

## SYNTHESIS AND PARAGENESIS OF Na-BEIDELLITE AS A FUNCTION OF TEMPERATURE, WATER PRESSURE, AND SODIUM ACTIVITY\*

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**Abstract**—In the chemical system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , the stability field of Na-beidellite is presented as a function of pressure, temperature, and Na- and Si-activity.  $\text{Na}_{0.7}$ -beidellite was hydrothermally synthesized using a stoichiometric gel composition in the temperature range from 275° to 475°C and at pressures from 0.2 to 5 kbar. Below 275°C kaolinite was the only crystalline phase, and above about 500°C paragonite and quartz developed instead of beidellite. An optimum yield of 95% of the  $\text{Na}_{0.7}$ -beidellite was obtained at 400°C and 1 kbar after 20 days. Gels with a Na-content equivalent to a layer charge lower than 0.3 per  $\text{O}_{20}(\text{OH})_4$  did not produce beidellite. They yielded kaolinite below 325°C and pyrophyllite above 325°C. With gels of a Na-content equivalent to a layer charge of 1.5, the Na-beidellite field shifted to a minimum between temperatures of 275° and 200°C. This procedure offers the potential to synthesize beidellite at low temperatures. Beidellite synthesized from  $\text{Na}_{1.0}$ -gel approach a  $\text{Na}_{1.35}$  composition and those from  $\text{Na}_{1.5}$ - and  $\text{Na}_{2.0}$ -gels a  $\text{Na}_{1.8}$  composition.

**Key Words**—Beidellite, Electron microprobe, Hydrothermal synthesis, Kaolinite, Paragonite, Pyrophyllite, Scanning electron microscopy, X-ray diffraction.

### INTRODUCTION

Hydrothermal synthesis of smectites has become important because of their high chemical purity and the ability to selectively vary the smectite structure (Torii and Iwasaki, 1986; Plee *et al.*, 1987; Schutz *et al.*, 1987; Klopogge *et al.*, 1990a, 1990b). Also the systematic incorporation of specific organic and inorganic complexes, generating pillared clays with a specified range of basal and lateral spacings, has stimulated interest in smectite synthesis (Lahav *et al.*, 1978; Breen *et al.*, 1985; Pinnavaia *et al.*, 1985; Sterte, 1986; Sterte and Shabtai, 1987; Singh and Kodama, 1988). Pillared clays may be used simultaneously as molecular sieves and catalysts, e.g., in oil cracking reactions involving large organic molecules (Barrer, 1978; Ocelli, 1983, 1987; Rupert *et al.*, 1987; W. J. J. Welters, personal communication).

Beidellite is a dioctahedral member of the smectite group and can be described by the general formula



(Ross and Hendricks, 1945; Weir and Greene-Kelly, 1962). In natural beidellites, *p*-values can vary between 0.4 and 1.2, with an average *p*-value of 0.66 (Klopogge *et al.*, 1990a). At this value, Al exhibits a completely

homogeneous random distribution over the tetrahedral sites according to the Loewenstein Al-O-Al avoidance rule (Loewenstein, 1954) and, therefore, it represents the most stable composition.

The first aim of this study was to locate the synthesis field of Na-beidellite from a gel with composition  $\text{Na}_{0.7}\text{Al}_{4.7}\text{Si}_{7.3}\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$  (*p* = 0.7) in terms of temperature, pressure, and time in order to produce optimum amounts of Na-beidellite in experiments at low temperature and pressure conditions within a short period of time. The second purpose was to investigate the variation of the Na-content of the beidellite with compositions of the starting gels ranging from pyrophyllite  $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4$  (*p* = 0.0) to paragonite  $\text{Na}_2\text{Al}_6\text{Si}_6\text{O}_{20}(\text{OH})_4$  (*p* = 2.0) and to establish the influence of temperature at a fixed pressure of 1 kbar on the synthesis field of Na-beidellite.

### EXPERIMENTAL AND ANALYTICAL TECHNIQUES

The starting materials for the Na-beidellite syntheses were gels prepared according to the procedure of Hamilton and Henderson (1968). The chemicals for the gel preparation were  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck No. 1063),  $\text{Na}_2\text{CO}_3$  (Merck No. 6392), and tetraethyl orthosilicate (T.E.O.S.) (Merck-Schuchardt No. 800658). Experimental charges were prepared according to Klopogge *et al.* (1990a). Fifty mg of the gel and 70  $\mu\text{l}$  water were placed into a gold capsule welded on one end. The capsule was closed by arc-welding, while its main body was constantly cooled in an ice-water bath. All capsules

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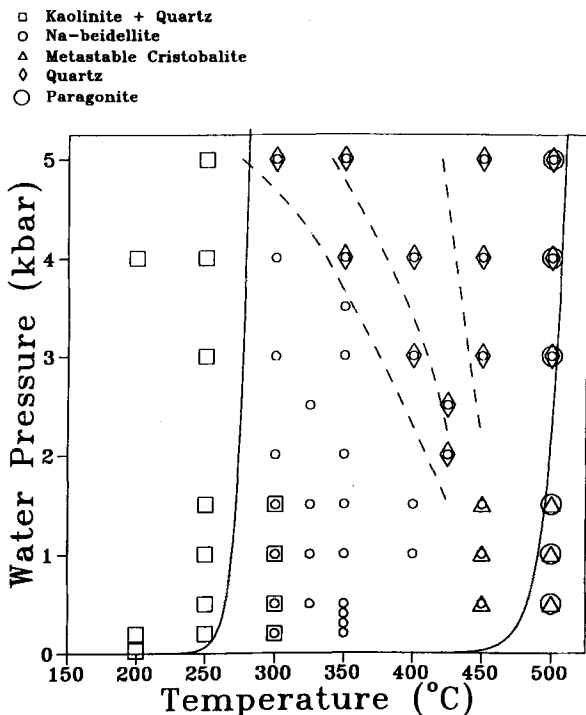


Figure 1. Experimental results on the Na-beidellite synthesis field from a gel with composition  $\text{Na}_{0.7}\text{Al}_{4.7}\text{Si}_{7.3}\text{O}_{22} \cdot x\text{H}_2\text{O}$ . Note the presence of  $\text{SiO}_2$  phases, including cristobalite. Dashed lines represent increasing amounts of  $\text{SiO}_2$ , with increasing temperature based on increasing intensities of the XRD lines.

were checked for leakage before the experiment. Experiments were carried out in a Tuttle-type, externally heated, cold-seal pressure vessel (Tuttle, 1949) using Ar gas as pressure medium. Standard run times of 10 days were used, except with the experiments to determine the crystallization curve for which run times up to 30 days were used. After quenching the pressure vessels with compressed cold air, the capsules were reweighed to check for leakage.

X-ray powder diffraction patterns were recorded with a Philips PW 1050/25 diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation. Beidellite identification was based on the  $d_{hkl}$  values of natural Ca-saturated beidellite determined by Weir and Greene-Kelly (1962) and on the  $d_{hkl}$  values of synthetic Na-beidellite determined by Kloprogge *et al.* (1990a, 1990b). The morphology and amounts of products have been investigated with a Cambridge S150 scanning electron microscope. The accuracy of the visual determination of the amounts is thought to be approximately 10%. Infrared spectra were measured on powdered samples in KBr tablets (concentration 1 wt. %) with a Perkin Elmer 580 IR spectrophotometer. Chemical analyses were made from suspensions of "diluted" samples emplaced on plastic holders, prohibiting fluorescence from nearby particles or background, using a JEOL JXA-8600 electron mi-

croprobe at 15 kV and 10 nA with minerals and synthetic compounds as standards. Raw count data were corrected with a Tracor Northern PROZA correction program.

## RESULTS

The synthesis conditions of beidellite and the development of other produced phases are summarized in a P-T diagram (Figure 1). At temperatures below 300°C, kaolinite and quartz are the predominant crystalline phases. All experiments producing kaolinite and quartz contain a considerable amount (20% to 50%) of amorphous material with a chemistry differing from the original gel composition. A small transition zone to the beidellite field seems to exist around 300°C due to the sluggish reaction kinetics of Na-beidellite in comparison to kaolinite, as evidenced by the disappearance of kaolinite when higher heating rates were used (approximately 30°C/min, unpublished data, J. T. Kloprogge). This transition zone with beidellite, kaolinite, quartz, and amorphous material disappears at water pressures above 2 kbar. Na-beidellite is the main crystalline phase in the temperature range 275°C–475°C. Saturation with ethylene glycol indicated full expandability of the beidellites formed between 300°C and 400°C. Five to 20% amorphous material is still present in Na-beidellite-rich yields. At 450°C, Na-beidellite is accompanied by cristobalite at pressures <2 kbar and by quartz over a wider temperature range and at pressures  $\geq 2$  kbar. The amount of quartz increases mainly with the synthesis temperature and less clearly with the pressure. At 500°C and pressures  $\leq 2$  kbar, paragonite is formed as the dominant phyllosilicate phase. Normal and ethylene glycol-saturated XRD analyses show that, at pressures  $\geq 2$  kbar, mixed-layer paragonite/beidellite is found with traces of quartz.

Calculations based on the microprobe analyses (Table 1a) reveal only a small variation in the composition of the beidellite with p-values between 0.5 and 0.7 at pressures below 2 kbar independent of the temperature. The variation of the composition was small even at 4 kbar. The Na analyses are consequently much lower than expected from the Si and Al analyses, presumably due to evaporation of Na during exposure to the electron beam in the microprobe (van der Pluijm *et al.*, 1988; Kloprogge *et al.*, 1990a).

Beidellite forms flakes with diameters up to 100  $\mu\text{m}$  and thicknesses of approximately 15 to 20  $\mu\text{m}$ . Only the crystal faces (001) have been observed. Most flakes show a package of platelets separated by small open spaces (Figure 2A). This is in contrast with kaolinite, which exhibits massive-looking flakes of a diameter up to 75  $\mu\text{m}$  and a thickness of approximately 5  $\mu\text{m}$  (Figure 2B). In all samples, variable amounts of amorphous material can be recognized as massive, mostly very small ( $\leq 25 \mu\text{m}$ ) fragments in the backscatter electron images produced by the microprobe and exhibit a vari-

Table 1. Selected microprobe analyses (wt. % oxides) and averages of a) beidellite and b) amorphous material from various runs using a gel with  $p = 0.7$  and c) beidellite from various gels. For the beidellite the structural formula based on 22 O is reported.

a) Beidellite from runs with gel composition $p = 0.7$ (62.7% SiO <sub>2</sub> , 34.2% Al <sub>2</sub> O <sub>3</sub> , 3.1% Na <sub>2</sub> O).												
Run:	542	427	543	549	554	641	593					
T (°C):	300	350	450	300	400	300	300					
P kbar:	0.5	0.5	0.5	1.5	1.5	2.0	4.0					
SiO <sub>2</sub>	55.99	56.76	56.56	59.39	59.45	60.69	59.90					
Al <sub>2</sub> O <sub>3</sub>	30.29	30.96	29.10	31.89	31.82	30.53	29.84					
Na <sub>2</sub> O	0.89	2.44	1.59	0.88	1.36	0.41	1.11					
Total	87.17	90.16	87.25	92.16	92.63	91.63	90.85					
Si	7.33	7.30	7.47	7.35	7.36	7.53	7.56					
Al <sup>IV</sup>	0.67	0.70	0.53	0.65	0.64	0.47	0.44					
Al <sup>VI</sup>	4.00	4.00	4.00	4.00	4.00	4.00	4.00					
Na	0.23	0.61	0.41	0.21	0.33	0.10	0.27					
Sum	12.23	12.61	12.41	12.21	12.33	12.10	12.27					
n <sup>1</sup>	3	10	3	14	13	8	15					
Mean p <sup>2</sup>	0.61	0.71	0.53	0.60	0.63	0.45	0.47					
s.d. <sup>3</sup>	0.25	0.13	0.29	0.21	0.11	0.13	0.11					
b) Average probe analyses of amorphous material from runs with gel composition $p = 0.7$ (62.7% SiO <sub>2</sub> , 34.2% Al <sub>2</sub> O <sub>3</sub> , 3.1% Na <sub>2</sub> O).												
Run:	542	542	543	543	549	554	641	593	593			
T (°C):	300	300	450	450	300	300	400	400	300	300	300	300
P kbar:	0.5	0.5	0.5	0.5	1.5	1.5	1.5	1.5	2.0	2.0	4.0	4.0
SiO <sub>2</sub>	73.25	64.96	84.31	72.44	67.84	65.19	64.67	59.45	71.42	51.49	71.32	68.47
Al <sub>2</sub> O <sub>3</sub>	24.39	29.81	12.29	21.30	31.57	31.04	33.31	31.93	28.05	27.92	21.81	26.04
Na <sub>2</sub> O	bd <sup>4</sup>	1.84	0.24	1.78	0.88	1.33	0.55	4.04	0.42	16.51	0.51	1.57
Total	97.64	96.61	96.84	95.52	100.29	97.56	98.53	95.42	99.89	95.92	93.64	96.08
c) Beidellites from runs at constant pressure of 1 kbar.												
Run E.:	694	716-2	711-2	712-1	711-3	712-2						
Na <sub>p</sub> :	1.0	1.5	1.5	1.5	2.0	2.0						
T (°C):	300	200	225	325	225	275						
SiO <sub>2</sub>	50.25	51.77	41.90	42.47	42.59	43.99						
Al <sub>2</sub> O <sub>3</sub>	34.77	38.78	35.38	35.80	35.39	36.12						
Na <sub>2</sub> O	3.41	6.73	6.19	7.18	6.63	6.57						
Total	88.43	97.28	83.47	85.45	84.61	86.68						
Si	6.61	6.37	6.01	6.02	6.06	6.10						
Al <sup>IV</sup>	1.39	1.63	1.99	1.98	1.94	1.90						
Al <sup>VI</sup>	4.00	4.00	4.00	4.00	4.00	4.00						
Na	0.87	1.61	1.72	1.97	1.83	1.77						
Sum	12.87	13.61	13.72	13.97	13.83	13.77						
n <sup>1</sup>	11	7	6	11	9	8						
Mean p <sup>2</sup>	1.39	1.68	1.87	1.91	1.92	1.89						
s.d. <sup>3</sup>	0.08	0.05	0.17	0.08	0.04	0.10						

<sup>1</sup> Number of analyses.

<sup>2</sup> Average of n analyses.

<sup>3</sup> s.d. = standard deviation.

<sup>4</sup> bd = below detection limit.

able composition as evidenced by the microprobe analyses (Table 1b).

The crystallization of Na-beidellite proceeds rather rapidly at 350°C and 1 kbar. After only one day, 15% Na-beidellite is produced. A maximum of 85% is reached after 14 days (Figure 3). A synthesis temperature of 400°C accelerates the crystallization and increases the maximum yield to 95% within 20 days. A longer run time does not significantly improve the Na-beidellite yield for the applied gel composition.

The synthesis field in relation to the gel composition is illustrated in a T-gel composition ( $\text{Na}_p\text{Al}_{4+p}\text{Si}_{8-p}\text{O}_{22}$ )

diagram at 1 kbar (Figure 4), in which p, with values between 0.0 and 2.0, represents the relative Na-content in the theoretical beidellite formula  $\text{Na}_p\text{Al}_{4+p}\text{Si}_{8-p}\text{O}_{20}(\text{OH})_4$ . The formation of Na-beidellite is dependent on both the temperature and the gel composition. Amorphous material of a variable composition is observed at temperatures below 200°C. In the composition range  $p < 0.4$ , kaolinite and quartz are formed below 325°C, while above 325°C pyrophyllite is produced. Above 350°C and at a Na-content of 0.7 and lower, pyrophyllite is formed instead of paragonite. At  $p = 0.7$ , beidellite forms between 450°C and 275°C. For  $p = 1.0$ , some

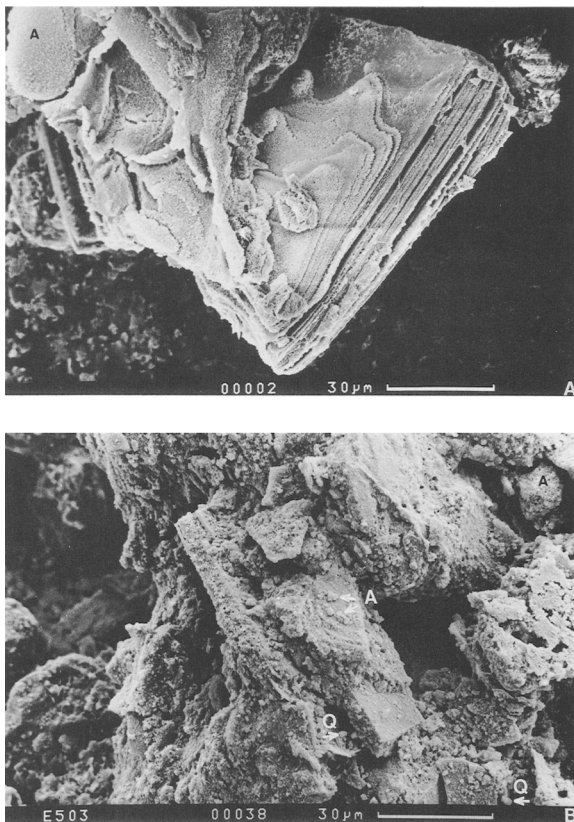


Figure 2. Scanning electron microscope photographs of A) Na-beidellite from run E427 and B) kaolinite from run E503. Note specks of quartz (a) and spheres of amorphous material (A).

bayerite is formed at 225°C as a crystalline phase. Increasing the Na-content to 1.5 results in a significant lowering of the Na-beidellite stability field to temperatures between 300°C and 175°C. The sodium content of the beidellite made from a gel of a composition of  $p = 1.5$  is significantly higher than expected from the gel composition and increases with the temperature from  $p = 1.68$  to 1.91 (Table 1c). The beidellite formed from a gel with a paragonite composition,  $p = 2.0$ , has a composition with  $p$  around 1.9.

Structural formulae calculated from the microprobe analyses (some characteristic analyses are given in Table 1b; all analyses are plotted in Figure 5), based on total Si + Al = 12, reveal the compositions of the beidellite, formed from gels with  $p$ -values of 1.0 and higher, to cluster around  $p$ -values of approximately 1.4 and 1.8 at a pressure of 1 kbar. Increasing the synthesis temperature results in a small increase in  $p$ -value.

DISCUSSION

Between 0.2 and 2 kbar, the temperature conditions for the  $Na_{0.7}$ -beidellite synthesis do not significantly depend on pressure, which agrees with the results of

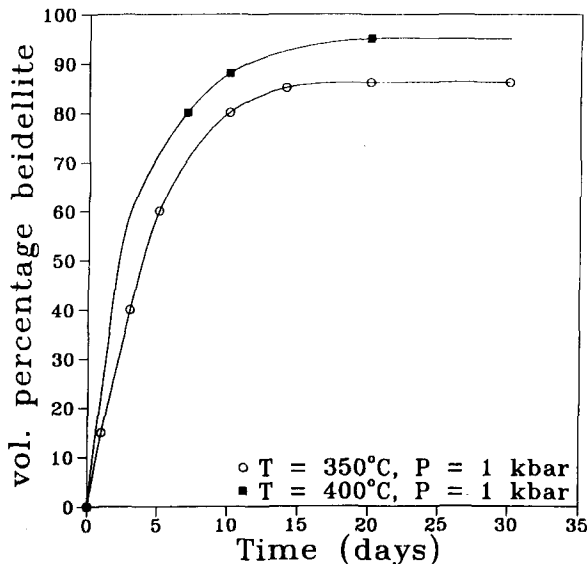


Figure 3. Beidellite yield in volume% estimated from SEM photographs as a function of the synthesis time at 350°C and 400°C at 1 kbar.

Sand *et al.* (1957). These authors observed the stability field to shift less than 25°C to higher temperatures in a similar pressure range. The conditions of 320°C/130 bar and 340°C/600 bar, which are applied for the syn-

- kaolinite + quartz
- beidellite
- ▲ pyrophyllite
- paragonite + SiO<sub>2</sub>
- ◆ amorph alone
- \* bayerite + amorph

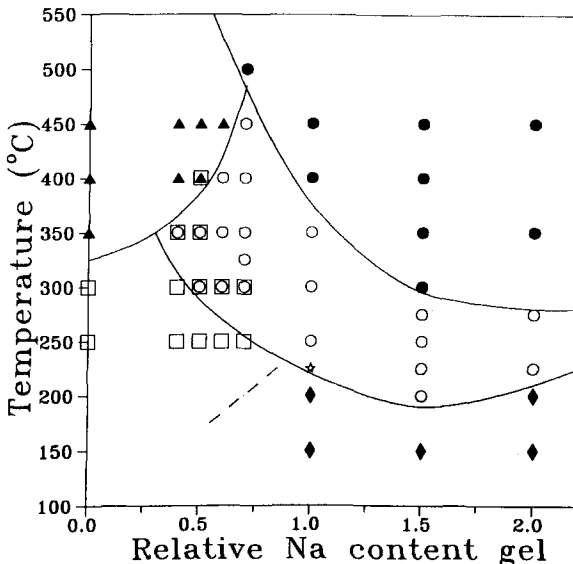


Figure 4. Experimental results at a constant pressure of 1 kbar of the synthesis field of Na-beidellite as a function of temperature and gel composition. The beidellite composition is variable, as shown in Table 1c. The presence of amorphous material or SiO<sub>2</sub> phase is not indicated.

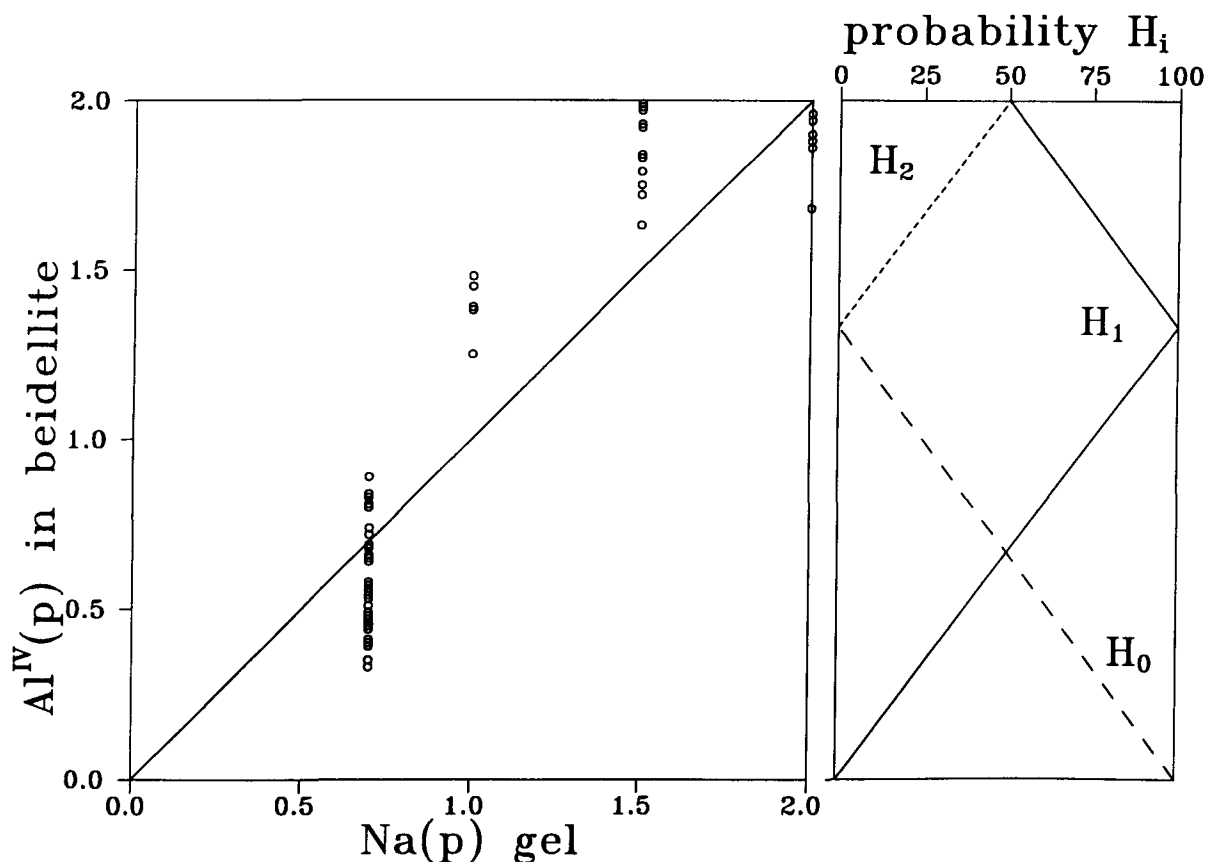


Figure 5.  $\text{Al}^{\text{IV}}$  content of the beidellite as a function of the starting gel composition and the probabilities  $H_i$ , where  $i$  represents the number of  $\text{Al}^{\text{IV}}$  per hexameric Si ring, as predicted by the HDC theory (Herrero *et al.*, 1985, 1987).  $H_1$  = solid line,  $H_2$  = short dash,  $H_3$  = long dash. The solid line on the left side gives the theoretical relationship between Na and  $\text{Al}^{\text{IV}}$  in beidellite.

thesis of beidellite from a gel with composition  $\text{Na}_{0.91}\text{Al}_{4.91}\text{Si}_{7.09}\text{O}_{20}(\text{OH})_4$  (Schutz *et al.*, 1987; Plee *et al.*, 1987), are within the field of pure beidellite. Eberl and Hower (1977) synthesized fully expandable  $\text{Na}_{0.68}$ -beidellite together with some quartz between 392° and 445°C at 2 kbar, which fits within our results. They found a 75%–90% expandable mixed-layer phase, consisting of beidellite- and some paragonite-like layers, and kaolinite between 260° and 350°C, where we observed fully expandable beidellite and a mixed-layer beidellite/paragonite phase at 500°C and pressures above 2 kbar.

The upper temperature limit of 470°C (Ames and Sand, 1958) and of 480°C (Sand *et al.*, 1957) for a  $\text{Na}_{0.66}$ -beidellite at a pressure of 1 kbar is comparable with our upper temperature limit of between 450°C and 500°C for the formation of  $\text{Na}_{0.7}$ -beidellite. The composition corresponding to  $p = 0.66$  is thought to represent the optimum substitution of Al for Si at the tetrahedral sites (Ames and Sand, 1958). The distribution of Al over the tetrahedral sheet is basically governed by the Al-O-Al avoidance rule (Loewenstein, 1954). The principle of the HDC (Homogenous Dis-

persion of Charges) (Herrero *et al.*, 1985, 1987) adds to the Loewenstein rule the fact that each hexameric ring of six Si tetrahedra in the tetrahedral sheet must contain a number of Al atoms as close as possible to the average Al/Si ratio corresponding to the composition. The right side of Figure 5 shows the probabilities of 0 ( $H_0$ ), 1 ( $H_1$ ), and 2 ( $H_2$ ) Al per hexameric ring as function of the composition (represented as  $\text{Al}^{\text{IV}}$ ). Homogeneous distributions are observed when one of the probabilities is 100% or two are 50%. The composition  $p = 0.66$  results in probabilities  $H_0$  and  $H_1$  of 50% for both hexameric rings with zero and one Al for  $\text{Na}_{0.66}$ -beidellite, supporting the suggestion of Ames and Sand (1958).  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra of  $\text{Na}_{0.7}$ -beidellite (as reported by Klopogge, 1992, and Klopogge *et al.*, 1990b and 1993) support this Al distribution. Our experiments with sodium contents  $p > 0.7$  in the starting gel result in a lowering of both the upper and the lower temperature limit of the beidellite synthesis field. The HDC theory indicates that at higher sodium contents the aluminum distribution over the tetrahedral sheet becomes less homogeneous, caused by the formation of hexameric rings with an unequal distri-

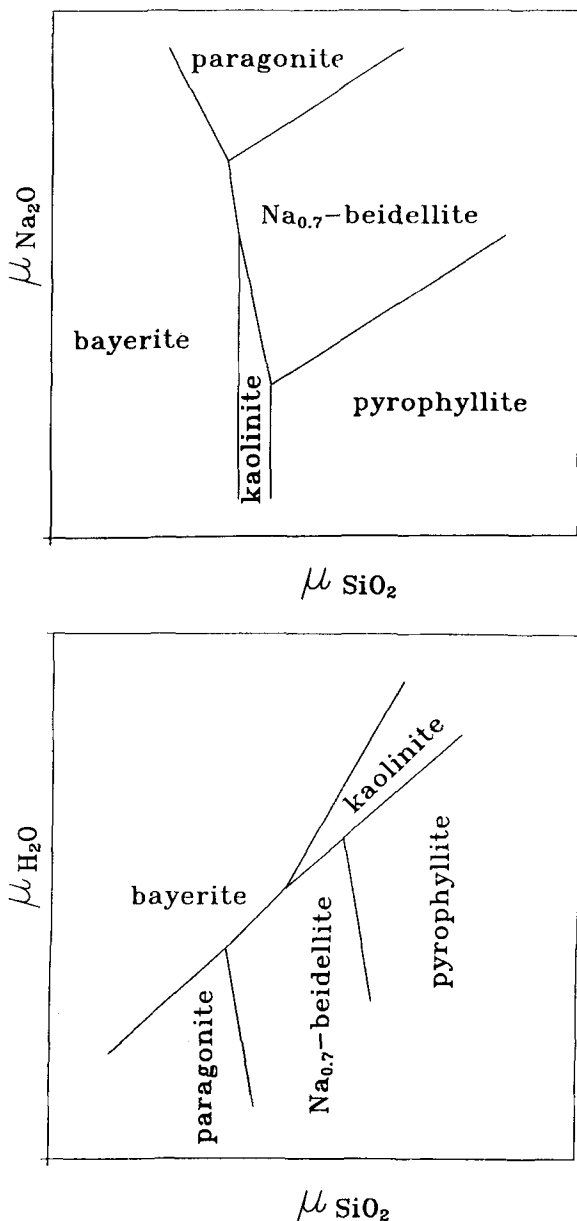


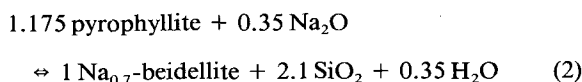
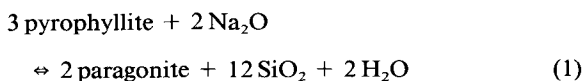
Figure 6. a = sodium-silica activity diagram at constant temperature and pressure based on Schreinemaker analyses; b = water-silica activity diagram.

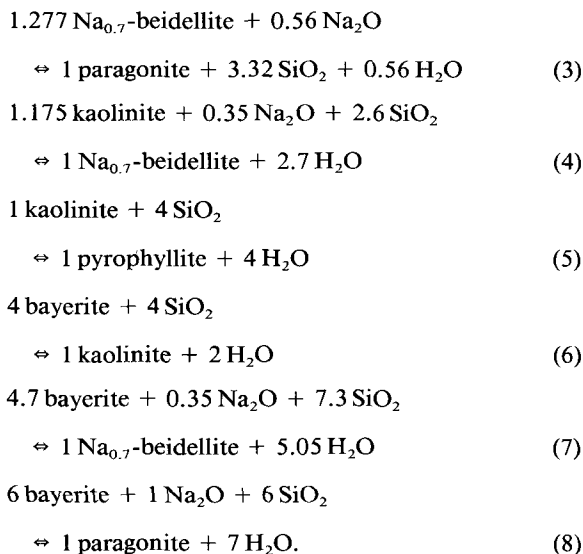
bution of one and two Al atoms per ring substituted. A homogeneous distribution of one and two Al atoms per hexameric ring is theoretically present when  $p$  has a value of 1.35. Two Al atoms in each ring ( $H_2$  100%) result in a paragonite composition with  $p = 2$ . Both distributions result in the formation of rather stable phyllosilicates. The microprobe analyses of beidellites formed from gels with  $p$ -values of one and higher (Table 1c) indicate that the system tends to form beidellite with average  $p$ -values of 1.4 and 1.9, approximating the above-mentioned homogeneous distributions (Figure 5, left side).

Examination of experiments with increasing synthesis temperatures at a constant pressure and gel composition in Figure 1 reveals a succession of minerals with increasing sodium content: kaolinite and quartz, beidellite, beidellite and  $SiO_2$ , and paragonite and quartz. The chemical potential of Na,  $\mu_{Na}$ , increases with the synthesis temperature. Velde (1985) has observed this sequence: kaolinite and quartz, via beidellite to paragonite, and finally zeolite. This sequence agrees well with our results. The rather constant composition of the beidellite demonstrates that the quartz crystallized from unreacted amorphous material. At high temperatures, the dissolution of silica, which is rapid as compared with the formation of beidellite, causes supersaturation of silica and, therefore, the formation of quartz. At low temperatures, the dissolution of silica is slow, thereby avoiding supersaturation and precipitation of a  $SiO_2$  polymorph (Kloprogge *et al.*, 1990a).

The temperature-composition diagram (Figure 4) exhibits a minimum in both the lower and upper temperature limits at  $p = 1.5$ . Although these temperature limits are comparable with the results of Koizumi and Roy (1959) in the  $p$ -range below 1.34, they still found an expandable phase together with a mica- or chlorite-like phase above the upper temperature limit, where we observe only paragonite. The existence of a minimum in the lower temperature limit offers the possibility of synthesizing large quantities of  $Na_{1.35}$ -beidellite at 200°C at pressures < 150 bar in simple Teflon-coated autoclaves. At these industrially viable conditions, it is possible to avoid the rather expensive synthesis procedures using high-pressure equipment as used in this study. This makes beidellite an economically interesting starting material for the synthesis of pillared clays, which can be used as heterogeneous, moderately acid catalyst and molecular sieve (e.g., Plee *et al.*, 1987; Schutz *et al.*, 1987).

To demonstrate the validity of our experimental results at fixed pressure, a geometric method to construct phase diagrams from the reaction coefficients of the solids, Schreinemaker analysis (Ferry and Burt, 1982) is used to construct  $\mu$ - $\mu$  diagrams (Figure 6), considering one of the components  $H_2O$ ,  $Al_2O_3$  or  $SiO_2$  as inert. Based on Figure 4, reactions between bayerite ( $Al[OH]_3$ ), kaolinite ( $Al_2Si_2O_7[OH]_4$ ), pyrophyllite ( $Al_2Si_4O_{10}[OH]_2$ ), paragonite ( $Na_2Al_2Si_6O_{20}[OH]_4$ ),  $Na_{0.7}$ -beidellite ( $Na_{0.7}Al_{4.7}Si_{7.3}O_{20}[OH]_4$ ), and quartz/cristobalite ( $SiO_2$ ) can be written, considering  $Al_2O_3$  to be inert:





The reaction between kaolinite and paragonite cannot be observed in Figure 4 and turns out to be metastable. Changing the beidellite composition in Reactions 2 and 3 does not change the orientation of the phase boundaries with pyrophyllite and paragonite, although the positions do change. The boundaries between kaolinite and beidellite defined by Reaction 4 and between bayerite and beidellite (Reaction 7) become less steep upon increasing sodium content of the beidellite. For low  $\mu_{\text{Na}_2\text{O}}$  and  $\mu_{\text{SiO}_2}$  values this diagram is in good agreement with the  $\mu(\text{K},\text{Na})\text{-}\mu(\text{Si})$  diagram reported by Velde (1985) and the ion activity diagrams reported by Garrels (1984), although they report gibbsite ( $\gamma\text{-Al}[\text{OH}]_3$ ) instead of bayerite ( $\alpha\text{-Al}[\text{OH}]_3$ ). This difference may be explained by the relatively high pH of approximately 8–9 in our experiments, favoring the formation of bayerite rather than gibbsite.

The phase boundary in the Na-free system between kaolinite and pyrophyllite at  $P = 1$  kbar and  $T$  between 300° and 350°C agrees well with the experimental result of  $325^\circ \pm 20^\circ\text{C}$  at 1 kbar reported by Thompson (1970) for Reaction 5.

### CONCLUSIONS

1) The synthesis field of  $\text{Na}_{0.7}\text{-beidellite}$  after 10 days run time is limited between the temperatures of 300°C and 450°C at pressures below 2 kbar (10 days run time). The beidellite has a rather constant composition of  $p = 0.6\text{--}0.7$ .

2) Below 300°C, kaolinite is the only crystalline phase produced for a gel composition of  $p = 0.7$ .

3) At 500°C, paragonite is the crystalline phyllosilicate instead of Na-beidellite, accompanied by quartz or metastable cristobalite.

4) At the high temperature and pressure side of the beidellite field, quartz or metastable cristobalite additionally results.

5) The composition of the beidellite synthesized from gels with  $p = 1.5$  and  $2.0$  is approximately  $\text{Na}_{1.4}\text{Al}_{5.4}\text{Si}_{6.6}\text{O}_{20}(\text{OH})_4$  and  $\text{Na}_{1.9}\text{Al}_{5.9}\text{Si}_{6.1}\text{O}_{20}(\text{OH})_4$ .

6) At 1 kbar, both the lower and upper temperature limits exhibit a minimum at 200° and 300°C starting with a gel with a composition of  $p = 1.5$ .

7) A maximum temperature of 450°C is observed at 1 kbar and a composition of  $p = 0.7$ , near the average natural composition.

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