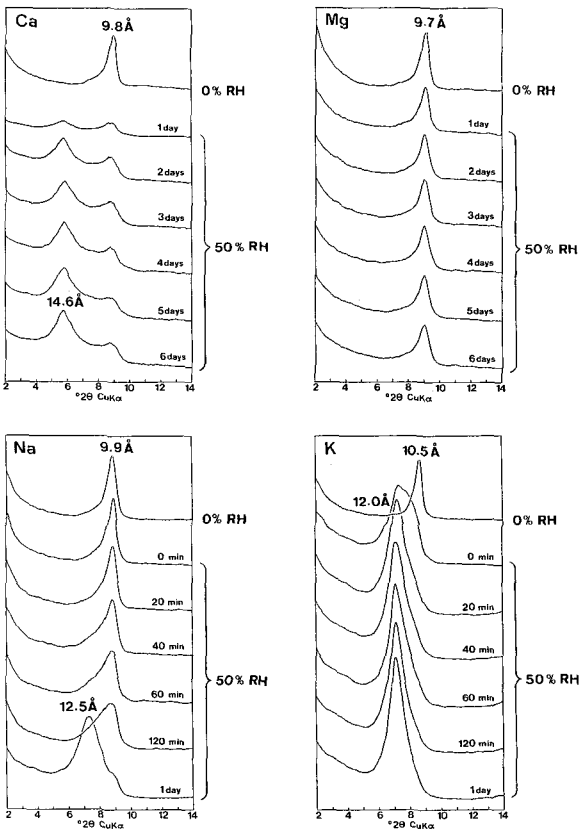


Figure 4. Changes in first-order reflections of homoionic (saturated with Ca, Mg, Na, or K) beidellite on exposure to air at 50% for various periods of time after heating at 800°C for 1 hr. 0% = at 0% RH; 1 to 6 days and 0 to 120 min signify exposure times to air at 50% RH.

completely restored. On saturation with deionized water after heating at 900°C, the Ca-, Na-, and K-saturated specimens showed segregation structures of the rehydrated and dehydrated forms (Figure 3). On the other hand, the Mg-saturated specimen did not rehydrate, and its dehydrated form, having a d(001) value of about 9.7 Å, remained after saturation with deionized water. Figure 2b shows variations of d(001) of rehydrated homoionic montmorillonites from Cheto. The irreversibe dehydration temperatures of the Mg-, Ca-, Na-, and K-saturated specimens were 400°, 600°, 600°, and 800°C, respectively. Thus, the present beidellite had an appreciably stronger rehydration ability than the montmorillonite. The differences in the rehydration properties of beidellite and montmorillonite are considered to be due to their different charge localization.

Rehydration rate of beidellite heated at 800°C in air

The XRD patterns of specimens heated at 800°C in air at 50% RH for various periods of time (Figure 4) indicate that rehydration rates were strongly influenced by the kind of interlayer cation. The Ca-saturated specimen showed a segregation structure of two-layer hydrated and dehydrated forms on exposure to air for 1 day. Although an increase in the amount of two-layer hydration was observed during exposure to air at 50% RH, the segregation structure remained even after 6 days. For the Mg-saturated specimen, the dehydrated form remained even after exposure for 6 days, whereas the first-order reflection of the dehydrated specimen broadened slightly. On the other hand, the Na- and K-saturated specimens rehydrated more rapidly than the Ca- and Mg-saturated specimens. The Na-saturated specimen almost completely rehydrated on expo-

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Table 1. Basal spacings and structure factors for various states of Na-saturated beidellites.

	Unheated			Heated at 400°C		
00l	d (Å)	|Fo|	Fc	d (Å)	|Fo|	Fc
1	12.7	109.8	−112.3	9.96	58.1	−43.5
2	6.23	45.9	−47.0	4.86	59.1	−56.9
3	4.16	23.8	−20.6	3.23	122.6	−126.6
4	3.097	152.2	154.9	2.442	19.3	−13.3
5	2.459	14.4	−9.7	1.936	84.4	87.9
6	2.059	81.8	−76.6	1.603	31.3	31.9
7	1.766	43.7	43.2	1.379	67.3	−69.4
8	1.544	44.9	42.1	1.204	30.9	35.9
9	1.376	41.2	−43.6			
10	1.239	40.1	36.3			

	Heated at 800°C			Rehydrated		
00l	d (Å)	|Fo|	Fc	d (Å)	|Fo|	Fc
1	9.89	45.9	−36.3	12.66	95.7	−92.4
2	4.90	63.1	−57.8	6.27	49.2	−44.9
3	3.25	149.1	−147.9	4.18	16.1	−19.0
4	2.442	19.5	21.7	3.116	168.9	166.3
5	1.951	64.7	74.0	2.495	19.2	−26.5
6	1.622	44.6	44.1	2.074	48.9	−57.8
7	1.389	75.1	−76.4	1.775	24.0	27.2
8	1.228	39.0	44.9	1.551	40.1	40.5
9				1.382	56.6	−54.3
10				1.249	36.8	45.4

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

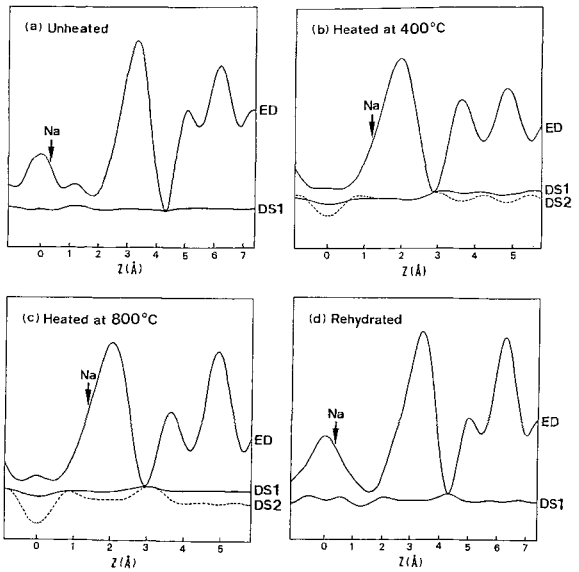


Figure 5. Electron density distribution and difference synthesis curves for Na-saturated beidellites. (a) unheated, (b) heated at 400°C, (c) heated at 800°C, and (d) rehydrated after heating at 800°C; ED = electron density distribution; DS1 = difference synthesis calculated by using Z-parameters obtained by refinement; DS2 = difference synthesis calculated by assuming that interlayer Na^+ ions are located at center of interlayer space.

sure for 1 day, whereas the K-saturated specimen showed a rapid rehydration and rehydrated completely on exposure within about 20 min. These results strongly indicate that the K- and Mg-saturated beidellite samples rehydrated rapidly and slowly, respectively, in agreement with those reported for homoionic rectorites by Kawano and Tomita (1989a).

Behavior of interlayer cation during dehydration and rehydration

The positions of interlayer cations for four different states of Na-saturated specimens, i.e., (1) unheated, (2) heated at 400°C, (3) heated at 800°C, and (4) rehydrated after heating at 800°C, were examined by means of one-dimensional Fourier analysis. The d-values of the basal reflections (Table 1) show a rational series, indicating that the specimens exhibited hydrated homogeneously. The electron density distribution (ED) and difference synthesis (DS) curves calculated by using ten reflections of unheated and rehydrated specimens and eight reflections of heated specimens are shown in Figure 5a to 5d. The ED curve of the unheated specimen has a broad peak in the interlayer region due to the interlayer Na^+ ions and water molecules. After refinement of the Z-parameters, the position of interlayer Na^+ ions was determined as shown in Figure 5a. Note that the DS curve shows a nearly flat line, suggesting that the interlayer Na^+ ions of the unheated specimen were located at very close to the center of the interlayer space. As for the specimen heated at 400°C, the DS curves (DS2 in Figure 5b) calculated by keeping the position of interlayer Na^+ ions fixed at the center of the interlayer space show a negative peak in interlayer region. The position of interlayer Na^+ ions, however, was determined to be near the basal oxygen plane by refinement of all atomic positions.

The negative peak of the DS curve was also reduced significantly (DS1 in Figure 5b) if it was calculated using the refined parameters. The DS curve (DS2 in Figure 5c) of the specimen heated at 800°C, calculated by fixing the interlayer Na^+ ions at the center of the interlayer space, showed a negative peak in interlayer region, also suggesting that the interlayer Na^+ ions were located at other positions instead of interlayer space. The DS curve (DS1 in Figure 5c), calculated using the refined structure, is considerably improved, suggesting that the interlayer Na^+ ions apparently migrated into hexagonal holes of the silicate layers and were located in deeper parts of the holes, compared with the specimen heated at 400°C. For the rehydrated specimens heated to 800°C, a large electron density was observed in the interlayer region of the ED curve, and the interlayer Na^+ ions were found to be as shown in Figure 5d. Pezerat and Méring (1967) reported one-dimensional Fourier synthesis curves of hydrated and dehydrated Na-saturated montmorillonites calculated by using 18 and 14 reflections, respectively. A positive peak due to the interlayer Na^+ ions was clearly present

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near the surface of the basal oxygen plane. Inasmuch as only ten or eight reflections were used in the present study, a significant positive peak due to Na^+ ions was not recognized in the ED curves. The position of the ions, however, could be definitely determined by least squares refinement. Insofar as the behavior of the interlayer Na^+ ions during dehydration and rehydration is concerned, these results suggest that the Na^+ ions apparently migrated from the interlayer space toward hexagonal holes of silicate layers during thermal dehydration and returned to the interlayer space on rehydration.

Structural rearrangement after dehydroxylation

The ED curve (Figure 5c) for the specimen heated at 800°C shows an increase in electron density near the octahedral cations and a decrease near the octahedral oxygens and hydroxyl ions, compared with that of the specimen heated at 400°C (Figure 5b). Similar results were also reported for sericite by Udagawa (1955), for muscovite by Eberhart (1963), for pyrophyllite by Wardle and Brindley (1972), for rectorite by Kawano and Tomita (1989a), and for montmorillonite by Kawano and Tomita (1989b). These observations have been explained as the removal of hydroxyl ions as H_2O and the relocation of residual oxygens to the same level as that of octahedral cations, as follows; $2OH^- \rightarrow H_2O + O^{2-}$. Although the detailed dehydroxylated structure is uncertain, two types of rearranged octahedral configurations may be present; a six-fold coordination octahedron (Grim and Bradley, 1948; Bradley and Grim, 1951) and a five-fold coordination octahedron (Wardle and Brindley, 1972).

DISCUSSION

Rehydration properties of beidellite and montmorillonite

The rehydration characteristics of homoionic (saturated with Ca^{2+}, Mg^{2+}, Na^+, or K^+) beidellites are: (1) the existence of strong rehydration tendency and (2) rehydration rates in the following order; $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$.

The dioctahedral smectite from Aterasawa, Yamagata Prefecture, Japan, having an intermediate composition between montmorillonite and beidellite, showed a lesser rehydration tendency than the present beidellite; i.e., the irreversible dehydration temperatures of Mg-, Ca-, Na-, and K-saturated specimens were 400°, 700°, 700°, and 900°C, respectively (Kawano and Tomita, 1989b). The Cheto montmorillonite had an appreciably weaker rehydration ability than the smectite from Aterasawa and the present beidellite (Figure 2). These results suggest that the rehydration abilities of dioctahedral smectite increased with decreasing octahedral negative charge. The rehydration ability of each homoionic smectite was greatest for the K-saturated material and smallest for the Mg-saturated material. Thus, the rehydration of dioctahedral smectite was also apparently strongly dependent on the size of the interlayer cations ($K^+ > Na^+ > Ca^{2+} > Mg^{2+}$, instead of their hydration energies ($Mg^{2+} > Ca^{2+} - Na^{2+} > K^+$; Rosseinsky, 1965), as well as on octahedral negative charge density.

Interpretation of rehydration mechanism of beidellite

The rehydration of smectite group minerals involves a re-coordination of water molecules to the dehydrated interlayer cations. Therefore, the behavior of the interlayer cations during dehydration and rehydration is significant in elucidating the rehydration mechanism of smectites. On the basis of Fourier analysis of the Na-saturated beidellite, the interlayer Na^+ ions migrated from interlayer space to shallow parts of the hexagonal holes on heating at 400°C and moved deeper into the holes on heating at 800°C. Thus, the interlayer Na^+ ions behaved similarly during dehydration to montmorillonite (Kawano and Tomita, 1989b). Significant differences in rehydration abilities of these minerals, however, were recognized, as mentioned above.

The negative layer charge of beidellite originates mainly from the tetrahedral sheets; the octahedral sheets are almost electrically neutral. This crystallochemical feature of beidellite seems to affect the behavior of the interlayer cations. Namely, no attractive electrostatis force exists between the octahedral sheets and the migrated interlayer cations. Migrated interlayer cations can therefore easily be extracted from the hexagonal holes and rehydration can then occur rapidly. For montmorillonite, however, the migrated interlayer cations are strongly attracted to the octahedral sheets, because the negative layer charge of montmorillonite originates mainly from substitution of Mg^{2+} for Al^{3+} in the octahedral sheets, thus, the migrated interlayer cations are easily fixed to the hexagonal holes. Consequently, the rehydration ability of beidellite is strong, but that of montmorillonite is weak.

The difference in rehydration rates of the homoionic beidellites is probably due to the sizes of saturating cations, rather than to their hydration energies. The small ionic radius of Mg^{2+} allows its easy migration into hexagonal holes, and the ion is fixed in the hexagonal holes. On the contrary, K^+ has large ionic radius, which makes its fixation difficult, and the ion can easily be extracted from the hexagonal holes. Accordingly, the rehydration rate of K-saturated beidellite is fast, whereas that of Mg-saturated beidellite is slow.

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