

## Holotype buddingtonite: An ammonium feldspar without zeolitic H<sub>2</sub>O

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### ABSTRACT

Holotype buddingtonite from the Sulphur Bank Quicksilver deposit, Lake County, California, was studied by XRD, IR, STEM, SEM, TGA, DTA and wet chemical analyses. Synthetic anhydrous ammonium feldspar was studied also for comparison. The holotype buddingtonite specimen (NMNH no. 11697400) contains admixtures of FeS<sub>2</sub>, anatase and, most importantly, montmorillonite. Montmorillonite is capable of reversible dehydration, and its admixture explains the zeolitic behavior previously ascribed to buddingtonite. It is concluded that buddingtonite is an anhydrous ammonium feldspar: i.e., free of zeolitic H<sub>2</sub>O, with no zeolitic properties.

### INTRODUCTION

Buddingtonite was first described by Erd et al. (1964) as an ammonium feldspar with zeolitic H<sub>2</sub>O, with the following formula: NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> · ½H<sub>2</sub>O. The mineral was studied by chemical analysis, XRD, thermal analysis, and IR. Buddingtonite was found initially as a hydrothermal replacement of plagioclase in certain parts of the Sulphur Bank Quicksilver deposit, Lake County, California (White and Robertson, 1962), and later in oil shales and hydrothermal deposits (Gulbrandsen, 1974; Kimbara and Nishimura, 1982; Loughnan et al., 1983). Buddingtonite has gained importance recently because of spatial relationships with Au deposits (Kydd and Levinson, 1986). All authors have accepted the hydrous formula that was proposed for buddingtonite. Pavlishin and Bagmut (1988) studied the substitution of K by NH<sub>4</sub><sup>+</sup> in feldspars of granites and pegmatites but did not mention the presence of any structural H<sub>2</sub>O in their ammonium-bearing feldspars. Solomon and Rossman (1988), however, did find minor amounts of structurally bound H<sub>2</sub>O (0.02 wt% H<sub>2</sub>O) in their ammonium-bearing feldspars, although there was no evidence for H<sub>3</sub>O<sup>+</sup> substitution in the alkali-cation sites.

Experimental studies of ammonium feldspars (Barker, 1964; Hallam and Eugster, 1976) were inconclusive with respect to the zeolitic character of buddingtonite. A study of the crystal structure of holotype buddingtonite concluded that buddingtonite has a feldspar structure in which

the H<sub>2</sub>O is not present in an ordered way (Kimball and Megaw, 1974). Moreover, structure and properties of synthetic ammonium feldspar are consistent with the anhydrous formula NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> (Voncken et al., 1988; Voncken, 1990). In addition, the lattice parameters and X-ray diffraction pattern of synthetic ammonium feldspar are essentially identical to those of natural ammonium feldspar, suggesting that differences in properties between natural and synthetic ammonium feldspar are due to impurities in the natural material. Pyrite, marcasite, anatase, and montmorillonite were found in the sample initially characterized by Erd et al. (1964).

This study presents new data on the natural holotype buddingtonite specimen studied originally in order to shed light on the nature of the zeolite-like behavior of the mineral. Pure synthetic ammonium feldspar was used for comparison.

### SAMPLE DESCRIPTION

Two samples, taken from the holotype specimen of buddingtonite (NMNH no. 11697400), were available for comparison with the synthetic material. The first sample was a 70-mg remnant of DW-1, initially described by Erd et al. (1964). This is the purest fraction of holotype buddingtonite. The second sample, designated here as 2821, has not been previously described. It consists of a 100-mg remnant of material, split from the original holotype specimen, that was crushed, treated with cold 1:1 HCl and 1:1 HNO<sub>3</sub>, and sedimented in H<sub>2</sub>O for over an hour to determine the associated clay minerals. Buddingtonite was the predominant mineral in this fraction. Pyrite and marcasite were eliminated and very minor anatase was still present. The smectite content was significantly greater than in DW-1.

Synthetic ammonium feldspar was prepared from NH<sub>3</sub>

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Fig. 1. SEM photograph of a synthetic ammonium feldspar crystal grown at 600 °C and 2 kbar. Flaky material on both sides of the crystal is carbon substrate material.

solution and an Al-Si gel at 600 °C and 2 kbar using the method of Voncken et al. (1988). A rapid-quench pressure vessel was used, allowing cooling to room temperature within 2 s. If quenching is insufficiently rapid, secondary tobelite develops (Voncken et al., 1988). The synthetic sample consisted of pure buddingtonite.

#### ANALYTICAL TECHNIQUES

X-ray powder diffraction photographs were obtained with an Enraf Nonius FR552 powder diffraction camera, using  $\text{CuK}\alpha$  radiation. For SEM analysis, the samples were Au-coated and studied using a Cambridge Stereoscan, operated at 10 KeV. For STEM-analysis, the samples were ground for 5 min in alcohol in an agate mortar, and a drop of the suspension was transferred to a Cu grid bearing a C film on one side. STEM analyses were performed with a JEOL 200C TEM, equipped with an energy-dispersive X-ray analyzer (Link Systems Ltd.), and operated at 120 or 200 KeV. The sample preparation for IR-spectroscopy was as follows: 2.5 mg of sample was mixed with 250 mg of KBr. Pellets were pressed in vacuum and subsequently dried for one night at 120 °C and analyzed using a Perkin Elmer 580 IR spectrometer. Thermal analyses (TGA and DTA) were obtained in air with a Dupont thermal analyzer at a heating rate of 10 °C/min. Wet chemical analyses of DW-1 were carried out for  $\text{NH}_4^+$ , which was determined by colorimetry after acid decomposition and Kjeldahl distillation.

#### RESULTS

A typical euhedral synthetic ammonium feldspar crystal is shown in Figure 1. The XRD pattern of the holotype sample DW-1 only showed buddingtonite lines, as did those of previous studies (Erd et al., 1964; Kimball and Megaw, 1974; Voncken et al., 1988). In the pattern of sample 2821, vague broad lines were visible with  $d$  values of 4.45, 3.04, 2.59, and 1.50 Å, which are interpreted as belonging to montmorillonite.

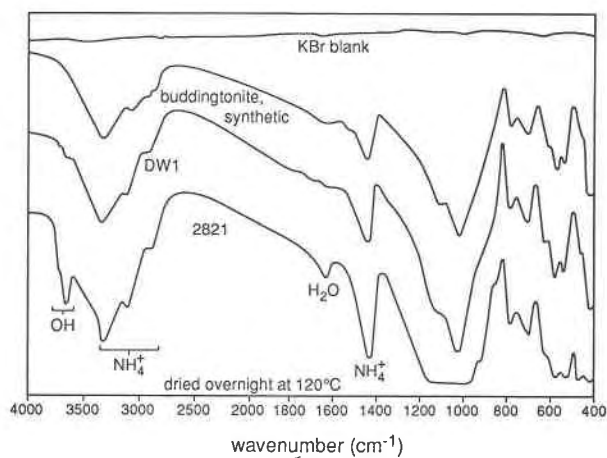


Fig. 2. IR spectra in the spectral range 4000–400  $\text{cm}^{-1}$  for natural buddingtonite and synthetic buddingtonite.

In the IR-spectra of the natural ammonium feldspars (Fig. 2), there are two distinct bands at 3750–3600  $\text{cm}^{-1}$ , which are characteristic of montmorillonite. These bands are most clearly visible in the spectrum of buddingtonite sample 2821. To highlight absorption features of the montmorillonite impurity, a KBr pellet with synthetic buddingtonite was put in the reference beam when natural buddingtonite was analyzed. Many of the resulting bands can be ascribed to montmorillonite, which may have  $\text{NH}_4^+$  in the interlayer (Table 1).

SEM analyses of DW-1 reveal typical buddingtonite crystals of  $\sim 5 \mu\text{m}$  in length, as well as blocky grains (Figs. 3a, 3b). Sometimes thick plates were visible. Figure 3b illustrates small thin flakes, visible as overgrowths on feldspar faces. The grain size of the thin flakes is  $\leq 1 \mu\text{m}$ . The amount of the flaky material in 2821 is estimated to be four times as large as in DW-1.

A STEM study of the samples DW-1 and 2821 confirms the presence of plates and flakes in both. The small thin flakes are extremely unstable under the electron beam. No analyses could be obtained. The larger and thicker plates, already observed by SEM, were identified as buddingtonite by means of electron diffraction patterns. Iron sulfide and what was probably  $\text{TiO}_2$  were identified a few times using qualitative energy dispersive X-ray analyses.

If the amounts of  $\text{NH}_4^+$  in wt%, determined by wet chemical methods, are recalculated to  $(\text{NH}_4)_2\text{O}$ , values of 8.5 and 8.3 wt% are found for DW-1. This agrees very well with the results of Erd et al. (1964, Table 3), who reported 8.34 wt%  $(\text{NH}_4)_2\text{O}$ . They reported that the holotype buddingtonite contains small amounts of K, Na, Ca, and Ba.

Erd et al. (1964) recorded a total weight loss of 12% for sample DW-1, whereas our TGA data for sample DW-1 shows a total weight loss of 10.8 wt% (Figs. 4a, 4b, Table 2). Thermogravimetric analyses (Figs. 4a, 4b) show a loss of bulk  $\text{NH}_3$  and  $\text{H}_2\text{O}$  from the material, starting at about 500 °C. There is a difference between

TABLE 1. IR vibrations of DW-1\*

cm <sup>-1</sup>	Inten- sity		Interpretation	Refer- ence
3710	sh	3703	OH-stretch montmorillonite	1
3630	s	3655	OH-stretch montmorillonite	1
		3640	OH-stretch montmorillonite	2
		3630	OH-stretch, tobelite	3
3400	sh	3410	H <sub>2</sub> O (montmorillonite)	2
3290	s	3290–3300	NH <sub>4</sub> <sup>+</sup>	4–10
3070	s	3070	NH <sub>4</sub> <sup>+</sup>	
2850	m	2850	NH <sub>4</sub> <sup>+</sup>	
1640	m	1630	H <sub>2</sub> O (montmorillonite)	2
1430	s	1430–1435	NH <sub>4</sub> <sup>+</sup>	4–10
1130	vs	1120	montmorillonite	2
1050	vs	1035	montmorillonite (broad band)	2
1000	vs			
920	sh	915	montmorillonite	2, 11
895	w	880	montmorillonite	2
785	m	795	montmorillonite	2
735	sh	731	buddingtonite or sanidine	2, 4
705	m	711, 715	buddingtonite	4, 5
		692	montmorillonite	2
630	sh	626	montmorillonite	2
580	st	575	montmorillonite	2
540	st	520	montmorillonite	2
470	st	464	montmorillonite	2
430	st	425	montmorillonite	2

Note: Abbreviations: s = strong, m = medium, w = weak, sh = shoulder. Reference numbers: 1 = Mortland et al. (1963); 2 = Van der Marel and Beutelspacher (1976); 3 = Voncken et al. (1987); 4 = Erd et al. (1964); 5 = Voncken et al. (1988); 6 = Shigorova et al. (1981); 7 = Vedder (1965); 8 = Solomon and Rossman (1988); 9 = Chourabi and Fripiat (1981); 10 = Krohn and Altaner (1987); 11 = Serratos (1962).

\* A sample of synthetic buddingtonite was in the reference beam during the analysis.

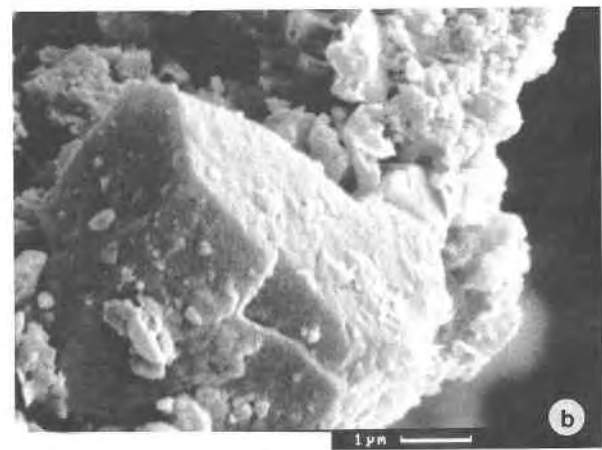
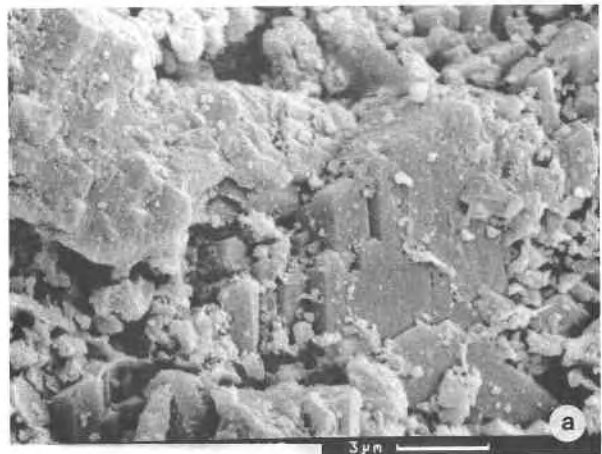


Fig. 3. (a) SEM photograph of a buddingtonite-bearing aggregate in holotype separate DW-1. (b) SEM photograph of a buddingtonite crystal in sample 2821. Overgrowth by an apparent phyllosilicate is visible.

the temperatures recorded at the start of the loss of NH<sub>3</sub> and H<sub>2</sub>O from buddingtonite given by Erd et al. (1964) (608 °C) and the present results (500 °C). However, Erd et al. (1964) applied a different heating rate (12 °C/min) in thermal analysis. Several weight-loss stages can be recognized in the thermogravimetric analysis of DW-1 (Fig. 4a). The rise of the curve at temperatures greater than 850 °C is due to the rise of the base line, as was proved with a corundum blank (not shown). The total weight loss for sample 2821 (Fig. 4b) is 14%. It largely occurs in two stages. This sample shows a large weight loss below 150 °C (5.0%).

The DTA patterns (Figs. 5a, 5b, 5c) display a large curve between 25 and 700 °C. This large curve is due to a difference in thermal conductivity between the silicate and the reference material (corundum) and does not represent thermal decomposition. A differential thermal analysis of pure synthetic NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> is shown in Figure 5a. In Figures 5b and 5c, DTA patterns of DW-1 and 2821 are shown. The DTA data are summarized in Table 3.

## DISCUSSION

The presence of iron sulfide and anatase is consistent with DTA results. Exothermic peaks in sample DW-1 between 350 and 490 °C can be attributed to decomposition of pyrite or marcasite (Smykatz-Kloss, 1974). The small exothermic peak at 980 °C in the DTA pattern of

DW-1 (Fig. 5b) may be attributed to the transition of anatase to rutile (Yamaguchi and Mukaida, 1989).

Our IR data indicate the presence of ammonium-bearing montmorillonite in DW-1 and 2821. The thin flakes, imaged with SEM and STEM, and which decompose very quickly, are interpreted as being ammonium-bearing montmorillonite.

Thermal analysis also confirms the presence of montmorillonite in DW-1 and 2821. In the DTA recording of sample 2821, peaks are found at 60, 110, and 150 °C. In the DTA recording of DW-1 (Fig. 5b), which according to SEM investigation contains smaller amounts of montmorillonite, only one peak is found at 100 °C. Loss of interlayer H<sub>2</sub>O in smectitic minerals may take place in several steps up to 200 °C (cf. Koster van Groos and Guggenheim, 1987a; Gotoh et al., 1988). Release of NH<sub>3</sub> from NH<sub>4</sub><sup>+</sup>-bearing montmorillonite is an endothermic process, which takes place gradually between 200 and 600 °C (Chourabi and Fripiat, 1981). Besides loss of interlayer H<sub>2</sub>O and NH<sub>3</sub>, dehydroxylation should also occur. De-

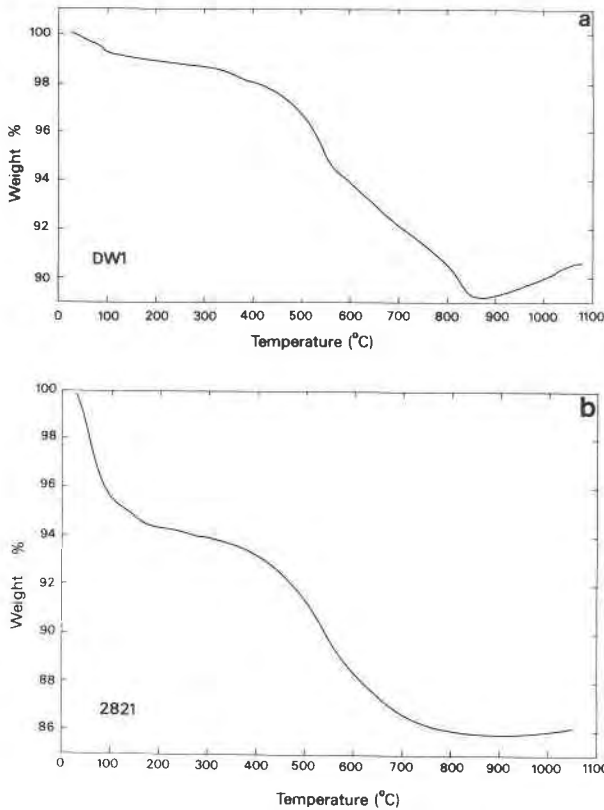


Fig. 4. (a) TGA curve of sample DW-1. (b) TGA curve of sample 2821.

hydroxylation, which is exothermic, may occur between 500 and 700 °C (Chourabi and Fripiat, 1981; Koster van Groos and Guggenheim, 1987b).

Differential thermal analyses of the natural buddingtonite samples (Figs. 5b, 5c) do not clearly indicate if deammoniation and dehydroxylation occur. However, the weight-loss curve (Fig. 5b) shows a change in slope somewhat above 550 °C. This may be explained by the combined weight loss from buddingtonite and montmorillonite in the temperature region 500–550 °C, with respect to the loss from buddingtonite alone at temperatures above 550 °C. At about 800 °C, the remaining Al-O-Si structure of buddingtonite breaks down, as indicated by the DTA curve of synthetic ammonium feldspar (Fig. 5a). A similar but smaller peak is recorded for DW-1. The sample 2821, containing less buddingtonite than DW-1, shows no peak here.

Although montmorillonite is shown to be present in both holotype buddingtonite samples, the precise amount of the clay mineral in DW-1 and 2821 is problematic. Erd et al. (1964) accepted the total amount of impurities in DW-1 to be less than 5%, of which less than 3% is FeS<sub>2</sub>. Calculation of the amount of montmorillonite on the basis of the chemical analysis is ambiguous, as the analysis of DW-1 includes buddingtonite and montmorillonite, and the latter mineral may have a wide range of

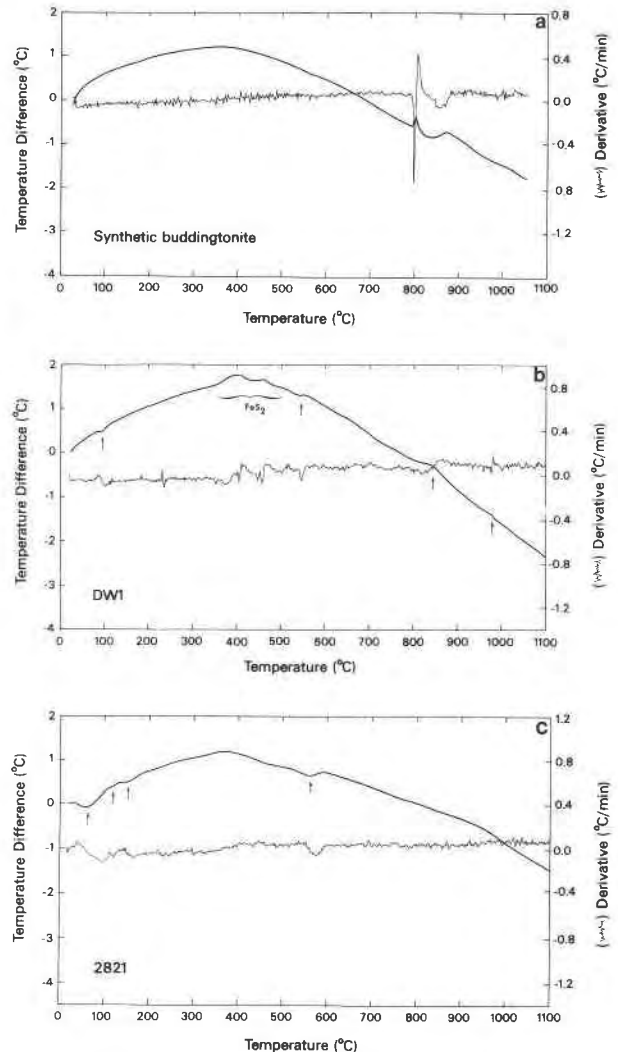


Fig. 5. (a) DTA curve of synthetic ammonium feldspar. (b) DTA curve of sample DW-1. Peaks marked with an arrow are listed in Table 3. (c) DTA curve of separate 2821. Peaks marked with an arrow are listed in Table 3.

compositions. Intensities of the IR bands at 3710 and 3630 cm<sup>-1</sup> can be used to calculate the relative amounts of montmorillonite in these samples. Values of  $I/I_0$  for the 3710 and 3630 cm<sup>-1</sup> bands from the DW-1 spectrum are 8.3 and 16.7 respectively, and for 2821 they are 31.3 and 63.8, respectively. This suggests that 2821 contains approximately four times as much montmorillonite as DW-1, which agrees reasonably well with the estimates from SEM photographs.

It is desirable to evaluate the contribution of the impurities to the total weight loss of holotype buddingtonite. On thermal decomposition, a feldspar with the ideal formula NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> would lose 10.1 wt% according to the reaction  $2\text{NH}_4\text{AlSi}_3\text{O}_8 \leftrightarrow 2\text{NH}_3 + \text{H}_2\text{O} + \text{Al}_2\text{O}_3 + \text{SiO}_2$ . A weight loss of 9.6% was found for synthetic NH<sub>4</sub>AlSi<sub>3</sub>O<sub>8</sub> by Voncken et al. (1988). The weight-loss data for DW-1

TABLE 2. A summary of weight losses detected with TGA

Synthetic NH <sub>4</sub> AlSi <sub>3</sub> O <sub>8</sub>		DW-1		2821	
T (°C)	wt. loss (%)	T (°C)	wt. loss (%)	T (°C)	wt. loss (%)
		0-150	1.0	0-150	5.0
		150-360	0.6	150-850	9.0
		360-410	0.5		
		410-550	3.0		
		550-800	4.2		
800-900	9.6	800-850	1.5		
		<b>Total</b>			
	9.6		10.8		14.0

can be corrected for the contribution of impurities by subtracting 1.0% for absorbed H<sub>2</sub>O and the loss of interlayer H<sub>2</sub>O from montmorillonite and 0.5% for the loss of volatiles from FeS<sub>2</sub>-decomposition. Therefore, 9.3% remains for buddingtonite and montmorillonite decomposition (dehydroxylation and ammonium loss) in DW-1. As the amount of montmorillonite in DW-1 is not known, the contribution of montmorillonite to the weight loss cannot be determined. The discrepancy between the chemical data for DW-1 and the thermogravimetric analyses can probably be attributed to this unknown contribution. Correction of the weight-loss data of 2821 for the loss of interlayer H<sub>2</sub>O from montmorillonite (a subtraction of 5%) leads to a value of 9% for ammonium loss and dehydroxylation. Again, there is an unknown contribution of dehydroxylation of montmorillonite. The corrected weight losses for both natural buddingtonite samples, however, suggest that buddingtonite is anhydrous, like synthetic ammonium feldspar. This agrees with the results of Voncken et al. (1988), who show similarity in structure and properties between synthetic and natural buddingtonite.

The presence of montmorillonite in the holotype buddingtonite sample is essential for the interpretation of the zeolitic behavior reported for buddingtonite. As the H<sub>2</sub>O content of montmorillonite varies with humidity, laboratory conditions will have an influence on the weight losses detected. The difference between the total weight-loss value found by Erd et al. (1964) for DW-1 and the present one (12% vs. 10.8%) is therefore not considered to be significant. Montmorillonite is well known for its

ability to dehydrate reversibly (e.g., Serratosa, 1962), and this perfectly explains the zeolitic behavior previously described and ascribed to buddingtonite.

It is concluded that buddingtonite contains no zeolitic H<sub>2</sub>O and should be considered to be anhydrous ammonium feldspar.

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TABLE 3. A summary of reactions detected with DTA

Synthetic NH <sub>4</sub> AlSi <sub>3</sub> O <sub>8</sub>		DW-1		2821	
T (°C)	Type	T (°C)	Type	T (°C)	Type
		100	endo	60	endo
				110	endo
				150	endo
		350-490	exo		
		550	endo or exo	550	endo or exo
800	exo	±850	exo		
875	exo	980	exo		

Note: endo = endothermic, exo = exothermic.

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