# HYDROTHERMAL SYNTHESIS OF AMMONIUM-BEIDELLITE

Key Words--Ammonium-beidellite, Hydrothermal synthesis, X-ray powder diffraction.

Hydrothermally synthesized smectites like beidellite (Plee *et al* 1987, Schutz *et al* 1987, Kloprogge *et al*  1990a, 1990b) and saponite (Suquet *et al* 1977, Kloprogge *et al* 1993a) are receiving increasing interest because of their high purity and their possible application as catalysts and molecular sieves. Highly acidic  $H<sup>+</sup>$ -smectites are usually prepared by heat or acid treatment of ammonium exchanged Na-smectites. An interesting new route would be the direct synthesis of ammonium-smectites. Recently, Kloprogge *et al*  (1993a) reported the hydrothermal preparation ofammonium-saponites from Si/Al/Mg gels and NH<sub>4</sub>OH solutions, without the conventional cation exchange techniques.

Beidellite with only tetrahedral A1-Si substitution and its corresponding acidity is therefore an interesting candidate to be synthesized in the ammonium-form. This note briefly describes the first laboratory experiments to synthesize ammonium-beidellite using urea  $(H, NCONH,$ ), glycine  $(H, NCH, CO, H)$ , ammoniumhydroxide (NH4OH), ammonium-chloride (NH4C1), and ammonium-aluminum-fluoride ( $[NH_4]_3AIF_6$ ) as ammonium sources. The  $[NH<sub>4</sub>]$ <sub>3</sub>AlF<sub>6</sub> was kindly supplied by P. J. Dirken, Dept. Geochemistry, Institute of Earth Sciences, State University of Utrecht, The Netherlands.

#### EXPERIMENTAL

#### *Materials and methods*

Si/AI gels containing 4.7 A1 per 7.3 Si were prepared according to the method of Hamilton and Henderson (1968). The syntheses were achieved after 7 days at 1 kbar pressure and a temperature of 250° or 350°C in a Tuttle-type, externally heated, cold seal pressure vessel, using gold capsules containing 50 mg gel and 50  $\mu$ l of one of the ammonium source solutions. No ammonium buffers were used as (e.g., Voncken *et a11987,*  1988) for the synthesis of buddingtonite and tobelite, an ammonium feldspar and ammonium mica respectively. After cooling, the samples were analyzed by  $X$ -ray diffraction  $(XRD)$  and Infrared spectroscopy  $(IR)$ . The final pH could not be determined due to the small amount of solution, which was completely adsorbed on the solid product.

## *Analytical techniques*

The X-ray powder diffraction patterns were recorded on a Philips PW 1050/25 diffractometer using *CuKa* 

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radiation. The scanning speed was  $1° 2 T$  min. The IR spectra were obtained on powdered samples in KBr tablets (sample concentration 1 wt %) using a Perkin Elmer 580 IR spectrophotometer.

#### RESULTS AND DISCUSSION

Table 1 summarizes all experiments performed and the phases observed. At 250°C most products are amorphous with only trace amounts of beidellite (E718-l) or kaolinite (E718-3). An exception is E725 containing the ammonium-aluminum-fluoride which resulted in the formation of trace amounts of ammonium-beidellite, ammonium-analcime, and  $NH<sub>4</sub>AlF<sub>4</sub>$  (Figure 1a). The large amount of amorphous material is thought to be due to the low temperature, in agreement with other observations (Kloprogge *et al* 1993b), that Na-beidellite,  $Na_{0.7}Al_{4.7}Si_{7.3}O_{20}(OH)_4 \cdot xH_2O$ , cannot be synthesized at 1 kbar at temperatures below 300°C. Therefore, additional experiments have been conducted at 350°C which is in the biedellite synthesis field (Kloprogge et al. 1993b). In all cases with alkaline solutions beidellite with a basal spacing between 10.5 and 10.8  $\AA$  is formed accompanied by ammonium-analcime (Figure lc). This indicates the formation of ammonium-analcime first incorporating all free  $NH<sub>4</sub>$ <sup>+</sup> before the beidellite starts to crystallize. In nature analcime,  $Na(AlSi, O_6) \cdot H_2O$ , is mostly a secondary mineral formed during late stage magmatic processes from alkaline fluids accompanying minerals like prehnite and zeolites in foid containing rock types. Furthermore it is a typical component of tuff-bearing alkaline saline lakes, mainly related to the brine composition (Deer *et al* 1992). Synthetic ammonium-analcime has been described by Barrer and Denny (1961). An exception is experiment E727-2 with an almost neutral pH, where only beidellite with a basal spacing of  $12.4$  Å is formed (Figure 1b). The presence of  $NH<sub>4</sub>$ <sup>+</sup> in the interlayer should result in a basal spacing near 12.4 A (Suquet *et al* 1977; Kloprogge *et al*  1993a) comparable to  $K^+$ . Saturation with ethylene glycol resulted in an expansion of the basal spacing to a value of approximately 17.0 A. Therefore, only the beidellite from E727-2 containing glycine is thought to be a real ammonium-beidellite. Glycine can be considered to be a zwitterion forming a  $H_3N^+CH_2COO^$ in solution reacting to  $NH<sub>4</sub><sup>+</sup> + HOCH<sub>2</sub>COO<sup>-</sup>$ . Hydroxy-acetic acid lowers the pH slightly and is a well known ligand for metals like Si forming stable fiverings (personal comment, K. Timmer), e.g.,



Figure 1. XRD patterns of a) E725: beidellite +  $NH<sub>4</sub>$ -analcime +  $NH<sub>4</sub>AlF<sub>4</sub>$ ; b) E727-2: ammonium beidellite and c) E726-1: beidellite + NH<sub>4</sub>-analcime. B = beidellite,  $A = am$ monium analcime,  $F = NH<sub>4</sub>AIF<sub>4</sub>$ .

$$
2 OCH_2COO^{2-} + Si^{4+} \rightarrow
$$

$$
O = C - O \t O - C = O
$$
  
\n| Si |  
\nH - C - O \t O - C - H  
\n| |  
\nH H H

The smaller basal spacings in the other experiments indicate the presence of  $H<sup>+</sup>$  instead. The use of  $[NH<sub>4</sub>]$ <sub>3</sub>AlF<sub>6</sub> and glycine results in the highest crystalline



Figure 2. IR spectra of E726-1: beidellite +  $NH<sub>4</sub>$ -analcime and E727-2: NH<sub>4</sub>-beidellite.

beidellite. In the first case it can be explained by the partial replacement of the clay hydroxyl groups by Ffollowing the breakdown reaction of  $[NH_4]_3AIF_6$ .  $NH<sub>4</sub>AlF<sub>4</sub> + 2F<sup>-</sup> + 2NH<sub>4</sub><sup>+</sup>$ . In the second case the lowering of the pH from near neutral to slightly acidic is thought to prohibit the formation of analcime resulting in the incorporation of the ammonium in the beidellite.

The infrared spectra (Figure 2) are not very informative due to overlap of the absorption maxima of the various phases present in each run. The  $NH<sub>4</sub>$  absorption maxima can easily be distinguished as a broad peak between  $33,240$  and  $3100$  cm<sup>-1</sup>, a shoulder at  $3020$  cm<sup>-1</sup> and a broad doublet at 1430 and 1400 cm<sup>-1</sup>. These values agree well with those observed for ammonium-saponite but are systematically shifted towards lower wavenumbers compared to tobelite, an ammonium-mica (Voncken *et al* 1987, Kloprogge *et al* 1993a). The NH4-beidellite sample E 727-2 shows a more distinct beidellite pattern in the range between 1100 and 400 cm<sup>-1</sup> with peaks at 1100, 1040, 938, 888, 810, 627, 537, and 480-465 cm<sup>-1</sup>, which agree well with the IR data of synthetic beidellite published by Kloprogge *et al* (1990a).

Table 1. Results and conditions of the experiments performed at 1 kbar.

Sample	T(C)	NH <sub>4</sub> source	pH (start)	Products
E718-1	250	urea (1 M)	9.27	trace beidellite $(10.4 \text{ Å})^1$ + amorphous
E718-2	250	<b>NH<sub>4</sub>OH</b> (25%)	14.12	amorphous
E718-3	250	$NHaCl$ (1 M)	5.60	trace kaolinite $+$ amorphous
E722-1	250	urea $(2 M)$	9.60	amorphous
E723	250	<b>NH<sub>4</sub>OH</b> (6.5%)	12.57	amorphous
E725	250	$[NH_4]_3AIF_6^2$		traces beidellite (10.3 Å), NH <sub>4</sub> -analcime, NH <sub>4</sub> AIF <sub>4</sub> + amorphous
E726-1	350	$[NH_4]_3AIF_6$	$\overline{\phantom{0}}$	beidellite (10.7 Å) + NH <sub>4</sub> -analcime
E726-2	350	urea $(1 M)$	9.27	beidellite (10.5 Å) + NH <sub>4</sub> -analcime
E726-3	350	NH <sub>4</sub> OH (6.5%)	12.57	beidellite (10.8 Å) + NH <sub>4</sub> -analcime
E727-2	350	glycine $(2 M)$	6.84	beidellite $(12.4 \text{ Å})$

<sup>1</sup> Numbers in parentheses represent the basal spacing observed by XRD.

2 Only slightly soluble in water.

## **CONCLUSIONS**

Hydrothermal treatment at 250°C does only succeed in the crystallization of  $H<sup>+</sup>$ -beidellite when using urea or  $[NH_4]_3$ AlF<sub>6</sub>. Increasing the temperature to 350°C results first in the formation of ammonium-analcime followed by  $H<sup>+</sup>$ -beidellite. The high crystallinity of the beidellite in the  $[NH_4]_3AIF_6$  experiments can be explained by the incorporation of fluor at hydroxyl sites. the formation of  $NH<sub>4</sub>$ -beidellite in the glycine experiment is explained by the slightly acidic fluid prohibiting analcime formation.

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