*Geologie en Mijnbouw* **69**: 351–357, 1990.

# Hydrothermal synthesis of Na-beidellite

J. Theo Kloprogge[1], Ad M.J. van der Eerden[1], J. Ben H. Jansen[1] & John W. Geus[2]
*[1] Department of Geochemistry, Institute of Earth Sciences, University of Utrecht, Budapestlaan 4, P.O. Box 80.021, 3508 TA Utrecht, The Netherlands; [2] Department of Inorganic Chemistry, Analytical Chemical Laboratory, University of Utrecht, Croesestraat 77a, 3522 AD Utrecht, The Netherlands*

Received 21 November 1989; accepted in revised form 28 February 1990

*Key words:* Na-beidellite, hydrothermal synthesis

## Abstract

Na-beidellite was hydrothermally synthesized using various starting materials at a range of P-T conditions. The best crystallized Na-beidellite was carefully investigated with XRD, SEM, TGA, MAS-NMR and IR-spectroscopy. Cell parameters are: a = 5.18 ± 0.005 Å; b = 8.96 ± 0.008 Å; c = 12.54 ± 0.011 Å; V = 581.9 ± 0.5 Å$^3$. Indexing is based on an orthorhombic cell. $^{29}$Si MAS-NMR reveal three peak positions: − 92.7 ppm (Si-OAl); − 88.4 ppm (Si-1Al); − 82.3 ppm (Si-2Al), indicating an Al$^{IV}$/Si ratio of 0.106 per unit cell. The presence of small amounts of F in the hydrothermal fluid causes a significant increase in crystallinity. Na-beidellite is the only crystalline product applying a starting gel of composition $Na_{0.7}Al_{4.7}Si_{7.3}O_{22}$. A $Na_{1.0}Al_{5.0}Si_{7}O_{22}$ gel results in Na-beidellite + paragonite and gels with higher Na content produce only paragonite.

## Introduction

The name Beidellite was given by Larsen & Wherry (1925) to a clay specimen from Beidell, Colorado, which they had earlier described as leverrierite (Larsen & Wherry 1917). Nowadays Beidellite is defined as a dioctahedral Al-smectite (Ross & Hendricks 1945, Weir & Greene-Kelly 1962) with the formula $(0.5Ca,Na,K)_p(Al^{VI})_4Si_{8-p}(Al^{IV})_pO_{20}(OH)_4.nH_2O$. Natural Beidellite exhibits an average layer charge (p) of 0.66, which represents the amount of Al$^{IV}$.

Smectites have received much attention due to their swelling behaviour in water and the possibility to form pillared clays with organic and inorganic complexes (Loeppert et al. 1979, Plee et al. 1987, Sterte & Shabtai 1987, Kloprogge et al. 1990). These pillared clays can be used as molecular sieves and catalysts in e.g. oil cracking reactions, comparable with the use of synthetic zeolites. However, natural smectites exhibit unreliable quality and large variation in impurity content. Therefore, hydrothermal synthesis has been attempted in recent years (Torii & Iwasaki 1986, 1987, Plee et al. 1987, Schutz et al. 1987).

In this paper we present results on the hydrothermal synthesis of Na-beidellite with a composition $Na_{0.7}Al_{4.7}Si_{7.3}O_{20}(OH)_4.nH_2O$ under a variety of conditions. The best crystallized samples were selected for characterization with XRD, IR, TGA, DTA, SEM and Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR).

## Starting materials and experimental methods

As starting material a Na-Al-Si gel with the required composition was prepared according to the method of Hamilton & Henderson (1968). The

*Table 1.* List of used chemicals

| | |
|---|---|
| $Na_2CO_3$ | Merck no. 6392 |
| $Al(NO_3)_3.9H_2O$ | Merck no. 1063 |
| TEOS $Si(OC_2H_5)_4$ | Merck-Schuchardt no. 800658 |
| Ethanol | Nedalco C.V. |
| NaOH | Merck no. 6498 |
| NaF | Merck no. 6449 |
| $H_2O$ | double distilled |

chemicals are listed in Table 1. The experiments were carried out in goldcapsules of 30 mm length and 2.4 mm internal diameter, placed in Tuttle-type, externally heated, cold-seal pressure vessels (Tuttle 1949) as described in detail by Bos et al. (1987) and Kloprogge et al. (1990).

X-ray powder diffraction patterns were recorded on a Philips PW 1050/25 diffractometer using Cukα radiation. Infrared absorption spectra were scanned on powdered samples in KBr tablets (1 wt% sample) with a Perkin Elmer 580 IR spectrophotometer. The morphology of the products was investigated with a Cambridge S150 scanning electron microscope. Thermogravimetrical analyses were made on a Dupont 1090 Thermal Analyzer. Chemical analyses were made on a JEOL JXA-8600 electron microprobe. $^{27}Al$ and $^{29}Si$ MAS-NMR spectra were recorded on a Bruker WM500 (11.7 Tesla) at the Department of Physical Chemistry, Faculty of Science, University of Nijmegen. Chemical shifts are reported in ppm relative to $[Al(H_2O)_6]^{3+}$ for $^{27}Al$ and to tetramethylsilane ($Me_4Si$) for $^{29}Si$.

## Results and discussion

### *Influence of temperature and pressure*

The experimental results under different conditions are summarized in Table 2. Variation in temperature indicates roughly four fields. At 250° C kaolinite is the only clay mineral formed, accompanied by a minor amount of quartz. The 300° C run represents a transition zone between the kaolinite and beidellite fields. At 350° C and 400° C beidellite is the predominant crystalline product. Higher temperature runs yielded beidellite accompanied by metastable $SiO_2$ in the form of cristobalite. In the beidellite field pressure can be as low as 200 bar

*Table 2.* Selected experimental results

| Run nr. | T (° C) | P (bar) | Run time (days) | Gel nr.[1] | Solution | Crystalline phases produced[2] |
|---|---|---|---|---|---|---|
| E520 | 250 | 1000 | 7 | 1 | $H_2O$ | Kaol + minor Qtz |
| E549 | 300 | 1000 | 7 | 1 | $H_2O$ | Beid + Kaol + minor Qtz |
| E432 | 350 | 1000 | 10 | 1 | $H_2O$ | Beid |
| E444 | 400 | 1000 | 10 | 1 | NaOH[3] | Beid + minor Qtz |
| E544 | 450 | 1000 | 7 | 1 | $H_2O$ | Beid + Crist + minor Qtz |
| E427 | 350 | 500 | 10 | 1 | $H_2O$ | Beid |
| E498 | 350 | 400 | 15 | 1 | $H_2O$ | Beid |
| E499 | 350 | 300 | 15 | 1 | $H_2O$ | Beid |
| E500 | 350 | 200 | 15 | 1 | $H_2O$ | Beid |
| E452 | 350 | 1000 | 10 | 1 | NaF/NaOH 0.2[3] | Beid |
| E453 | 350 | 1000 | 10 | 1 | NaF/NaOH 1.0[3] | Beid |
| E454 | 350 | 1000 | 10 | 1 | NaF[3] | Beid |
| E598 | 350 | 1000 | 7 | 2 | $H_2O$ | Beid + Par |
| E583 | 350 | 1000 | 7 | 3 | $H_2O$ | Par |
| E584 | 350 | 1000 | 7 | 4 | $H_2O$ | Par |

[1] Gel nr. 1 = $Na_{0.7}Al_{4.7}Si_{7.3}O_{22}$, 2 = $Na_{1.0}Al_{5.0}Si_{7.0}O_{22}$, 3 = $Na_{1.5}Al_{5.5}Si_{6.5}O_{22}$, 4 = $Na_{2.0}Al_{6.0}Si_{6.0}O_{22}$.

[2] Kaol = Kaolinite, Qtz = Quartz, Beid = Na-beidellite, Par = Paragonite.

[3] 0.01 Mol/l $Na^1$.

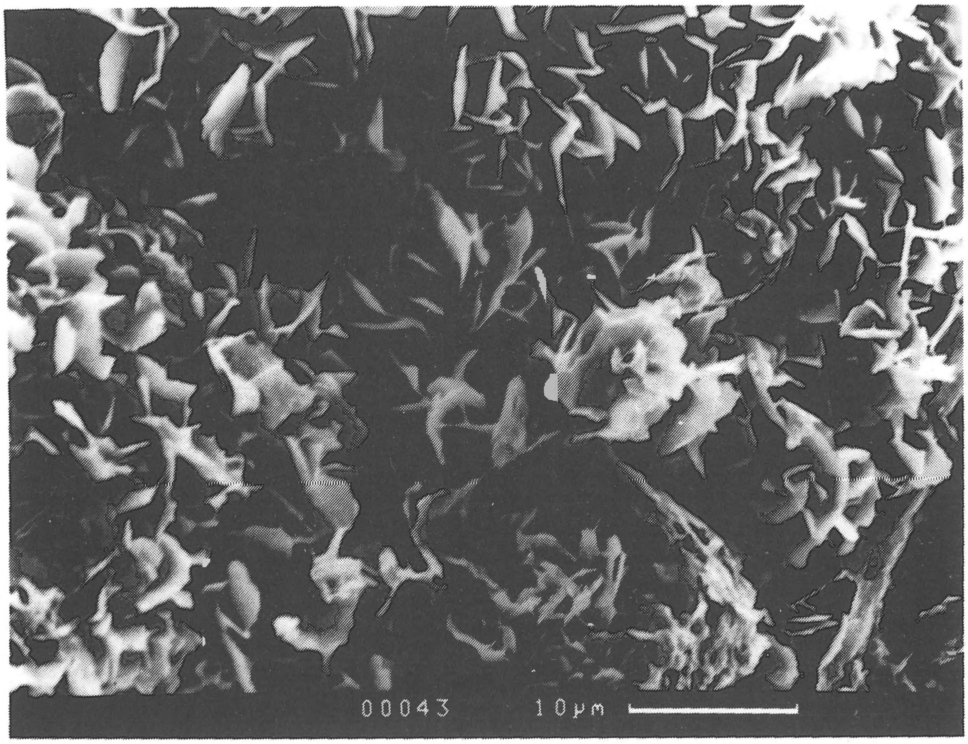

*Fig. 1.* Scanning electron microscope (SEM) photograph of Na-beidellite flakes.

without any change in crystallization. A more detailed investigation of the pressure/temperature influence on the stability of beidellite is in progress.

## Gel composition

The layer charge of beidellite can vary between 0.4 and 1.2. Run E598 started with a gel that would be expected to give a beidellite with a layer charge of 1.0. However, the result of this run consists of amorphous material and a mixture of beidellite and low crystalline paragonite, $Na_{2.0}Al_6Si_6O_{20}(OH)_4$. The beidellite must have a lower layer charge than 1.0. Unfortunately the two minerals could not be separated mechanically for chemical analyses.

*Table 3.* X-ray pattern of synthetic Na-beidellite

| hk + 001 | d(calc) | d(obs) | $I/I_0$ | cell parameters |
|---|---|---|---|---|
| 001 | 12.54 | 12.56 | 100 | orthorhombic |
| 002 | 6.27 | 6.25 | 30 | |
| 02, 11 | 4.48 | 4.45 | 90 | a(A) = 5.18 ± 0.005 |
| 004 | 3.14 | 3.13 | 40 | b(A) = 8.96 ± 0.008 |
| 20, 13 | 2.59 | 2.56 | 45 | c(A) = 12.54 ± 0.011 |
| 24 | 1.679 | 1.68 | 20 | $V(A^3)$ = 581.9 ± 0.5 |
| 33 | 1.495 | 1.49 | 35 | |
| 06 | 1.493 | | | |

*Table 4.* Chemical analysis (by microprobe) and structural formula

| | wt% | formula based on 22 O | |
|---|---|---|---|
| $SiO_2$ | 56.76 | tetrahedral Si | 7.30 |
| $Al_2O_3$ | 30.96 | Al | 0.70 |
| $Na_2O$ | 2.44* | | |
| LOI | 9.65 | octahedral Al | 4.00 |
| total | 99.81 | | |
| | | interlayer Na | 0.61* |
| | | CEC (meq/100 gr) | 68 |

* low, due to evaporation during analyses.

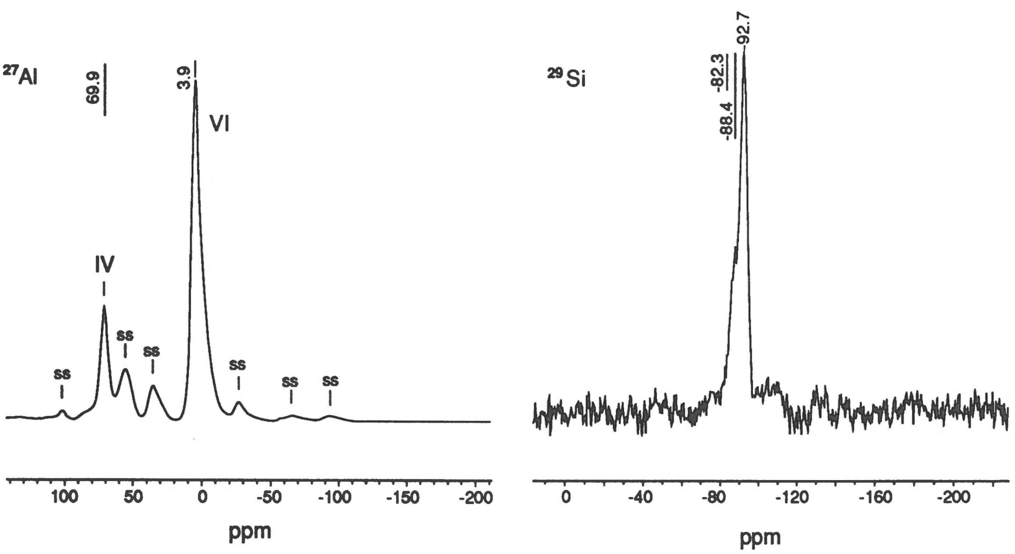

*Fig. 2.* 11.7-T $^{27}Al$ and $^{29}Si$ MAS-NMR spectra of synthetic Na-beidellite.

Higher Na contents ($Na_{1.5}Al_{5.5}Si_{6.5}O_{22}$ and $Na_{2.0}Al_{6.0}Si_{6.0}O_{22}$) resulted in the crystallization of only paragonite.

### *Characterization*

The beidellite of run E432 was extensively investigated. The product of this run exhibited small flakes of beidellite of approximately 30 μm together and approximately 10 wt% unreacted amorphous material (Fig. 1). The XRD pattern (Table 3) is comparable with that of natural beidellite from Unterrupsroth (Nadeau et al. 1985). Cell parameters were calculated with a least squares refinement program on 7 reflections; computer calculated reflections are consistent with that of beidellite. The structural formula of the synthetic beidellite, based on microprobe analyses, is $Na_{0.61}Al_{4.7}Si_{7.3}O_{20}(OH)_4$, which is in agreement with the gel composition $Na_{0.7}Al_{4.7}Si_{7.3}O_{22}$, except for the sodium that was apparently evaporized during the microprobe analyses (Table 4). The Al substitution in the tetrahedral layer based on the analytical data is 0.7 Al per unit cell. This substitution can be established in situ from MAS-NMR spectra (Fig. 2). The $^{27}Al$

*Table 5.* $^{27}Al$ and $^{29}Si$ NMR peak positions (chemical shift δ in ppm) for synthetic and natural beidellite

| | $^{27}Al$ | | $^{29}Si$ | | |
|---|---|---|---|---|---|
| | $Al^{IV}$ | $Al^{VI}$ | Si-0Al | Si-1Al | Si-2Al |
| Nadeau et al. (1985) | 69.2 | 2.34 | − 92.6 | − 87.7 | − 83.2[1] |
| natural beidellite | 69.1 | 2.46 | − 92.3 | − 87.3 | − 82.5[2] |
| Diddams et al. (1984)<br>synthetic beidellite | ± 70 | ± 5 | − 93 | − 88 | |
| Plee et al. (1985)<br>synthetic beidellite | 69.3 | 3.0 | − 95.2 | − 90.2 | − 85.6 |
| This study<br>synthetic beidellite | 69.9 | 3.9 | − 92.7 | − 88.4 | − 82.3 |

[1] size fraction < 1.4 μm, [2] size fraction > 3.0 μm.

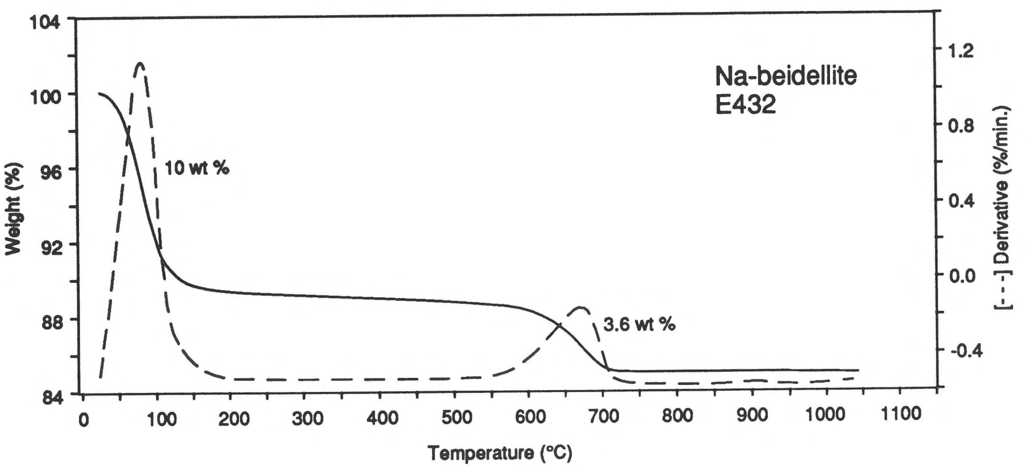

*Fig. 3.* TGA (solid line) and DTG (dashed line) plot of Na-beidellite.

NMR spectrum reveal that most Al is in octahedral coordination (3.9 ppm) and a small amount in tetrahedral coordination (69.9 ppm). Due to the differences in peak width and side band structure it is not possible to make a quantitative assessment by simply comparing peak heights. These problems are not encountered with $^{29}$Si NMR, so the ratio $Al^{IV}/Si$ can be calculated from the formula (Sanz & Serratosa 1984, Nadeau et al. 1985)

$$\frac{2Si^2 + (Si^1 - 4Si^2)/3}{Si_0 + Si^1 + Si^2}$$

where $Si^0$, $Si^1$ and $Si^2$ represent the intensity of the NMR peaks for Si atoms with zero (− 92.7 ppm), one (− 88.4 ppm) and two Al (− 82.3 ppm). The

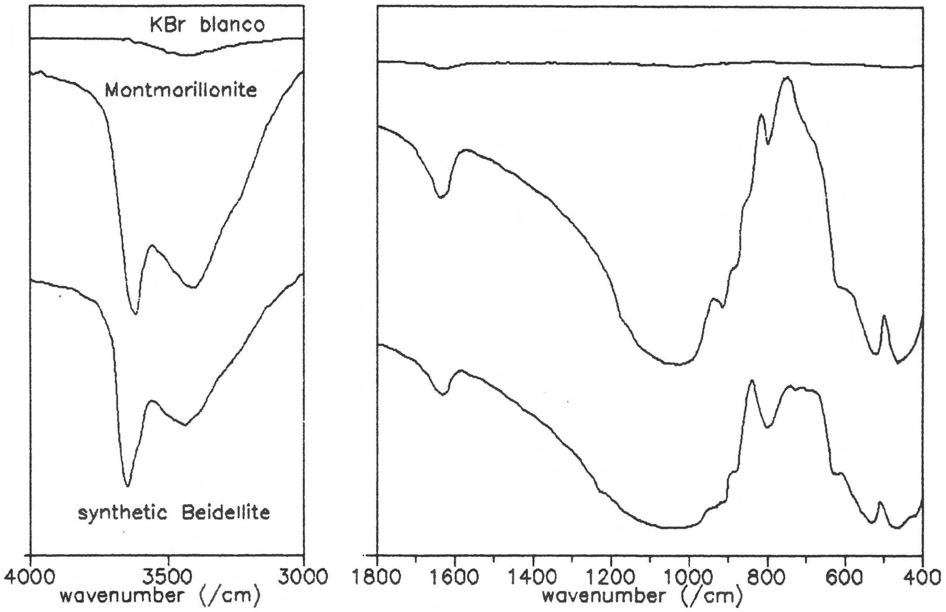

*Fig. 4.* IR-spectrum of synthetic Na-beidellite. An IR-spectrum of natural montmorillonite is drawn for reference. A spectrum of a KBr blanco is displayed at the top of the figure.

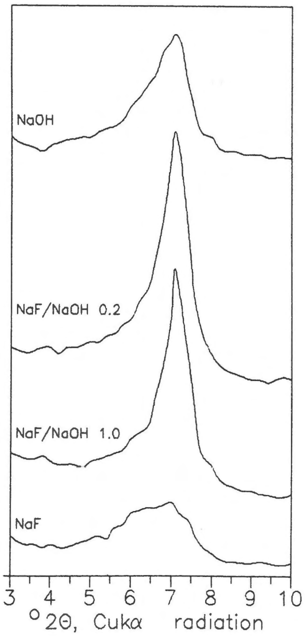

*Fig. 5.* Partial XRD-pattern of the 001 reflection displaying the influence of NaF on the beidellite crystallinity.

ratio $Si^0$:$Si^1$:$Si^2$ is around 42:20:7 predicting an Al substitution of 0.76 per unit cell, which, within instrumental accuracy, is similar with the analytical data. The peak positions agree with those reported by Diddams et al. (1984) for synthetic beidellite and by Nadeau et al. (1985) for natural beidellite (Table 5).

The TGA show two major steps of weight loss (Fig. 3). Below 100° C approximately 10% adsorped water is lost, equivalent with 5 mole water per unit cell, after correction for amorphous material. Between 600 and 700° C 3.6% water is lost by dehydroxylation, corresponding with 4.3% based on dry weight. Ideal beidellite should loose 4.9%, equivalent with 2 mole $H_2O$. The discrepancy of 0.6% is equivalent with 12.5% unreacted, amorphous material, in agreement with the approximation based on SEM photographs.

A typical IR spectrum is displayed in Fig. 4. The IR-vibrations are consistent with the data of Van der Marel & Beutelspacher (1976). Band positions in the region 4000–1200 $cm^{-1}$ are dominated by OH stretching vibrations. In the region below 1200 $cm^1$ SiO and AlOH bending vibrations are visible. The vibrations at 3445 and 1635 $cm^{-1}$ belong to adsorped $H_2O$.

### *Influence of F*

The presence of small amounts of NaF in combination with NaOH in the hydrothermal fluid has a marked influence on the crystallinity of the beidellite (Fig. 5). In the runs with mixtures of NaF-NaOH in solution the crystallinity is strongly increased. Pure NaF solution produced very badly crystallized Na-beidellite. The IR spectra exhibit less adsorption on the AlOH bending vibrations at 935, 881 and 800 $cm^1$. TGA reveals a weight loss due to dehydroxylation of 2.2 wt%. This indicates that the beidellite crystallinity increases when a part of the OH is replaced by F. These results are in agreement with the data presented by Torii & Iwasaki (1986) for trioctahedral Mg-smectite. The replacement of OH by F has no effect on the swelling behaviour of the Na-beidellite. It is possible that the pressure and temperature needed for beidellite synthesis can be decreased when an optimum amount of F is added to the hydrothermal fluid.

## Conclusions

1. Beidellite is synthesized at temperatures in the range of 350° C to 400° C and pressures down to 200 bar.
2. Hydrothermal treatment of a gel with an amount of Na, corresponding with a beidellite with a theoretical layer charge of 1.0 and more, results in the crystallization of paragonite instead of beidellite at 350° C and 1000 bar.
3. Characterization of beidellite with MAS-NMR quantified $Al^{IV}$ substitution in the tetrahedral Si-layer. $Al^{IV}$ substitution was 0.76 per unit cell, which is in sufficient agreement with the value of 0.70 based on microprobe analysis.
4. The presence of a small amount of F in the hydrothermal fluid during Na-beidellite synthesis increases the crystallinity of beidellite, without effecting its swelling behaviour.

## Acknowledgements

The authors wish to thank H.M.V.C. Govers for the X-ray powder diffraction patterns, T. Zalm for the TGA and DTA curves, R.P.E. Poorter for the microprobe analyses and J. Pieters for help with the electron microscopy. G. Nachtegaal is specially thanked for the technical assistance at the NMR facility at Nijmegen.

## References

Bos, A., G.J.L.M. de Haas, J.H.L. Voncken, A.M.J. van der Eerden & J.B.H. Jansen 1987 Hydrothermal synthesis of ammonium phlogopite – Geol. Mijnbouw 66: 251–258

Diddams, P.A., J.M. Thomas, W. Jones, J.A. Ballantine & J.H. Purnell 1984 Synthesis, characterization and catalytic activity of Beidellite-Montmorillonite layered silicates and their pillared analogues – J. Chem. Soc. Chem. Comm. 1984: 1340–1342

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

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

Larsen, E.S. & E.T. Wherry 1917 Leverrierite from Colorado – J. Wash. Acad. Sci. 7: 208–217

Larsen, E.S. & E.T. Wherry 1925 Beidellite, a new mineral name – J. Wash Acad. Sci. 15: 465–466

Loeppert, R.H., M.M. Mortland & T.J. Pinnavaia 1979 Synthesis and properties of heat-stable expanded smectite and vermiculite – Clays Clay Miner. 27: 201–208

Nadeau, P.H., V.C. Farmer, W.J. McHardy & D.C. Bain 1985 Compositional variations of the Unterrupsroth beidellite – Am. Mineral. 70: 1004–1010

Plee, D., F. Borg, L. Gatineau & J.J. Fripiat 1985 High-resolution solid-state $^{27}$Al and $^{29}$Si nuclear magnetic resonance study of pillared clays – J. Am. Chem. Soc. 107: 2362–2369

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

Ross, C.S. & S.B. Hendricks 1945 Minerals of the Montmorillonite group – U.S. Geol. Surv. Prof. Pap.: 205–B

Sanz, J. & J.M. Serratosa 1984 $^{29}$Si and $^{27}$Al high-resolution MAS-NMR spectra of phyllosilicates – J. Am. Chem. Soc. 106: 4790–4793

Schutz, A., W.E.E. Stone, G. Poncelet & 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

Sterte, J. & J. Shabtai 1987 Cross-linked smectites. V. Synthesis and properties of hydroxy-silicoaluminum montmorillonites and fluorhectorites – Clays Clay Miner. 35: 429–439

Torii, K. & T. Iwasaki 1986 Synthesis of new trioctahedral Mg-smectite – Chem. Letters 1986: 2021–2024

Torii, K. & T. Iwasaki 1987 Synthesis of hectorite – Clay Sci. 7: 1–16

Tuttle, O.F. 1949 Two pressure vessels for silicate-water studies – Geol. Soc. Amer. Bull. 60: 1727–1729

Van der Marel, H.W. & H. Beutelspacher 1976 Atlas of infrared spectroscopy of clay minerals and their admixtures – Elsevier, (Amsterdam): 396 pp

Weir, A.H. – R. Greene-Kelly 1962 Beidellite – Am. Miner. 47: 137–146