Hydrothermal synthesis of beidellite from aluminosilicate glass by varying water/solid ratio

Hirohisa YAMADA*, Katsuaki YOSHIOKA** and Hiromoto NAKAZAWA*

*National Institute for Research in Inorganic Materials, Namiki I, Tsukuba, Ibaraki, 305 JAPAN
**Nippon Paint Co., Ltd., Minamishinagawa 4-1-15, Shinagawa, Tokyo, 140 JAPAN

Abstract
Beidellite was synthesized from sodium aluminosilicate glass at a hydrothermal pressure of 100 MPa and at temperatures of 250, 300, 350, 400 and 450°C. The initial water/solid ratio of the starting materials was varied in the range 0.155 to 2.17. The run products were analyzed by the powder X-ray diffraction (XRD) method. Correlations among the water/solid ratio, temperature of synthesis, yield of beidellite and its crystallinity indicated: (1) Amount of water intercalated in the structure was limited to three layers even in water-excess condition of synthesis at high pressure and temperature. (2) Beidellite, crystallized from glass by hydration, was in the form of a two-dimensional flake. The dimensions and thickness of a flake were independent of the temperature of synthesis and the water/solid ratio, and were not increased by further hydration.

Introduction
It is evident that smectite could not be crystallized without water, and that water is one of the essential constituents in smectite. On the other hand, water is easily intercalated between the layers of smectite. In other words, water cleaves and dissociates the structural units of smectite. Therefore the role of water in the formation of smectite is conflicting and has not been yet determined. Most of the previous hydrothermal experiments for smectite were carried out in water-excess conditions (Koizumi and Roy, 1959; Iiyama and Roy, 1963; Eberl and Hower, 1977; Suquet et al., Eberl, 1978). Beidellite is known to have better crystallinity and better morphology in comparison with other smectites (Güven and Pease, 1975; Güven et al., 1977), and in this experiment, we have attempted to elucidate the role of water in the synthesis. Synthesis of beidellite was performed under hydrothermal conditions, varying the initial water/solid ratio. The crystallinity and the productivity of beidellite were investigated in relation to the water content. The results were, furthermore, compared with the previous results obtained for the montmorillonite –H₂O system (Nakazawa et al., 1991).
Experimental

Starting material and hydrothermal synthesis

A mixture of Na₂CO₃, Al₂O₃ and SiO₂ in the stoichiometric dehydroxylated Na-beidellite composition, Na₀.₆₆Al₄(Al₀.₆₆Si₇.₃₄)O₂₂, was fused using an infrared focussing-image furnace and quenched into water. The chemical composition of the quenched glass was determined by an electron microprobe analyzer (EPMA) to be Na₀.₆₆Al₄.₄₆Si₇.₄⁰O₂₂. The composition was slightly richer in SiO₂ and poorer in Al₂O₃ compared with that of the ideal one. The inhomogeneity of the glass was not detected by EPMA and was estimated to be less than 1%. The glass was pulverized in an alumina mortar with distilled water or ethyl alcohol. The crushed glass was fractionated to be <10 μm by hydraulic elutriation or by filtering with a 10 μm sieve. Two-hundred milligram lots of the fractionated glass (<10 μm) were sealed in Au-tube together with 30.9, 61.8, 113.4 and 422.6 mg of distilled water, respectively. Weight ratios of the water/solid were thus 0.155, 0.309, 0.567 and 2.113, respectively. If the glass were to react completely with the water to form beidellite, and the water were to be entirely spent as OH and as interlayer water, the following reaction should take place:

\[
\text{Na}_{0.66}\text{Al}_4(\text{Si}_{7.34}\text{Al}_{0.66})\text{O}_{22} + m\text{H}_2\text{O} \\
\rightarrow \text{Na}_{0.66}\text{Al}_4(\text{Si}_{7.34}\text{Al}_{0.66})\text{O}_{20}(\text{OH})_4\cdot n\text{H}_2\text{O}
\]  \hspace{1cm} (1)

where \( n = m - 2 \). If this assumption is true, the amount of water in the starting materials of different water/solid ratios corresponds to \( n = 4, 10, 20 \) and 80, for the chemical formula in equation (1). The \( n \)-value is used hereafter to indicate water content of both starting mixtures and run products. The four charges with different \( n \)-values were treated simultaneously in each experiment, using a rapid-quench type hydrothermal apparatus (Yamada et al., 1988). The experiments were carried out at temperatures from 250°C to 450°C under a pressure of 100 MPa and for a duration of 7 days. After quenching, the run products were examined by powder X-ray diffraction method.

Characterization by powder X-ray diffraction (XRD)

A well known characteristic of smectite is that its interlayer spacing is a function of the relative humidity of the atmosphere. The basal spacing of the heidellite samples at the growth condition and that in the open air are assumed to be different because of completely different environments. The XRD pattern of the 001 reflection of each run product was, therefore, recorded as quickly as possible after quenching and opening of the capsule to observe the initial state of the sample. For this, the product was not pulverized finely but mounted on a sample holder and flattened by a microspurtle.

For more quantitative observation by XRD, the sample was dried in a desiccator with silica gel for 7 days after pulverizing in an alumina mortar. A 30 mg portion of the sample was mounted on a quartz plate of an off-Bragg cut, without compression,
to avoid the influence of preferred orientation. The powder X-ray diffraction intensities of 001 and 11,02 reflections were then measured by the planimetry of their diffraction profiles recorded. The ethylene glycolated samples were also examined by XRD method; the products were oriented using water on a slide glass, and then placed in a sealed container with ethylene glycol, and heated in an oven at 60°C for more than 16 h. The samples were further investigated by the so-called "Greene-Kelly test" (Greene-Kelly, 1953; Lim and Jackson, 1986); 50 mg of each product was put into a test tube and then washed 3 times with aqueous 1 M LiCl and 3 times with 80% ethanol. A Li-exchanged sample was then placed on a gold plate and heated overnight at 300°C in a furnace. The sample was cooled, pulverized, spread out on a slide, placed in a sealed glass container with glycerol, and heated in an oven at 90°C for more than 16 h. The sample was then examined by XRD.

Results

*Phases synthesized by hydrothermal runs*

Run products identified by XRD are summarized in Table 1. The variations of phases were independent on the initial water/solid ratio of starting materials but were dependent on the temperature of synthesis. In the temperature range from 300°C to 400°C, a single phase of beidellite was formed, of which the (001) spacing expanded to about 17 Å with ethylene glycol and to 18 Å after the Greene-Kelly test (Fig. 1b). The integrated intensity of hk-bands is larger than that of synthetic montmorillonite, but the full width at half maximum intensity (FWHM) is the same as that of the montmorillonite (Nakazawa et al., 1991). The crystallinity and yield of beidellite, which are discussed in detail later, were dependent on both the initial water/solid ratio and temperature. At 250°C, beidellite coexisted with kaolinite and an amorphous phase (Fig. 1a). At 450°C, Na-rectorite (regularly interstratified paragonite/beidellite) and dioctahedral smectite with octahedral charge (DSm(M)) coexisted with silica minerals (cristobalite and quartz). The characterization of Na-rectorite is as follows: The d-spacing of the 001 reflection was about 27 Å for a glycolated sample (EG) and was about 28 Å after the Greene-Kelly test (GK) (Fig. 1c). This is explained by the regular stacking of beidellite (17 Å for EG, 18 Å for GK) and nonexpandable mica layer (10 Å for EG and GK). DSm(M) has the following characteristics: The basal spacing expanded to 17 Å for EG, shrank to 9.6 Å for GK and the d(06) was 1.49 Å. These features indicate that this phase is a dioctahedral smectite having octahedral charges, and that it shows the same swelling behaviour as that of montmorillonite. The chemical composition of the smectite is Mg-free and is thus Al-rich as compared with that of ideal montmorillonite.

The colour of the products was mostly white, as expected from the chemical composition. However, some samples synthesized from starting glass which was
Hydrothermal synthesis of beidellite

TABLE 1. Phases identified in hydrothermal products.

<table>
<thead>
<tr>
<th>Temp.(°C)</th>
<th>n</th>
<th>Run Products*</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>4</td>
<td>Beid, Kaol, Amor</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>Beid, Kaol, Amor</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>Beid, Kaol, Amor</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>Beid, Kaol, Amor</td>
</tr>
<tr>
<td>300</td>
<td>4</td>
<td>Beid</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>Beid</td>
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<tr>
<td>20</td>
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<td>Beid</td>
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<td>80</td>
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<td>Beid</td>
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<tr>
<td>350</td>
<td>4</td>
<td>Beid</td>
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<td>10</td>
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<tr>
<td>20</td>
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<td>Beid</td>
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<tr>
<td>80</td>
<td></td>
<td>Beid</td>
</tr>
<tr>
<td>400</td>
<td>4</td>
<td>Beid</td>
</tr>
<tr>
<td>10</td>
<td></td>
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<tr>
<td>20</td>
<td></td>
<td>Beid</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>Beid</td>
</tr>
<tr>
<td>450</td>
<td>4</td>
<td>Beid, DSm(M), Crist, Qtz</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>Na-rect, DSm(M), Crist, Qtz</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>Na-rect, DSm(M), Crist, Qtz</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>Na-rect, DSm(M), Crist, Qtz</td>
</tr>
</tbody>
</table>

*Abbreviations used, Beid: beidellite, Na-rect: Na-rectorite (regularly interstratified paragonite and beidellite), DSm(M): dioctahedral smectite with octahedral charge, Kaol: kaolinite, Amor: amorphous material, Crist: cristobalite, Qtz: quartz.

pulverized and filtered with ethyl alcohol, were light bluish purple; the depth of this colour decreased with an increase in water content. The XRD pattern indicated no difference with white smectite. Therefore the colour may be due to some organic impurities formed from the alcohol, as will be discussed elsewhere.

**Basal spacing of quenched beidellite**

The product synthesized at a high water/solid ratio of n = 80 was found to coexist with free water (ph = 7). Those of n = 20 seemed to be wet and those of n < 20 seemed to be rather dry. XRD patterns of 001 reflection of beidellite synthesized at temperatures of 350°C and 400°C are shown in Fig. 2. As described before, the patterns were obtained as soon as possible after quenching and opening of the capsules. The d(001) spacing, which is an indicator of the number of water-layers, appears to be a function of the initial water/solid ratio of the starting material. As the initial water/solid ratio increased, the number of water-layers was changed from one (n = 4) to three (n = 80). An interesting
observation was that the number of water layers was limited to three, and such beidellite coexisted with free water. After the samples were dried in a desiccator with silica gel for 7 days, the 001 reflection of all samples was changed to sharp single-peak corresponding to the interlayer distance of one water-layer. When the samples were left in the open air, the d(001) varied depending on the relative humidity (a phenomenon which is usually experienced – See Fig. 2, dashed line). Therefore a broadening of the 001 reflections, as seen in Fig. 2, is reasonably interpreted as being due to a transitional state of hydration from that at the synthesis to that at the XRD measurement in the open air. The observed d-spacings of quenched samples, thus, indicate the number of water-layers in the “as-grown” beidellite. Similar observations were made for montmorillonite (Nakazawa et al., 1991).

**Water content dependency of productivity and crystallinity of beidellite**

The X-ray intensities of 001 and 11,02 reflections of beidellite are plotted against the water contents of starting mixtures in terms of mole fraction, n (Fig. 3). Because the products synthesized at temperatures of 250°C and 450°C coexisted with other phases, they are excluded from Fig. 3. The yield of beidellite, evaluated by integrated intensities, is obviously dependent on the temperature of synthesis; indicating the reaction kinetics from glass to beidellite. The n-value dependency of the productivity is observed in the low water content region (n <10), but the productivity is almost constant in the high
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**Fig. 2.** X-ray powder diffraction patterns of the 001 reflection recorded as soon as possible after quenching (solid line) and recorded after keeping it in open air for a long time (dashed line): (a) samples synthesized at 350°C and (b) at 400°C.

The FWHMs of 001 and 01,22 reflections of the run products, i.e. those normal and parallel to 2:1 layer, are shown against the water content of starting materials in Fig. 4. The crystallinity, estimated from the FWHMs normal and parallel to (001), are almost independent on both the n-value and the temperature of synthesis.

**Discussion**

*Maximum hydration state of beidellite at high temperature and high pressure*

The amount of intercalated water in beidellite at high pressure and high temperature can be estimated from the basal spacing of quenched samples recorded as soon as possible after quenching and opening of the capsule (Nakazawa et al., 1991). According to the present result, beidellite with three water layers coexists with free water in a water-excess
condition \( n = 80 \). This result is not consistent with the swelling behaviour of Na-smectite at ambient conditions. When Na-smectite swells with the water of \( n = 80 \), the d(001) spacing is about 40 Å (Norrish, 1954; Fukushima, 1984). The coexistence of free water and beidellite with three water-layers indicates, therefore, that the swelling behaviour at high pressure and high temperature is different to that at ambient conditions, and the maximum hydration state of beidellite in three water-layers. Beidellites with one and two water-layers were observed for synthesis with low water content. When the samples are in open air, the amount of intercalated water changes easily depending on relative humidity (Fig. 2). The fact that the swelling of beidellite at high P,T is not infinite demonstrates that this swelling is not an osmotic one, but beidellite rather seems to have respective numbers of water-layers corresponding to the pressure-temperature conditions. This interpretation is consistent with the result by Colten (1986), who observed
montmorillonite intercalated two water-layers in an in-situ experiment at 45 MPa and 200°C, and also consistent with the previous observations on montmorillonite (Nakazawa et al., 1991).

**Formation mechanism of beidellite from glass**

Comparison of the FWHMs of 001 and 11,02 reflections, i.e. those normal and parallel to 2:1 layer, indicates that beidellite initially synthesized from glass is a thin flake, whose geometry is quite stable within a broad range of synthesis temperatures and water/solid ratios (Fig. 4). On the other hand, the productivity of beidellite from glass increases for a water content less than \( n = 10 \), but is saturated above this value. The temperature of synthesis is also a parameter for the increase of beidellite formation (Fig. 3). These observations leads to the conclusion that the size and thickness of a two-dimensional flake of beidellite is not increased by the maturity of beidellite formation and that the increase in the productivity is due to an increase in the number of thin flakes.

The phenomena that the thin crystal does not grow but that the number of crystallites increases, are not explained by the mechanism of precipitation from hydrothermal solution. This is probably explained by the mechanism of the hydration reaction of glass. This process is analogues to a model for formation of hydrous melt by mixing of \( \text{H}_2\text{O} \) and silicate melts (Burnham, 1975).

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**References**


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