

## 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, Klopogge *et al* 1990a, 1990b) and saponite (Suquet *et al* 1977, Klopogge *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, Klopogge *et al* (1993a) reported the hydrothermal preparation of ammonium-saponites from Si/Al/Mg gels and NH<sub>4</sub>OH solutions, without the conventional cation exchange techniques.

Beidellite with only tetrahedral Al-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<sub>2</sub>NCONH<sub>2</sub>), glycine (H<sub>2</sub>NCH<sub>2</sub>CO<sub>2</sub>H), ammonium-hydroxide (NH<sub>4</sub>OH), ammonium-chloride (NH<sub>4</sub>Cl), and ammonium-aluminum-fluoride ([NH<sub>4</sub>]<sub>3</sub>AlF<sub>6</sub>) 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/Al gels containing 4.7 Al 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 μl of one of the ammonium source solutions. No ammonium buffers were used as (e.g., Voncken *et al* 1987, 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 CuKα

radiation. The scanning speed was 1° 2 θ 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 (E718-1) 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 (Klopogge *et al* 1993b), that Na-beidellite, Na<sub>0.7</sub>Al<sub>4.7</sub>Si<sub>7.3</sub>O<sub>20</sub>(OH)<sub>4</sub>·xH<sub>2</sub>O, cannot be synthesized at 1 kbar at temperatures below 300°C. Therefore, additional experiments have been conducted at 350°C which is in the beidellite synthesis field (Klopogge *et al* 1993b). In all cases with alkaline solutions beidellite with a basal spacing between 10.5 and 10.8 Å is formed accompanied by ammonium-analcime (Figure 1c). 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<sub>2</sub>O<sub>6</sub>)·H<sub>2</sub>O, 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 Å (Suquet *et al* 1977; Klopogge *et al* 1993a) comparable to K<sup>+</sup>. Saturation with ethylene glycol resulted in an expansion of the basal spacing to a value of approximately 17.0 Å. 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<sub>3</sub>N<sup>+</sup>CH<sub>2</sub>COO<sup>-</sup> 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 five-rings (personal comment, K. Timmer), e.g.,



## CONCLUSIONS

Hydrothermal treatment at 250°C does only succeed in the crystallization of H<sup>+</sup>-beidellite when using urea or [NH<sub>4</sub>]<sub>3</sub>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<sub>4</sub>]<sub>3</sub>AlF<sub>6</sub> 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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