Hydrothermally Grown Buddingtonite, an Anhydrous Ammonium Feldspar ($NH_4AlSi_3O_8$)

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Abstract. Ammonium feldspar was grown hydrothermally from a gel, having a stöchiometric $Al_2O_3 \cdot 6SiO_2$ composition. As a source for NH_4^+, a 25 percent NH_3 solution was used. Internal Cr/CrN and graphite/methane buffers fixed the fugacity of NH_3 during the experiments. Unit cell parameters of the synthetic ammonium feldspar are a: 0.8824 (5) nm, b: 1.3077 (8) nm, c: 0.7186 (4) nm, β: 116.068 (12)°, V: 0.7448 (34) nm^3. The X-ray powder diffraction pattern is measured and indexed in accordance to the space group $C2/m$. Infrared and thermal gravimetric analyses provide no evidence for the presence of structurally bound water molecules in the crystal structure of synthetic ammonium feldspar. Hydrothermally grown anhydrous ammonium feldspar is shown to be identical to the mineral buddingtonite by the similarity of the data between the synthetic and natural materials. There may be justification for considering natural buddingtonite as an anhydrous feldspar with the ideal formula $NH_4AlSi_3O_8$. Reexamination of natural specimens is desirable.

Introduction

The mineral buddingtonite ($NH_4AlSi_3O_8 \cdot 1/2H_2O$) was first described by Erd et al. (1964) as a monoclinic ammonium feldspar with zeolitic water. It occurs as a replacement of plagioclase in an ammonium rich hot spring system of Sulphur Bank, Lake County, California. Wet chemical, infrared, thermogravimetric and differential thermal analyses provided supportive evidence for the presence of zeolitic water in natural buddingtonite. Erd et al. (1964) stated that the mineral is an anhydrous phase above 430° C. Gulbrandsen (1974) found buddingtonite in the Meade Peak Member of the Phosphoria Formation, SE Idaho, USA, where it is the principal constituent of a mudstone interval between two phosphate rich beds. It is probably of diagenetic origin. Kimbara and Nishimura (1982) found buddingtonite in the Tōshichi Spa, Iwate Prefecture, Japan. The mineral occurs as a replacement of plagioclase in a hydrothermally altered pyroclastic rock. Loughnan et al. (1983) described the occurrence of uniformly distributed buddingtonite throughout the upper part of the Condor Oilshale Deposit in Queensland, Australia. The buddingtonite in the Condor

Deposit is also thought to be of a probable diagenetic origin.

Synthetic ammonium feldspar is reported in only a few studies. Barker (1964) synthesized a nearly pure buddingtonite (97.3 percent of the theoretical NH_4^+) through a cation exchange reaction between NH_4Cl and synthetic alkali feldspar (Or_5Ab_{95}) at 550° C and 2000 bar. Hallam and Eugster (1976) determined the stability relations of the ammonium silicates buddingtonite and tobelite, the ammonium analogue of muscovite (Higashi 1982). They used the Cr/CrN and graphite/methane buffers and proved that relatively high values of f_{NH3} are necessary for the formation of ammonium feldspar.

Because the presence of structurally bound water molecules remains questionable, we have examined synthetic ammonium feldspar by means of X-ray diffraction, thermal analysis, infrared absorption and scanning electron microscopy.

Experimental Techniques

The starting material for the ammonium feldspar synthesis consisted of coprecipitated gels, with a composition of $Al_2O_3.6SiO_2$, prepared according to the method of Hamilton and Henderson (1968). The chemicals used for the gel preparations were $Al(NO_3)_3$ (Merck no. 1063, p.a.) and T.E.O.S. (Merck-Schuchardt No. 800658, p.a.). A 25 percent NH_3 solution (Merck No. 5432, p.a.) was the ammonium source. Ammonia was added in excess. Chromium powder (Ventron No. 00672), chromium nitride powder (Ventron No. 49112) and graphite (Norit) were applied for the buffering of the ammonia fugacity during the reaction, following the method described by Hallam and Eugster (1976).

The Al—Si gel was placed in an unsealed platinum tube. This tube was tightly crimped on both sides and placed in a larger platinum tube, welded on one side, and containing Cr and CrN in known amounts. Subsequently, the ammonia was added. The outer tube was welded with a carbon-arc while it was constantly cooled in a water bath. The platinum capsule was placed in a larger gold capsule, welded on one side and containing a known amount of graphite. The gold capsule was welded under cooling from a water bath. The synthesis experiments were carried out in externally heated cold seal pressure vessels (Tuttle 1949). Argon gas was the pressure medium. The experiments were

Table 1. Experimental results. $P=2$ Kbar

Run nr.	T in °C	Run time in days	Quench time in min[a]	Phases produced
RK18	550	10	15	buddingtonite + minor tobelite[b]
RK21[c]	590–550	5	15	buddingtonite + minor tobelite[b]
RK33[c]	660–570	10	15	tobelite + quartz
JV85A-E88	600	14	15	buddingtonite + minor tobelite
JV85B-E89	600	14	15	buddingtonite + minor tobelite
JV110-E205	600	18	15	buddingtonite + minor tobelite
JV110-E206	600	18	15	buddingtonite + minor tobelite
JV110-E207	600	18	15	buddingtonite + minor tobelite
JV96A-E127	600	14	5	buddingtonite
JV96B-E128	600	14	5	buddingtonite
JV96C-E129	600	14	5	buddingtonite

[a] times by approximation for cooling to room temperature. Quench times differ slightly for different run temperatures

[b] SEM-photographs of the run products are shown in Figure 3a and b

[c] slow cooling to the lower temperature

run at 2 kbar total pressure in the temperature range region of 660–550° C at either constant or decreasing temperature. For the latter experiments a programmable temperature controller (Eurotherm) was used. The experimental conditions and results are summarised in Table 1. Temperatures were measured with chromel-alumel thermocouples and are considered to be accurate to $\pm 5°$ C. The pressure was read from a bourdon-type pressure gauge which was calibrated against a Heise precision gauge of which the accuracy is ± 10 bar. After quenching with compressed cold air the capsules were reweighed to check for leakage. The buffer materials were checked by XRD and appeared never to be exhausted. Optical examination with a polarising microscope showed ammonium feldspar as colourless grains, generally about 10–30 μm length. The largest crystals appeared to be too small for a well oriented determination of the optical properties. In general, the yield of successful ammonium feldspar synthesis runs was at least about 98 percent. If no other phases could be identified with XRD, optical microscope and SEM, the sample was considered to be pure buddingtonite. Tobelite is often found as a minor phase (Table 1) and it is considered to occur as a run product from insufficiently rapid quenching, because its stability field is traversed during cooling.

Analytical Methods

The X-ray powder diffraction patterns have been obtained with a Guinier FR552 (Enraf Nonius) focussing camera using CuKα1 radiation. Heating stage X-ray diffraction was carried out using a HT Guinier CuKα1 (Enraf Nonius FR553) focussing powder camera. A heating rate of 25° C per h was applied from 20° C to 1020° C. For determination of the unit cell parameters, silicon powder was taken as internal standard. Peak positions and intensities have been recorded in this procedure with a double beam recording microdensitometer (MK IIICS; Joyce and Loebl & Co Ltd). The unitcell refinements were made with the computer program UNITCELLC (Strom 1976a). Thermogravimetric analysis were made in air with a Dupont 1090 Thermal Analyser with a heating rate of 10° C per minute. Infrared

Table 2. X-ray powder diffraction data of hydrothermally grown buddingtonite

hkl	d_{hkl} obs (Å)	I/I_o	hkl	d_{hkl} obs (Å)	I/I_o
110	6.78	25	022	2.899	20
020	6.54	35	$\bar{3}$11	2.870	15
001	6.47	25	$\bar{1}$32	2.776	10
$\bar{1}$11	5.93	50	$\bar{3}$12	2.656	20
$\bar{2}$01	4.336	100	$\bar{2}$41	2.611	30
111	3.989	45	240	2.522	15
130	3.820	75	$\bar{1}$51	2.434	12
$\bar{1}$31	3.643	15	330	2.260	15
$\bar{1}$12	3.470	40	060	2.180	18
220	3.390	90	241	2.154	12
$\bar{2}$02	3.323	60	$\bar{1}$52	2.116	8
040	3.269	40	$\bar{4}$22	2.056	15
002	3.234	90	222	1.994	15
131	3.020	40	400	1.982	15
$\bar{2}$22	2.963	25			
041	2.918	20			

absorption spectra were measured from powdered samples in KBr disks, with a Perkin Elmer 580 IR spectrophotometer. For morphological analysis, the run products were examined by means of a Cambridge S150 or M600 scanning electron microscope.

## Results

X-ray Powder Diffraction

The d_{hkl} values of buddingtonite, given by Erd et al. (1964), Gulbrandsen (1974), Kimbara and Nishimura (1982) and Loughnan et al. (1983) are indexed according to a primitive P-cell. Kimball and Megaw (1974) suggest a C-cell symmetry for the holotype buddingtonite. We have indexed the pattern of synthetic ammonium feldspar according to a C centered unit cell, as in the case of high sanidine (Ribbe 1963). The d_{hkl} values of the hydrothermal ammonium feldspar and their intensities are listed in Table 2. The lattice

Table 3. Unit cell parameters of hydrothermally grown buddingtonite

Space group	a (nm)	b (nm)	c (nm)	$\beta(°)$	V (nm^3)
C2/m	0.8824 (5)	1.3077 (8)	0.7186 (4)	116.068 (12)	0.7448 (34)[a]
	0.8804 (2)	1.3024 (3)	0.7183 (1)	116.105 (18)	–[b]

[a] This work

[b] D.E. Appleman in Kimbal and Megaw (1974). Natural holotype buddingtonite from the Sulphur Bank Deposit. Figures in parentheses represent the estimated standard deviation and refer to the last decimal place
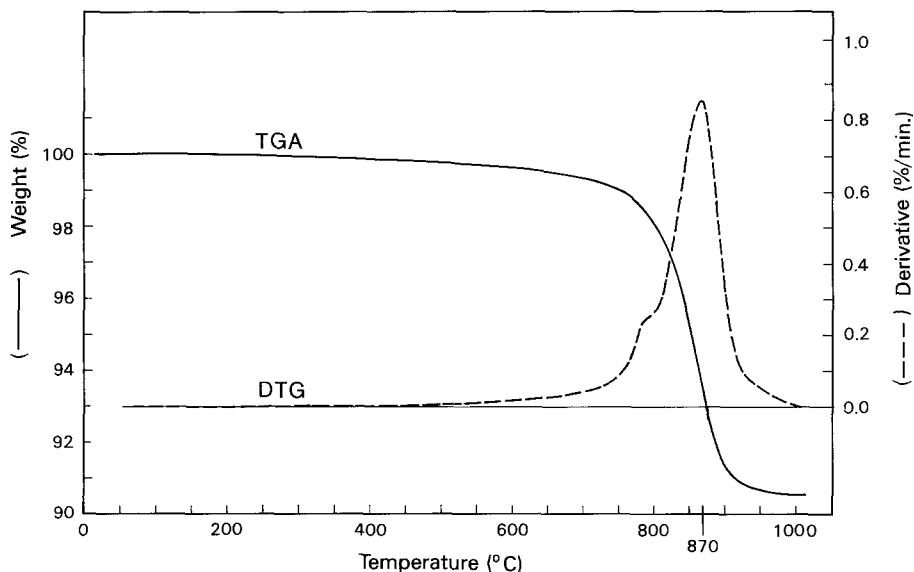

Fig. 1. TGA (solid line) and DTG (dashed line) curve of ammonium feldspar

parameters are given in Table 3. They are in good agreement with the values reported by Kimball and Megaw (1974) for natural buddingtonite from the Sulphur Bank Deposit.

In HT-XRD, the ammonium feldspar pattern does not change up to approximately 650° C. Above this temperature many lines grow weaker and eventually fade in the temperature region of 770 to 830° C. Above 830° C the structure is amorphous. These results agree with those of Loughnan et al. (1983). They mention that the XRD-pattern of a heated natural buddingtonite from the Condor Oilshale Deposit remains virtually unaffected up to 500° C. Remnants of the feldspar pattern could be traced by them to about 750° C. The temperature interval of 770 to 830° C found for the breakdown of the synthetic ammonium feldspar in HT-XRD marks the onset of its decomposition in the thermogravimetric analysis of Figure 1. In the TGA the silicate decomposed between 800 and 900° C. In a TGA applying the same heating rate as in the HT-XRD, the decomposition took place between 750 and 850° C.

Thermogravimetric Analysis

The decomposition reaction of anhydrous ammonium feldspar may be written as follows:

$$2\ NH_4AlSi_3O_8 \rightarrow 2\ NH_3 + H_2O + 6\ SiO_2 + Al_2O_3$$
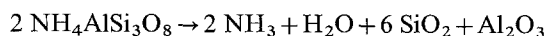
Taking the formula as $NH_4AlSi_3O_8$, the ideal weight loss should be 10.1 weight percent. Figure 1 shows a thermogra-

vimetric analysis of pure ammonium feldspars. Below 400° C no weight losses are detected. At about this temperature, the sample starts to lose weight very slowly. The total weight loss is approximately 9.5 weight percent and it occurs mainly between 800 and 900° C. It is in good agreement with the ideal value. A DTG-curve, calculated from the weight loss data shows a large peak at 870° C with a small shoulder at about 800° C. The peak and the shoulder may be attributed to the loss of $2NH_3 + H_2O$ according to the above reaction. A TGA (not shown), with the same heating rate as the HT-XRD, yielded a loss of 9.6 weight percent. If we assume that ammonium feldspar is represented by the formula $NH_4AlSi_3O_8 \cdot 1/2H_2O$, like natural buddingtonite, the ideal weight loss would be 13.1 weight percent. This value diverges strongly from the experimental results. Erd et al. (1964) report, however, a weight loss of 12.0 weight percent for natural holotype buddingtonite. Loughnan et al. (1983) recorded a total weight loss of 11.7 weight percent for natural buddingtonite, heated to 600° C.

IR-Spectroscopy

Figure 2 shows the spectra of the KBr carrier material, at 20° C and when dried at 120° C and the spectra of ammonium feldspar from the run JV110-E206 (Table 1) at 20, 120 and 450° C in the spectral range of 4000–400 cm^{-1}. A spectrum of synthetic tobelite, $NH_4Al_2Si_3AlO_{10}(OH)_2$, (Voncken et al. 1987) is added for reference. The absorption
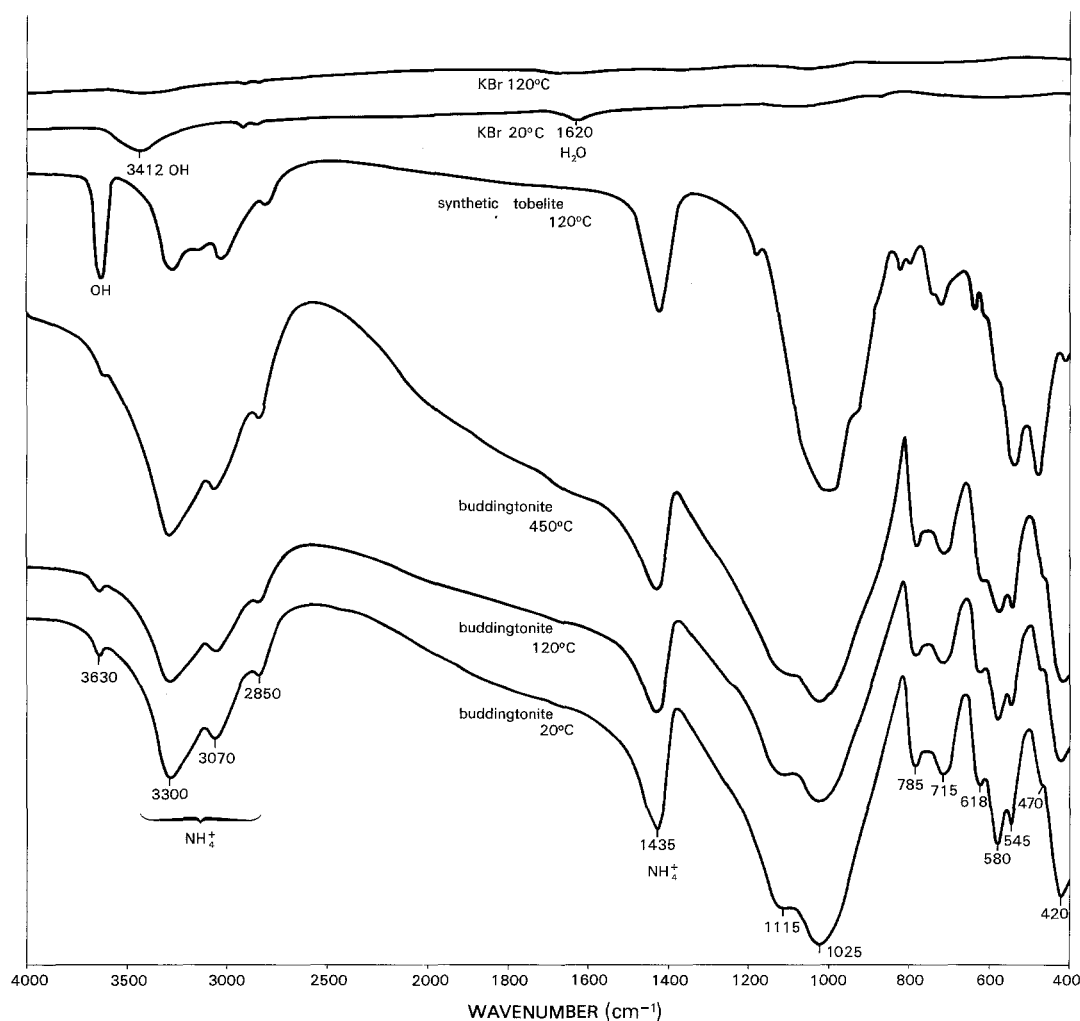
Fig. 2. IR spectra of KBr blank at 20° C and 120° C, and of ammonium feldspar (run JV110-E206) at 20, 120 and 450° C. The ammonium feldspar spectrum at 20° C was corrected for the KBr spectrum at 20° C by placing the blanc KBr disk in the reference beam. A spectrum of synthetic tobelite is added for reference

maxima of synthetic ammonium feldspar are listed in Table 3, together with the IR data given by Erd et al. (1964). The maxima at 3300, 3070, 2850 and 1435 cm^{-1} are due to the stretching and bending vibrations of ammonium (Shigorova et al. 1981; Hori et al. 1986). An excellent agreement exists between the absorption maxima of the synthetic and natural buddingtonite, except for the absorption maxima at 3412, 1620 and 731 cm^{-1}, which occur in the natural buddingtonite spectrum. Erd et al. (1964) assigned the 3412 cm^{-1} frequency to residual water in stretching mode and the 1620 cm^{-1} to the bending mode vibrations of water. They attributed the band at 3650–3500 cm^{-1} to structurally bound water as a results of a comparison between the IR-spectra of buddingtonite and NH$_4^+$-montmorillonite. Even though the maximum at 3630 cm^{-1} in our buddingtonite spectra could be explained by the presence of water molecules (Hofmeister and Rossman 1985; Beran 1986), there exists another and more plausible explanation. The mineral tobelite has one of its strongest absorption maxima at 3630 cm^{-1} (Voncken et al. 1987). As tobelite occurs in several runs as a secondary phase (Table 1), the absorption maximum at 3630 cm^1 in our ammonium feldspar spectra can better be explained by the presence of small amounts of the ammonium mica.

Crystal Morphology

The structure of the feldspars is formed by tetrahedra of (Si, Al)O$_4$, linked to each other in three dimensions. Large cations fill the open spaces in the tetrahedral network. The crystal faces of high sanidine can be classified by the PBC method into relatively slow growing F-faces and others, less important for the crystal morphology. The most important of the F-faces (F$_1$ faces) are parallel to at least two PBC's of strong Si, Al-bonds. They are {110}, {001}, {010}, {$\bar{2}$01}, {111}. F$_2$ faces which are parallel to one PBC with only Si, Al bonds and one PBC with additional weaker K−O bonds, are {130}, {021}, {$\bar{2}$21}, {$\bar{1}$12}, {100} and {$\bar{1}$01} (Woensdregt 1982).

The crystals shown in the Figures 3a and 3b could be indexed either by direct measurement of interfacial angles or by means of the computer program CAMERA (Strom 1976b). The pictures display characteristic habits of hydrothermally grown buddingtonite crystals. The experiments were made at either constant (550° C) or decreasing temperature (10° C per day, from 590 to 550° C), but no difference in crystal morphology was observed. The tiny euhedral crystals (up to 0.05 mm) show {010}, {110}, {100}, {001} and {$\bar{1}$01}, while {130} is occasionally observed.
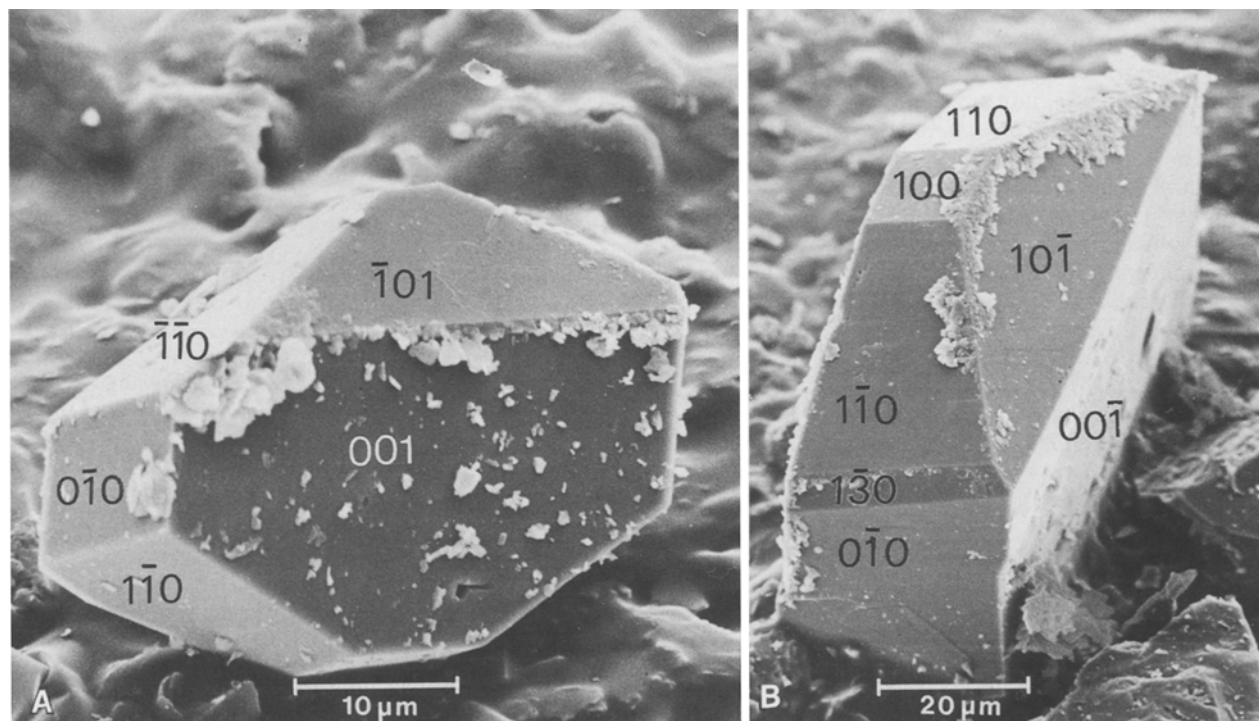
Fig. 3. (A) Buddingtonite crystal, grown at 550° C, 2 kbars. (B) Buddingtonite crystal, grown at 590–550° C, 2 kbars. The white flakes on the crystal faces are small NH_4-mica crystals (tobelite), believed to have been formed during quenching

Table 4. IR absorption maxima of hydrothermally grown and natural buddingtonite in cm^{-1}

(1)[a]	(2)[b]	(1)[a]	(2)[b]
3630[c]	3650–3600	785	785
–	3412	–	731
3300	3296	715	711
3070	3068	618	621
2850	2848	580	583
–	1620	545	546
1435	1419	470	466
1115	1117	420	425
1025	1034		

[a] This study
[b] Erd et al. (1964)
[c] attributed to tobelite impurity

The morphology of hydrothermally grown ammonium feldspar does not essentially differ from that of natural buddingtonite (Erd et al. 1964), and the agreement between the habits of buddingtonite and high sanidine is an indication that their crystal structures are very similar.

Discussion

In the feldspar structure little space is left for structural water, the cations occupy the main part of the cavities in the tetrahedral framework. Erd et al. (1964) reported for natural buddingtonite the chemical composition NH_4Al-$Si_3O_8 \cdot 1/2H_2O$, suggesting a zeolitic nature for the half mole of water. Kimball and Megaw (1974) stated in their interim report on the X-ray structural investigations of the holotype buddingtonite specimen: "If the chemical formula proposed for buddingtonite by Erd et al. (1964) is correct,

the half mole of water would appear to be completely disordered."

The X-ray powder diffraction pattern of synthetic ammonium feldspar can be indexed satisfactorily on the basis of the $C2/m$ space group symmetry. There are some slight differences between the X-ray powder diffraction pattern of the synthetic ammonium feldspar and reported patterns of natural buddingtonites. The 6.47 and 2.116 Å reflections in the pattern of the synthetic material have not been observed in patterns of natural material. A reflection at 3.60 Å, observed in all natural buddingtonite patterns, except the one given by Loughnan et al. (1983), could not be identified with certainty in the pattern of the synthetic silicate. The 3.129 Å reflection reported by Erd et al. (1964) does not belong to buddingtonite and represents an impurity (R.C. Erd, pers. comm., 1987). The differences observed in the X-ray powder diffraction patterns may be caused by differences in the techniques applied. We used a Guinier powder camera, in contrast to the other workers mentioned above, who used a diffractometer. The X-ray diffraction and morphological data indicate a close similarity between synthetic ammonium feldspar and high sanidine.

The calculated density from our unit cell volume is 2.29 g·cm^{-3}. From the unit cell data of Erd et al. (1964), using the anhydrous formula, a value of 2.31 g·cm^{-3} can be calculated, and similarly, a value of 2.30 g·cm^{-3} is obtained from the data of Kimbara and Nishimura (1982). Erd et al. (1964) calculated a value of 2.38 g·cm^{-3}, using the hydrous formula. These authors measured, however, a specific gravity of 2.32 g·cm^{-3} for the holotype material. Gulbrandsen (1974) measured a specific gravity of 2.36 g·cm^{-3}, but stated that the analysed grains were typically clouded with minute inclusions, that are presumed to be mostly organic matter, illite and iron oxide. Its appears, that our calculated density is in good agreement with values

calculated for natural buddingtonites and the measured value for the holotype material.

HT-XRD analysis of synthetic ammonium feldspar gives no indication of a significant change in the crystal structure upon heating. The TGA curve shows the absence of zeolitic water since no weight loss is observed beneath $400°$ C. Structural water in alkali feldspar may however persist up to $900°$ C (Beran 1986). Volatiles are slowly released between 400 and $800°$ C, whereas the decomposition of ammonium feldspar takes place very rapidly at higher temperatures. The maximum rate of weight loss is reached at $870°$ C. The total weight loss is in accordance with the formula $NH_4AlSi_3O_8$. Although we explain the 3630 cm^{-1} band in the IR-spectra by the presence of secondary tobelite, very minor replacement of M-site ammonium by structural water remains possible. As the molecular weights of water and ammonia are very similar, this would result in only a very minor change in the TGA data.

The DTA curves of Erd et al. (1964) show 2 broad exothermic peaks, the first one at 608 and the second one at $814°$ C. They state: "the larger broad exothermic peak at $608°$ C probably represents loss of ammonia, and the significance of the smaller exothermic peak at $814°$ C is not known." These authors attribute a small endothermic band at $119°$ C to loss of water. The unexplained DTA peak suggests the presence of an unidentified phase in the original sample. The occurrence of an unidentified ammonium-bearing phyllosilicate could explain the larger weight loss recorded for natural type buddingtonite with respect to its synthetic counterpart in TGA. If we take, on the basis of our experimental results, tobelite as a possible impurity, about 30 percent by weight of this mineral would be necessary to explain the difference in weight loss between the holotype buddingtonite and our synthetic material. There is no sign of any of the tobelite reflections in the XRD-pattern of the holotype buddingtonite. Small amounts of montmorillonite are present, but do not show on the X-ray diffraction pattern of the type material (R.C. Erd, pers. comm., 1987).

At present, the large differences in TGA results between synthetic and natural material can not be explained. Re-examination of natural buddingtonite might shed more light on this subject.

Conclusions

1) Hydrothermally grown anhydrous ammonium feldspar is shown to be identical to the mineral buddingtonite as is borne out by the similarity of the data between the synthetic and natural materials.

2) Synthetic ammonium feldspar and high sanidine have similar crystal structures, as is evidenced by X-ray diffraction and crystal morphology data.

3) There may be justification for considering natural buddingtonite as an anhydrous feldspar with the ideal formula $NH_4AlSi_3O_8$.

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