Clays and Clay Minerals, Vol. 43, No. 1, 135–137, 1995.

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^+-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 of ammonium-saponites from Si/Al/Mg gels and NH_4OH 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_2NCONH_2), glycine ($H_2NCH_2CO_2H$), ammonium-hydroxide (NH_4OH), ammonium-chloride (NH_4Cl), and ammonium-aluminum-fluoride ($[NH_4]_3AlF_6$) as ammonium sources. The $[NH_4]_3AlF_6$ 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 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 (E718-1) 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_4AlF_4 (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 Å is formed accompanied by ammonium-analcime (Figure 1c). This indicates the formation of ammonium-analcime first incorporating all free NH_4^+ before the beidellite starts to crystallize. In nature analcime, $Na(AlSi_2O_6) \cdot H_2O$, 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_4^+ in the interlayer should result in a basal spacing near 12.4 Å (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 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 $H_3N^+CH_2COO^-$ in solution reacting to $NH_4^+ + HOCH_2COO^-$. 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.,

Copyright © 1995, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1995.0430117 Published online by Cambridge University Press

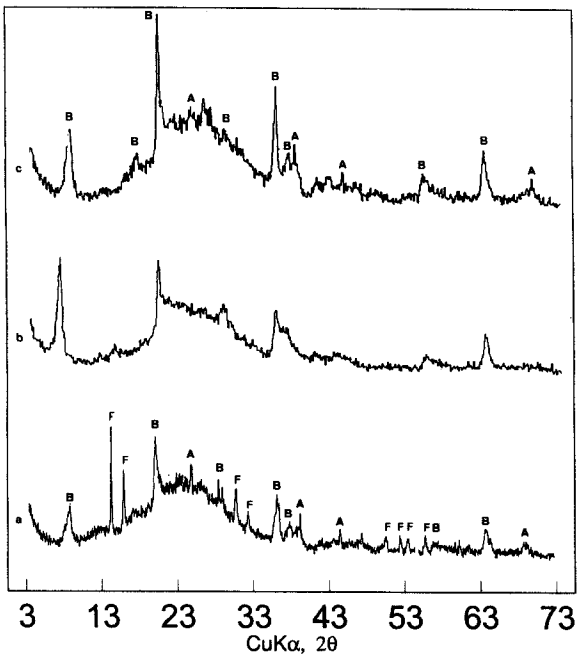
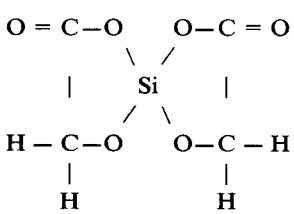


Figure 1. XRD patterns of a) E725: beidellite + NH_4-analcime + NH_4AlF_4; b) E727-2: ammonium beidellite and c) E726-1: beidellite + NH_4-analcime. B = beidellite, A = ammonium analcime, F = NH_4AlF_4.

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



The smaller basal spacings in the other experiments indicate the presence of H^+ instead. The use of $[NH_4]_3AlF_6$ and glycine results in the highest crystalline

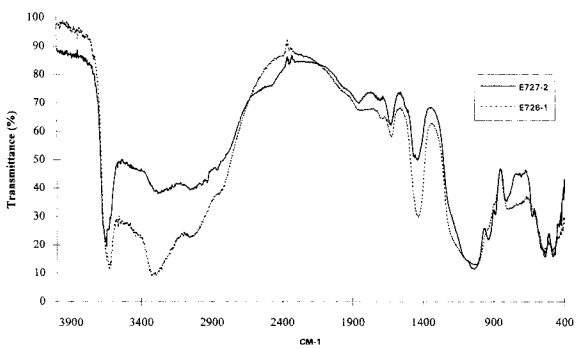


Figure 2. IR spectra of E726-1: beidellite + NH_4-analcime and E727-2: NH_4-beidellite.

beidellite. In the first case it can be explained by the partial replacement of the clay hydroxyl groups by F^- following the breakdown reaction of $[NH_4]_3AlF_6$ – $NH_4AlF_4 + 2F^- + 2NH_4^+$. 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_4 absorption maxima can easily be distinguished as a broad peak between 33,240 and 3100 cm^{-1}, a shoulder at 3020 cm^{-1} and a broad doublet at 1430 and 1400 cm^{-1}. 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 NH_4-beidellite sample E 727-2 shows a more distinct beidellite pattern in the range between 1100 and 400 cm^{-1} with peaks at 1100, 1040, 938, 888, 810, 627, 537, and 480–465 cm^{-1}, 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_4 source	pH (start)	Products
E718-1	250	urea (1 M)	9.27	trace beidellite (10.4 Å)[1] + amorphous
E718-2	250	NH_4OH (25%)	14.12	amorphous
E718-3	250	NH_4Cl (1 M)	5.60	trace kaolinite + amorphous
E722-1	250	urea (2 M)	9.60	amorphous
E723	250	NH_4OH (6.5%)	12.57	amorphous
E725	250	$[NH_4]_3AlF_6$[2]	—	traces beidellite (10.3 Å), NH_4-analcime, NH_4AlF_4 + amorphous
E726-1	350	$[NH_4]_3AlF_6$	—	beidellite (10.7 Å) + NH_4-analcime
E726-2	350	urea (1 M)	9.27	beidellite (10.5 Å) + NH_4-analcime
E726-3	350	NH_4OH (6.5%)	12.57	beidellite (10.8 Å) + NH_4-analcime
E727-2	350	glycine (2 M)	6.84	beidellite (12.4 Å)

[1] Numbers in parentheses represent the basal spacing observed by XRD.
[2] Only slightly soluble in water.

https://doi.org/10.1346/CCMN.1995.0430117 Published online by Cambridge University Press

CONCLUSIONS

Hydrothermal treatment at 250°C does only succeed in the crystallization of H^+-beidellite when using urea or $[NH_4]_3AlF_6$. Increasing the temperature to 350°C results first in the formation of ammonium-analcime followed by H^+-beidellite. The high crystallinity of the beidellite in the $[NH_4]_3AlF_6$ experiments can be explained by the incorporation of fluor at hydroxyl sites. the formation of NH_4-beidellite in the glycine experiment is explained by the slightly acidic fluid prohibiting analcime formation.

TPD-TNO, Department of J. T. KLOPROGGE
Inorganic Materials Chemistry
P.O. Box 595, 5600 AN Eindhoven
The Netherlands

Department of R. VOGELS
Inorganic Chemistry
Heterogeneous Catalysis
Utrecht University
P.O. Box 80083, 3508 TB Utrecht, The Netherlands

REFERENCES

Barrer, R. M., and P. J. Denny. 1961. Hydrothermal chemistry of the silicates. Part IX. *J. Chem. Soc.* 971–982.

Deer, W. A., R. A. Howie, and J. Zussman. 1992. *An Introduction to the Rock-Forming Minerals.* Harlow, England: Longman Scientific & Technical, 696 pp.

Hamilton, D. L., and C. M. B. Henderson. 1968. The preparation of silicate compositions by a gelling method. *Mineral. Mag.* **36**: 832–838.

Kloprogge, J. T., J. B. H. Jansen, and J. W. Geus. 1990a. Characterization of synthetic Na-beidellite. *Clays & Clay Miner.* **38**: 409–414.

Kloprogge, J. T., A. M. J. van der Eerden, J. B. H. Jansen, and J. W. Geus. 1990b. Hydrothermal synthesis of Na-beidellite. *Geologie & Mijnbouw* **69**: 351–357.

Kloprogge, J. T., J. Breukelaar, J. B. H. Jansen, and J. W. Geus. 1993a. Development of ammonium-saponites from gels with variable ammonium concentration and water content at low temperatures. *Clays & Clay Miner.* **41**: 103–110.

Kloprogge, J. T., A. M. J. van der Eerden, J. B. H. Jansen, J. W. Geus, and R. D. Schuiling. 1993b. Synthesis and paragenesis of Na-beidellite as function of temperature, water pressure and sodium activity. *Clays and Clay Miner.* **41**: 423–430.

Plee, D., L. Gatineau, and J. J. Fripiat. 1987. Pillaring processes of smectites with and without tetrahedral substitution. *Clays & Clay Miner.* **35**: 81–88.

Schutz, A., W. E. E. Stone, G. Poncelet, and J. J. Fripiat. 1987. Preparation and characterization of bidimensional zeolitic structures obtained from synthetic beidellite and hydroxy-aluminum solutions. *Clays & Clay Miner.* **35**: 251–261.

Suquet, H., J. T. Iiyama, H. Kodama, and H. Pezerat. 1977. Synthesis synthesis and swelling properties of saponites with increasing layer charge. *Clays & Clay Miner.* **25**: 231–242.

Voncken, J. H. L., R. J. M. Konings, J. B. H. Jansen, and C. F. Woensdregt. 1988. Hydrothermally growth buddingtonite, an anhydrous ammonium feldspar. *Phys. Chem. Miner.* **15**: 323–328.

Voncken, J. H. L., J. M. A. R. Wevers, A. M. J. van der Eerden, A. Bos, and J. B. H. Jansen. 1987. Hydrothermal synthesis of tobelite, $NH_4Al_2Si_3O_{10}(OH)_2$, from various starting materials and implications for its occurrence in nature. *Geologie & Mijnbouw* **66**: 259–269.

(*Received 7 June 1994; accepted 16 September 1994; Ms. 2514*).

https://doi.org/10.1346/CCMN.1995.0430117 Published online by Cambridge University Press