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BUDDINGTONITE, AN AMMONIUM FELDSPAR WITH ZEOLITIC WATER[1]

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ABSTRACT

Buddingtonite, the first ammonium aluminosilicate found in nature, occurs in Quaternary andesite and older rocks hydrothermally altered by ammonia-bearing hot-spring waters below the water table at the Sulphur Bank quicksilver mine, Lake County, California. Typically, it occurs as compact masses pseudomorphous after plagioclase, and as crystals as much as 0.05 mm diameter lining cavities.

Buddingtonite is biaxial (+), $\alpha=1.530$, $\beta=1.531$, $\gamma=1.534$ all ±0.002, 2V not determined, $X\wedge a=4°$, $Z=b$, $Y\wedge c=19°$. H $5\frac{1}{2}$, G2.32$\pm$0.01.

Chemical analysis of purest separate gave: SiO_2, 63.80; Al_2O_3, 19.16; Fe_2O_3, 1.85; MgO, 0.21; CaO, 0.04; BaO, 0.26; Na_2O, 0.06; K_2O, 0.62; $(NH_4)_2O$, 7.95; TiO_2, 0.99; H_2O^-, 0.88; H_2O^+, 3.28; S, 1.59; total 100.69 $(-O+S)=100.10$ per cent.

Buddingtonite is monoclinic; $P2_1$ or $P2_1/m$; $a=8.571$, $b=13.032$, $c=7.187$, $\beta=112°44'$ $\pm1'$; $a:b:c=0.658:1:0.551$; cell volume, 740.42Å^3; cell contents $4[NH_4AlSi_3O_8\cdot1/2H_2O]$; calculated density, 2.38_8 gcm^{-3}.

From 370° to 430° C, buddingtonite is the ammonium analogue of monoclinic K-feldspar; below about 370° C with normal atmospheric moisture, buddingtonite adsorbs zeolitic water.

The new mineral is named for Professor Emeritus Arthur F. Buddington.

INTRODUCTION

During a recent study of the major hot-spring mercury ore deposit at Sulphur Bank, Lake County, California (White and Roberson, 1962), White found an abundant hydrothermal mineral with an *x*-ray pattern similar to that of the hydrothermal K-feldspar that commonly replaces intermediate plagioclase in many hot-spring systems that are closely associated with volcanism (White, 1955; Sigvaldason and White, 1961, 1962).

However, hydrothermal K-feldspar had not been found previously in close association with mercury deposits, and experimental work by Hemley (1959) on the K_2O-Al_2O_3-SiO_2-H_2O system had shown that formation of K-feldspar is favored by high proportions of potassium to hy-

[1] Publication authorized by the Director, U. S. Geological Survey.

drogen ions and by high temperature; the hot-spring system now active at Sulphur Bank is relatively low in temperature, and the waters have a relatively low proportion of potassium to hydrogen ions. If the mineral in question was indeed K-feldspar, major changes in temperature and water composition with time were indicated.

Selective staining of the altered rocks for K-feldspar and chemical analysis, proved that potassium was indeed a minor component. An *x*-ray spectrometer analysis of pyroxene andesite almost completely replaced by the unknown mineral revealed a small amount of iron and traces of other elements but failed to indicate any major cation. Because the present thermal waters have the maximum known proportions of ammonium and boron to the major cations of normal thermal and mineral waters, Roberson (White and Roberson, 1962, p. 409) searched qualitatively for both components and found that ammonium was abundant, but boron was minor.

In spite of the recognized feldspar-like properties of the new mineral (White and Roberson, 1962, p. 409), it was tentatively assigned to the zeolite group because of its associated water, confirmed chemically. It is now classified as a feldspar with zeolitic water, in view of the data presented in this report.

The mineral is named in honor of Professor Emeritus Arthur F. Buddington, Department of Geology, Princeton University. The name should be pronounced bŭd.dĭng.tŏn.īt. The mineral name has been approved by the Commission on new minerals, International Mineralogical Association.

Occurrence

Details of occurrence are described by White and Roberson (1962); in summary, buddingtonite occurs near and below the water table of an active, hot-spring system as a hydrothermal replacement of a Quaternary andesite lava flow and older rocks. In one drill hole, the mineral extends below this water table to depths of about 400 feet, where present temperatures are about 100° C. (White and Roberson, 1962, p. 419). Only small amounts of the mineral were found in cuttings at greater depths in the same drill hole, and these amounts could have been derived by contamination from higher levels. A second deep hole drilled late in 1961 and completed at a depth of 1,390 feet provided cuttings only from depths below 1,100 feet. In spite of the fact that the cuttings contain pyrite and some other evidence of hydrothermal alteration, no trace of buddingtonite was found in whole-rock *x*-ray diffraction patterns. In specimens collected in the early 1880's by G. F. Becker from the old Herman Shaft (see review by White and Roberson, 1962, p. 409), buddingtonite occurs in abun-

dance down to the fifth level (315 feet below surface) but is absent in the three specimens of the Becker collection from greater depths. Present evidence supports but does not completely prove that buddingtonite at Sulphur Bank forms at relatively low temperatures, perhaps less than 120° C. Buddingtonite is the most abundant and most widely distributed mineral of hydrothermal origin at Sulphur Bank. It is absent in the acid environment related to oxidizing H_2S near and above the water table. In some places pyroxene andesite is almost completely replaced by buddingtonite, with only a few percent of other minerals such as sulfur, stibnite, pyrite, marcasite, ammoniojarosite(?), gypsum, barite, montmorillonite and anatase. In lake deposits and in rocks of the Franciscan Formation underlying the pyroxene andesite, quartz, chlorite, and mica are ordinarily stable or metastable, but albitic plagioclase has been partly to completely replaced by buddingtonite, preserving in its orientation some evidence of the original zoning and twinning. Clastic K-feldspar persists in the lake beds in at least some places, but some may have been replaced elsewhere by buddingtonite. All mercury-bearing ore specimens that have been tested contain buddingtonite except where cinnabar is associated with acid-leached rocks at and immediately above the former water table of the hot-spring system. Buddingtonite, however, is more widely distributed than cinnabar on the borders at moderate depths of the system.

Origin

The present water of the hot-spring system is concluded by White (1957, p. 1678–1679; White and Roberson, 1962, p. 421–422) to be unlike waters of probable magmatic or connate origin, and a metamorphic origin by dehydration of older rocks (Franciscan?) far below the present surface is favored. Most of the energy of the system may have come from the Quaternary volcanism of the area. Outstanding characteristics of supposed metamorphic water are the very high contents of CO_2 and boron relative to chloride (White *et al.*, 1963) and a high content of ammonia. The 460 to 540 ppm of NH_4 characteristic of the rising waters of the Sulphur Bank system are near the maximum recorded for thermal and mineral waters, and are probably the highest known anywhere in its proportion of ammonium to total cations (about 26 weight per cent or 31 ionic equivalent per cent). If the hypothesis of metamorphic origin of the water is correct, the ammonium has probably been released from clay minerals and micas, where it proxies readily for potassium because of identical charges and similar ionic radii.

Buddingtonite may occur elsewhere in environments relatively high in ammonium. The mercury-depositing hot-spring system of Ngawha,

New Zealand, is similar in many respects to Sulphur Bank (White *et al.*, 1963, p. F50–F51; White, 1955, p. 123–124), and its waters are relatively high in ammonium. Buddingtonite may also be found in the thermal system of the Geysers, California (Allen and Day, 1927), which is characterized at depth by superheated steam. As much as 1,400 ppm of NH_4 has been found at the surface in small acid hot springs.

Buddingtonite is likely to be found in epithermal ore deposits and fossil hot-spring systems characterized by high contents of ammonium in the waters. It is also likely to occur where ammonium is abundantly available from organic activity of various kinds.

Crystallography

X-ray data. The unit-cell parameters of buddingtonite were first derived from the *x*-ray powder-diffraction data (Table 1) by David B. Stewart and Daniel E. Appleman with a digital computer program for least-squares refinement of unit-cell parameters (Evans *et al.*, 1963). This program uses an initial set of approximate parameters to index the diffraction data, and proceeds to obtain the set of parameters that best fits the observed data by a cyclical process of refinement and reindexing. In the present study, the cell parameters and space group of sanidine were used as the initial approximation. After refinement, the presence of additional lines suggested that the unit cell of buddingtonite, although similar to that of sanidine, was primitive rather than *C*-centered. The final set of refined unit-cell parameters with their approximate standard errors is given in Table 2. Table 1 contains the d-spacings calculated from these refined unit-cell parameters and the observed d-spacings. The agreement is good.

A single-crystal investigation of buddingtonite was carried out by our colleague Malcolm Ross, using Buerger precession techniques. Although the available crystals were extremely small and imperfect, measuring about 0.05 mm on edge, the monoclinic unit-cell parameters and space group were obtained by using unfiltered molybdenum radiation and exposure times of approximately 100 hours. The *hk*0, 0*kl*, 1*kl*, *hk*1, and *hkh* reciprocal lattice nets were photographed. The condition limiting the possible reflections is

$$0k0{:}k = 2n$$

so that the space group is either $P2_1$ or $P2_1/m$. Table 2 lists the unit-cell data obtained by the single-crystal techniques. The agreement with the data obtained by least-squares refinement of the *x*-ray powder data is satisfactory.

TABLE 1. *X*-RAY DIFFRACTION DATA FOR BUDDINGTONITE AND FOR SYNTHETIC K-FELDSPAR

Calculated[1]		Observed				
		Buddingtonite Sulphur Bank mine, Lake County[2] California		K-feldspar (High sanidine, synthetic)[3]		
hkl	d_{hkl}	d_{hkl}	I	d_{hkl}	I	hkl
100	7.91					
110	6.76	6.75	16	6.65	6	110
001	6.63					
020	6.52	6.52	96	6.51	9	020
$\bar{1}01$	6.45					
011	5.91	5.91	33	5.869	9	$\bar{1}11$
$\bar{1}11$	5.78					
120	5.03					
021	4.65					
$\bar{1}21$	4.59					
101	4.32	4.33	65	4.241	50	$\bar{2}01$
$\bar{2}01$	4.18					
111	4.10					
$\bar{2}11$	3.98	3.98	33	3.947	20	111
200	3.95			3.87	3B	200
130	3.81	3.81	100	3.789	80	130
210	3.78					
031	3.63	3.63	12	3.623	15	$\bar{1}31$
131 121	3.60	3.60	5			
$\bar{1}02$	3.59					
$\bar{2}21$	3.52			3.557	12	$\bar{2}21$
$\bar{1}12$	3.462	3.462	23	3.459	50	$\bar{1}12$
220	3.380	3.381	72	3.328	100	220
002	3.314	3.314	34	3.287	60	$\bar{2}02$
040	3.258	3.258	62	3.258	35	040

(*continued on next page*)

[1] All calculated spacings listed for $d_{hkl} \geq 2.500$. Indices from least-squares refinement of *x*-ray powder data by David B. Stewart and Daniel E. Appleman (Table 2) using digital computer program (Evans, *et al.*, 1963).

[2] Split of analyzed sample DW-1. *X*-ray diffractometer data are: Chart X-2501; Cu/Ni radiation $\lambda CuK_\alpha = 1.5418A$; aluminum powder used as internal standard; scanned at $\frac{1}{4}°$ per minute from 10–90°2θ. Faint lines due to FeS_2, anatase, and ammoniojarosite(?), have been omitted.

[3] *X*-ray Powder Data File card 10-353.

TABLE 1—(*continued*)

Calculated[1]		Observed				
		Buddingtonite Sulphur Bank mine, Lake County[2] California		K-feldspar (High sanidine, synthetic)[3]		
hkl	d_{khl}	d_{khl}	I	d_{khl}	I	hkl
$\bar{2}02$	3.227	3.225	69	3.223	80	002
012	3.212					
$\bar{1}22$	3.145					
$\bar{2}12$	3.132	3.129	3			
131	3.064					
140	3.012	3.014	39	2.995	50	131
$\bar{2}31$	3.011					
022	2.954	2.954	13			
201	2.933			2.932		
041	2.924					
230						
						$\bar{2}22$
$\bar{1}41$	2.908	2.910	20	2.905	20	041
$\bar{2}22$	2.891	2.894	15	2.889		022
211	2.861	2.862	9			
$\bar{3}01$	2.857					
$\bar{3}11$	2.790					
$\bar{1}32$	2.768	2.767	9	2.766	15	$\bar{1}32$
102	2.707					
221	2.675					
112	2.650	2.650	12			
300	2.635					
032						
$\bar{3}21$	2.616					
$\bar{3}02$	2.612					
141	2.602	2.604	23	2.608	12	$\bar{3}12$
$\bar{2}32$	2.590					
310	2.583			2.582	30	221
$\bar{2}41$	2.569					$\bar{2}41$
$\bar{3}12$	2.561					
240	2.514	2.515	11			
		2.432	12			
		2.381	7			
		2.319	6			
		2.175	28	2.171	20B	060
		2.151	8			
		2.058	6			
		1.989	8			

(*continued on next page*)

TABLE 1—(*continued*)

Calculated[1]		Observed				
		Buddingtonite Sulphur Bank mine, Lake County[2] California		K-feldspar (High sanidine, synthetic)[3]		
hkl	d_{khl}	d_{khl}	I	d_{khl}	I	hkl
		1.979	8			
		1.947	3			
		1.859	7			
		1.802	13			
		1.797	19	1.793	—	$\bar{2}04$
		1.759	6			
		1.654	6			
		1.614	4			
		1.509	15			
		plus additional lines all with I≤10		plus additional lines		

Morphology. Most buddingtonite is anhedral and cryptocrystalline, but some tiny euhedral crystals up to 0.05 mm line cavities and cracks. Measurement of approximate interfacial angles was made using a petrographic microscope and was found to be in reasonably good agreement with those calculated from the unit-cell data. Forms noted are {001}, {010}, {110} and {$\bar{1}$01}. Buddingtonite corresponds closely to orthoclase in habit (Fig. 1) and in interfacial angles. Possible twinning was noted in several crystals but could not be determined definitely, owing to the minute size of the crystals and to the low birefringence.

PHYSICAL AND OPTICAL PROPERTIES

Buddingtonite has good {001} and distinct {010} cleavages; however rupture takes place more commonly by subconchoidal fracture than by cleavage. The mineral is brittle; its hardness ($5\frac{1}{2}$) was determined by rubbing minute crystals on clear faces of apatite (H-5), analcime (5), and orthoclase (6), and also by rubbing the mineral between glass slides. The surfaces were then examined for scratches under the microscope; only orthoclase remained unscratched by buddingtonite. Marcasite, with hardness 6 to $6\frac{1}{2}$, has positive relief compared to buddingtonite in polished section.

Individual crystals of buddingtonite are colorless, transparent, and

TABLE 2. UNIT-CELL DATA FOR BUDDINGTONITE, $NH_4AlSi_3O_8 \cdot 1/2H_2O$, AS OBTAINED BY SINGLE-CRYSTAL TECHNIQUES AND BY LEAST-SQUARES REFINEMENT OF *X*-RAY POWDER DATA

	Single-crystal data[1]	*X*-ray powder data[2]
Crystal system	Monoclinic	Monoclinic
d_{100}	7.92Å	7.905Å
d_{010}	13.04	13.032
d_{001}	6.62	6.629
β	113°±1°	112°44′±1′
—	(for β=112°44′)	
a	8.59±0.06Å	8.571±0.003Å
b	13.04±0.05	13.032±0.003
c	7.18±0.05	7.187±0.001
$a:b:c$	—	0.658:1:0.551
Cell volume	742 Å^3	740.42 Å^3
Cell contents	$4[NH_4AlSi_3O_8 \cdot 1/2H_2O]$	$4[NH_4AlSi_3O_8 \cdot 1/2H_2O]$
Space group	$P2_1$ or $P2_1/m$	—
Density (calc.)	2.38 gcm^{-3}	2.38$_8$ gcm^{-3}
Specific gravity (meas.)	2.32±0.01[3]	
	2.347[4]	

[1] Obtained by Malcolm Ross, using Buerger precession techniques. Unfiltered Mo radiation, λMoK_α=0.7107Å.

[2] Derived by David B. Stewart and Daniel E. Appleman using a digital computer program for least-squares refinement of unit-cell parameters (Evans, *et al.* 1963).

[3] Determined (Lee) by the sink-float method and centrifuging using bromoform-acetone mixtures whose specific gravities were checked with a Westphal balance.

[4] Pycnometric determination (Fahey) at 25 C on the analyzed sample which contained slightly more inclusions of FeS_2.

have a vitreous luster, but the compact material is translucent, cloudy, and has an earthy luster. The powder and streak of the compact material are light gray (Munsell color N7) to darker yellowish gray, depending upon the abundance of iron sulfide or clay mineral impurities. The analyzed sample is light olive gray (5Y 6/2). Buddingtonite is not fluorescent.

Buddingtonite is colorless in transmitted light. It is biaxial (+) with the following optical properties:

α=1.530±0.002	X$\wedge a$=+4°
β=1.531±0.002	Z=b
γ=1.534±0.002	Y$\wedge c$=19°

The axial angle, 2V, was not determined.

CHEMICAL PROPERTIES

Analysis. The material used for analysis (Table 3) was crushed to −200 mesh and was separated from the fines by settling in water. After a pass

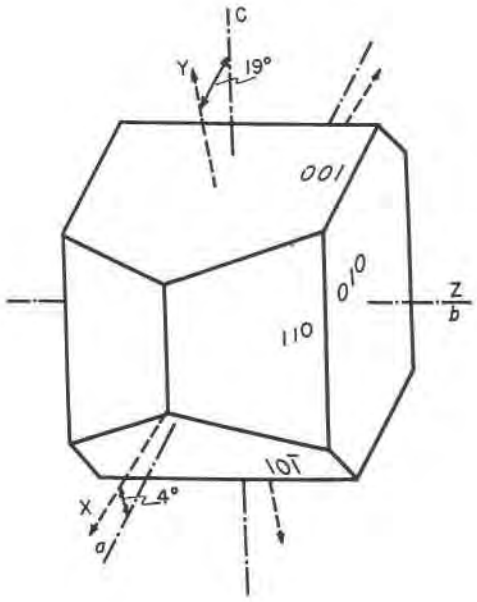


FIG. 1. Typical habit and optical orientation of buddingtonite.

TABLE 3. CHEMICAL ANALYSIS OF BUDDINGTONITE

	Weight percent	Recalc.[1]	Molecular proportions		Ratios[2]
SiO_2	63.80	66.89	1.1132		5.98
Al_2O_3	19.16	20.09	0.1970		1.06
Fe_2O_3	1.85	—			
MgO	0.21	0.22	.0055		
CaO	0.04	0.04	.0007		
BaO	0.26	0.27	.0018		
				0.1760	0.95
Na_2O	0.06	0.06	.0010		
K_2O	0.62	0.65	.0069		
$(NH_4)_2O$	7.95	8.34	.1601		
H_2O	3.28	3.44	.1909		1.03
H_2O^-	0.88	—			
TiO_2	0.99	—			
S	1.59	—			
Total	100.69	100.00			
Oxygen correction for S	0.59				
	100.10				

J. J. Fahey, analyst.

[1] Recalculated to 100 percent after subtracting FeS_2, S, TiO_2, and H_2O^-.

[2] Formula: $(NH_4)_2O \cdot Al_2O_3 \cdot 6SiO_2 \cdot H_2O$ or $NH_4AlSi_3O_8 \cdot \frac{1}{2}H_2O$.

through the Frantz isodynamic separator, final purification was achieved by centrifuging in heavy liquids. Approximately 4 gm were submitted for analysis. The purity of the sample was checked optically and with *x*-ray diffraction. Buddingtonite was not mechanically separated completely from its associated impurities, which are chiefly marcasite and montmorillonite. The chemical analysis shows that FeS_2 is less than 3 per cent; the amount of montmorillonite is low enough to be undetected in the *x*-ray pattern of the analyzed material. In addition to these impurities there are inclusions of anatase, ammoniojarosite(?), and liquid or gas; a grain count showed less than 0.05 per cent quartz. The total amount of impurities is probably less than five per cent.

The methods used in the analysis, except that for the determination of ammonia, were standard methods of chemical analysis contained *in* "Applied Inorganic Analysis," by Hillebrand *et al.* (1953).

The ammonia was determined by expelling it from the mineral with a strong solution of NaOH, collecting it in an excess (35.00 ml) of 0.1 normal H_2SO_4 and titrating the excess acid with 0.1 normal NaOH. One milliliter of 0.1 normal H_2SO_4 is equivalent to 0.0017032 gm NH_3 or 0.005208 gm $(NH_4)_2O$.

The detailed procedure is as follows: To the sample ($\frac{1}{2}$ gm) in a 500 ml Kjeldahl flask that contains 20 to 30 glass beads to minimize bumping, is added 300 ml H_2O and approximately 50 gm NaOH. The flask is immediately connected to a trap which in turn is connected to a vertical water-cooled glass condenser, the delivery end of which is placed below the surface of 35 ml of 0.1 normal H_2SO_4 contained in a 300 ml Erlenmeyer flask. The function of the trap is to prevent any of the strong solution of sodium hydroxide contained in the Kjeldahl flask from entering the condenser and reacting with the standard H_2SO_4 in the Erlenmeyer flask.

The Kjeldahl flask is heated until the sodium hydroxide solution gently boils, care being taken to prevent violent bumping. The heating is continued until about 150 ml distillate is in the Erlenmeyer flask that contains the standard sulfuric acid. This takes about one hour, in which time the ammonia of the sample has been completely displaced and has reacted with the standard sulfuric acid.

The results of a quantitative spectrographic analysis of buddingtonite are shown in Table 4. Because the sample was not entirely pure, the values reported represent the maximum concentrations of the minor elements present in buddingtonite.

Considering the low summation of total cations and the excess of water over that required by the proposed ideal formula, it is tempting to postulate the presence of oxonium ion (also known as hydronium) in the bud-

dingtonite structure. The presence of oxonium ion has been suggested for various minerals and a summary is given by Ginzburg and Yukhnevich (1962). However, Christ (1960, p. 338) has pointed out " . . . formation of hydronium ions in crystals appears to take place only in the hydrates of strong acids, as for example $HNO_3 \cdot 3H_2O$ . . . . " The presence or absence of the oxonium ion in minerals is thus a matter of some debate. We can give no positive proof of the existence of this ion in buddingtonite (*see* Infrared Absorption Analysis). Alternative possibilities are larger

TABLE 4. SPECTROGRAPHIC ANALYSIS OF BUDDINGTONITE[1]

Cu	0.0036
Mn	0.0082
Co	0.0007
Ni	0.0003
Cr	0.010
V	0.0064
Ga	0.0020
Sc	0.0020
Y	0.007
Yb	0.0007
Ti	0.70
Zr	0.015
Be	0.0004
Mg	0.22
Ca	0.026
Sr	0.0040
Ba	0.20
B	0.045

[1] Harry Bastron, analyst. Data given in percent. Looked for but not found: Ag, Au, Hg, Ru, Pd, Ir, Pt, Mo, Re, Ge, Sn, Pb, As, Sb, Bi, Zn, Cd, Tl, In, La, Th, Nb, Ta, Li, P. For limits of sensitivity, see Bastron *et al.*, 1960. Amounts of major elements reported in Table 3.

amounts of impurities than we have assumed or that there has been some loss of ammonia since the formation of the mineral, although the resistance to acid attack, slight ionic exchange capability under normal exchange conditions, and dehydration and infrared studies suggest that NH_4^+ is tightly bound within the structure.

Synthesis. A compound similar to buddingtonite has been synthesized by Barker (1962), using $KAlSi_3O_8$ and dry NH_4Cl at 650–700° C. and 2,000 bars confining pressure. A comparison of the *x*-ray powder data for the synthetic compound and for buddingtonite shows them to be nearly identical. A detailed account of this work and earlier attempts to synthesize

an ammonium feldspar are being given in an accompanying paper by Barker.

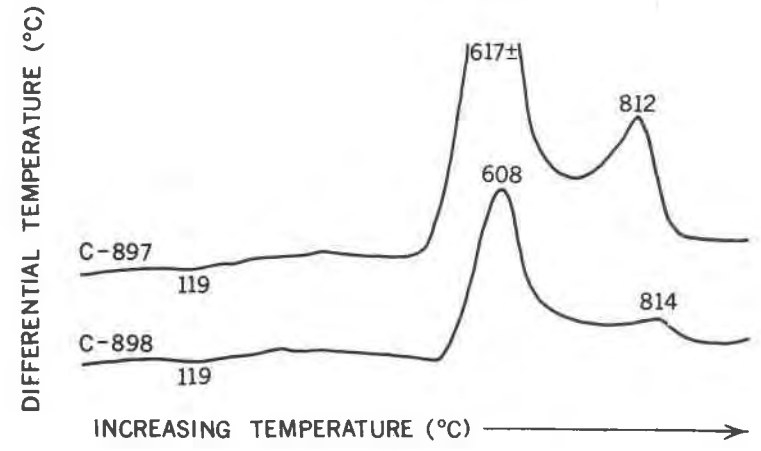
Solubility. The solubility of buddingtonite was not determined, but the mineral showed no sign of attack after 20 hours in hot 1:1 HCl or after 2 hours in warm 1:1 HNO_3 and, except for the disappearance of lines due to marcasite, the x-ray pattern remained unchanged.[1] A split of the analyzed sample, previously ground to $-100+200$ mesh and washed with water, was ground to a soft powder in a hand mortar, leached with distilled water, and the leachate allowed to evaporate. Synthetic boussingaltite, $(NH_4)_2(Mg, Fe)(SO_4)_2 \cdot 6H_2O$, and koktaite, $(NH_4)_2Ca(SO_4)_2 \cdot H_2O$, were precipitated from the solution, indicating that ammonia is probably released upon destruction of the structure by fine grinding. It is also possible that some of the ammonia and calcium may originally have been present in the fluid inclusions.

Pyrognostics. When heated in a closed tube below red heat, buddingtonite gives off water and ammonia. The associated iron sulfide decomposes and the sulfur oxidizes, yielding SO_3 which then combines with the ammonia. Crystals of $(NH_4)_2SO_4$ precipitate from the solution in the cool portion of the tube. At red heat in an open crucible, buddingtonite turns white, minute cracks appear, and numerous vermiform channels may be seen under the microscope. Outlines of the minute crystals are preserved, but their edges are rounded; the material has become a glass with $n=1.491$ and with numerous inclusions. After one week at about 1000° C., mullite, α-cristobalite and α-tridymite crystallize from the glass. Before the blowpipe buddingtonite fuses imperfectly to a glass plus crystalline material; its fusibility is about the same as that of orthoclase ($=5$), which is notably higher than that of any of the zeolites.

Differential Thermal Analysis

The DTA data shown in Fig. 2A were obtained by George T. Faust who has discussed previously the apparatus and techniques (Faust, 1948, 1950). Acid-treated samples of buddingtonite were used to eliminate thermal effects due to the decomposition of FeS_2. The shallow endothermic trough at 119° C. is interpreted as loss of water, 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. The products of the relatively rapid DTA heating are poorly crystallized, having an x-ray pattern that shows only a broad hump centered at 4.08 Å (α-cristobalite?) and a few lines due to anatase (partly inverted to rutile).

[1] Partial chemical analysis of one of the samples (DW-1) after acid-treatment showed no loss of ammonia and less than 0.2 per cent iron.



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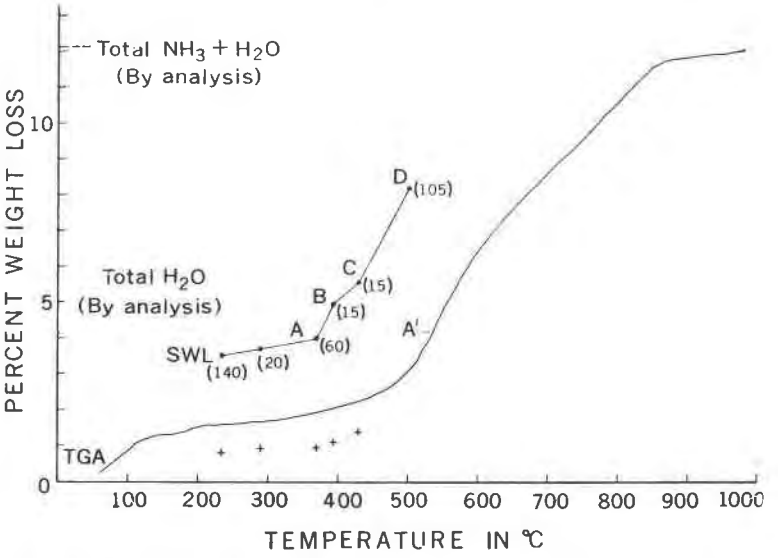

B

FIG. 2A. DTA curves for acid-treated buddingtonite sample DW-1, record C-897, and sample 582-M, record C-898. The curves were obtained as photographic records; heating rate 12 C. per minute; resistances of 600 and 900 ohms respectively in the galvanometer circuit.

FIG. 2B. Dehydration curves for buddingtonite. SWL—static weight-loss curve; time in minutes at temperature is shown in parentheses; per cent weight regained at room temperature after rehydration from circled points is shown by crosses. TGA—thermogravimetric curve.

Dehydration

A static weight loss (SWL) upon heating and a thermogravimetric analysis (TGA) were used to determine the dehydration characteristics of buddingtonite, with results shown as Fig. 2B. In the static method buddingtonite was heated in a covered platinum crucible in an electric furnace at various temperatures and periods of time. The sample was weighed as soon as possible after each removal from the furnace, again after twenty minutes, and finally after standing overnight to determine the extent of rehydration. Buddingtonite is completely anhydrous by 370° C. (point A, Fig. 2B), but it regains considerable moisture after twenty minutes and essentially rehydrates after standing overnight at room temperature and humidity. The slope ABC in Fig. 2B represents oxidation of the FeS_2 impurity, with essentially no loss of ammonia. Buddingtonite rehydrates up to point C (430° C.), but beyond this point on slope CD NH_4 is continuously driven off (as $NH_3+\frac{1}{2}H_2O$) with simultaneous destruction of the structure. *X*-ray and optical examination of a sample heated at 500° C. 105 minutes (point D) indicate that buddingtonite still persists.

The thermogravimetric analysis was made by E. J. Young using a Chevenard thermobalance with a heating rate of 300° C./hr. At this relatively rapid rate of heating the entire curve is displaced horizontally from the static curve toward higher temperatures and buddingtonite would appear to be anhydrous at 535° C. (point A′ in Fig. 2B) compared to the value 370° C. measured by the static method. The total weight loss of 12.0 per cent is in reasonable agreement with the 12.11 per cent ammonia plus total water reported in the chemical analysis of a separate sample.

The half mole of water present in buddingtonite thus appears to be zeolitic in nature. Some water is probably also contributed by liquid inclusions and by the montmorillonite impurity, but the amount is considered to be negligible. The reversible dehydration below 430° C. and the destruction of the buddingtonite structure above this temperature may be written:

1) $2NH_4AlSi_3O_8 \cdot 0.5H_2O \rightleftarrows 2NH_4AlSi_3O_8 + H_2O$
2) $6NH_4AlSi_3O_8 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 16SiO_2 + 6NH_3 + 3H_2O$

Ion Exchange

The ion exchange values for buddingtonite (Table 5) were determined by Harry C. Starkey (written communication, 1963). According to Starkey, the values for exchangeable NH_4 for both the heated and the unheated samples are based on single determinations; the ammonium was determined by distillation of an untreated sample. The water-soluble values are also based on single determinations; the rest of the values are

averages of duplicate runs. Because small portions of the samples were used, any error will have been magnified. An ammonium chloride batch method was used for determining the exchange capacity and exchangeable cations other than NH_4. The unheated sample was leached overnight (16 hrs) in 1N neutral NH_4Cl; the heated sample was leached overnight (16 hrs) in 1N NH_4Cl at 118° C. in a pressure cooker. The Ca in solution was apparently increased on heating. This may be due to dissolution of some of the sample, although some zeolites will give an apparent increase in exchange capacity under these conditions. The values for the amount of NH_4 and Ca soluble in water are included to point out that some of the Ca and NH_4 listed as exchangeable does not come from the exchange position, but originates from sample dissolution or from soluble salts present as impurities. Determinations of Na and K were made by flame

TABLE 5. ION EXCHANGE VALUES (IN M.E./100 G) FOR BUDDINGTONITE

	Na	K	Ca	Mg	NH_4	Sum of cation	Determined capacity
Unheated	—	—	11.8	—	9.0	20.8	14.1
Heated	—	—	23.6	—	9.0	32.6	19.4
Water soluble NH_4—1.7							
Water soluble Ca —7.0							

Harry C. Starkey, analyst.

photometry, but neither was found. Ca and Mg were determined by versene titration but only Ca was identified.

The figure for Ca may still include some other cations because it exceeds by several times the amount of Ca determined by chemical analysis. The figure for NH_4 shows that only about 3 per cent of the total NH_4 was exchanged or dissolved from buddingtonite.

In a study of feldspar surfaces as ion exchangers, Marshall (1962) found that under mild conditions most cations in the reacting solution affect only a thin layer 1 to 2 unit-cells deep, but that ammonium and hydrogen ions apparently penetrate more deeply into and are incorporated by the structure. Barker (1962) has shown that the K or Na of alkali feldspars can be almost entirely exchanged by NH_4 under hydrothermal pressures and temperatures.

Further study of ion exchange relationships in buddingtonite is clearly needed. The structural state of buddingtonite can be clarified by exchanging ammonium with sodium and potassium, and by replacing the cations in feldspars of known structural state by ammonium.

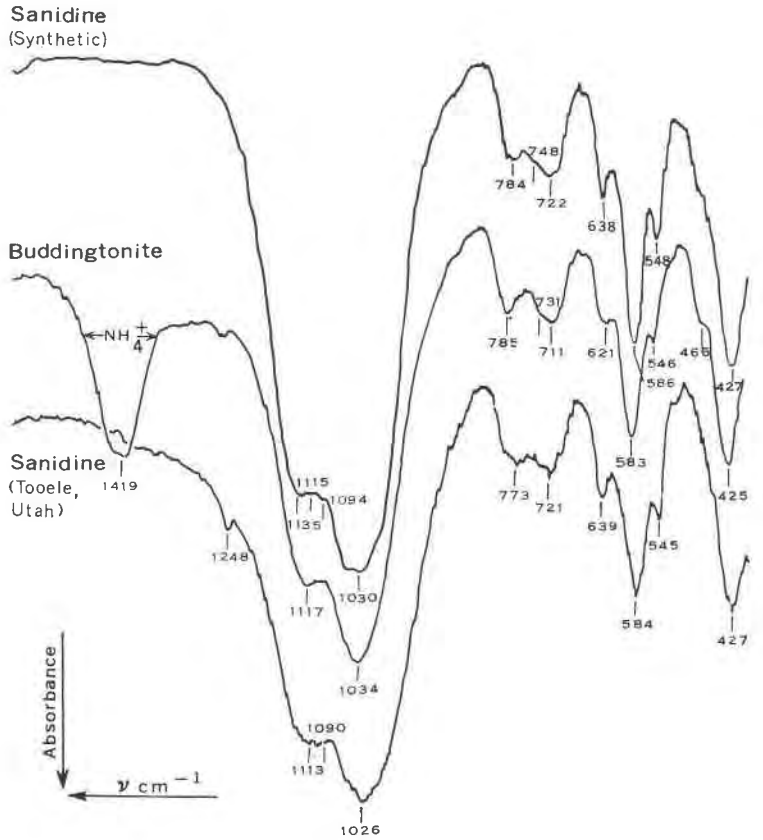

FIG. 3. Infrared spectra of buddingtonite and synthetic and natural sanidine in the region 1600–400 cm^{-1}. R. J. P. Lyon, analyst. Sanidine, synthesized by Julian Hemley, sample 3051, run A5769. Buddingtonite, sample DW-1, run 6077. Sanidine, Tooele, Utah, sample GC-3154, run 6072.

INFRARED ABSORPTION ANALYSIS

Spectra of buddingtonite compared with those of natural and synthetic sanidine (Lyon, 1963, p. 67) in the region 1600–400 cm^{-1} are shown in Fig. 3. These curves were prepared by R. J. P. Lyon of Stanford Research Institute, who noted the similarity in the framework structures between monoclinic K-feldspar and buddingtonite indicated by their infrared spectra. The only major differences between the curves are the presence of the absorption maxima for the NH_4^+ ion, residual water (H_2O^-), and lattice water (H_2O^+) in the curve for buddingtonite. The infrared absorption curve of buddingtonite shows little or no similarity to the curves of

the more common zeolites studied by Lyon. A comparison of the infrared frequencies for the NH_4^+ ion and for H_2O reported by Mortland *et al.* (1963) for NH_4-montmorillonite and those measured in the present study of buddingtonite are shown in Table 6. According to Mortland *et al.*, shifting of the peaks toward high frequencies indicates a state of greater freedom for the NH_4^+ ion. From the shift of most of the NH_4^+ peaks of buddingtonite toward lower frequencies it would appear that the NH_4^+ ion is more tightly bonded in the feldspar-like framework than it is in NH_4-montmorillonite.

Residual water (H_2O^-) with an absorption at 3412 cm^{-1} was removed from the spectrum when the sample was dried overnight at 110° C. at a

TABLE 6. ASSIGNMENT AND INFRARED FREQUENCIES (IN CM^{-1}) FOR NH_4^+ AND H_2O IN BUDDINGTONITE AND NH_4-MONTMORILLONITE

Assignment	Buddingtonite	NH_4-montmorillonite[1]
Lattice water ($\sim H_2O^+$) (unbonded OH stretching)	3650–3600	3703–3655
Residual water ($\sim H_2O^-$) (bonded OH stretching)	3412	3425–3412
NH stretching	3296	3280
NH stretching	3068	3080
NH stretching	2848	2860
H-O-H bending	1620	1620
NH_4^+ bending	1419	1442–1427

[1] Data from Mortland *et al.* (1963).

pressure of 253 mm Hg. Lattice water (H_2O^+) with a peak at 3600 cm^{-1} was completely removed after drying for 48 hours at 200° C. at 253 mm Hg. Comparison of the infrared curves of buddingtonite dried at 200° C. and of natural material shows that there is no loss of NH_4^+ under these conditions.

We could find no evidence of the presence of oxonium ion in the infrared spectrum of buddingtonite. Ginzburg and Yukhnevich (1962) attribute a peak at 1670 cm^{-1} to the oxonium ion in their study of the infrared spectra of amphibole, whereas White and Burns (1963) ascribe a peak at about 3470 cm^{-1} to this ion in their study of hydrogen-saturated micas. No absorption maxima occur at these positions in the infrared curve of buddingtonite.

MINERALOGICAL CLASSIFICATION

Buddingtonite is closely related to orthoclase and sanidine (Table 7) in its *x*-ray powder pattern, unit-cell size, crystal morphology, optical

TABLE 7. COMPARISON OF CRYSTALLOGRAPHIC, OPTICAL AND PHYSICAL DATA FOR BUDDINGTONITE, ORTHOCLASE AND SANIDINE

	Buddingtonite	Orthoclase[1]	Sanidine[2]
Cell contents	$4[NH_4AlSi_3O_8 \cdot \frac{1}{2}H_2O]$	$4[KAlSi_3O_8]$	$[4KAlSi_3O_8]$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/m$ or $P2_1$	$C2/m$	$C2/m$
a	8.571 ± 0.003Å	8.562Å	8.564Å
b	13.032 ± 0.003	12.996	13.030
c	7.187 ± 0.001	7.193	7.175
β	$112°44' \pm 1'$	116°0.9′	115°59.6′
Cell volume	740.42Å^3	719.29Å^3	719.65Å^3
Density (calc.)	2.38_8 gcm^{-3}	2.57_0 gcm^{-3}	2.56_9 gcm^{-3}
Specific gravity (meas.)	2.32 ± 0.01	2.563	2.555
Indices of refraction:			
α	1.530 ± 0.002	1.519	1.519
β	1.531 ± 0.002	1.523	1.523
γ	1.534 ± 0.002	1.524	1.523
Optical orientation	$X \wedge a = 4°$ $Z = b$ $Y \wedge c = 19°$	$X \wedge a = 5°$ $Z = b$ $Y \wedge c = 21°$	$X \wedge a = 5°$ $Y = b$ $Z \wedge c = 21°$
Cleavage	{001} good {010} distinct	{001} perfect {010} good	{001} perfect {010} good
Hardness	$5\frac{1}{2}$	6	6
Fusibility	5	5	5

[1] Crystallographic and optical data adapted from Cole, *et al.* 1949.
[2] Sanidinized orthoclase, data from same source as[1].

properties, hardness, fusibility, resistance to chemical attack and infrared absorption properties. Further classification depends upon details of the crystal structure which may remain unknown unless more suitable material can be found for single-crystal structural analysis. The possibility that there may be zeolites with a feldspar framework expanded to provide room for water molecules has been suggested by Smith and Rinaldi (1962, p. 211). Buddingtonite is evidently the ammonium analogue of monoclinic K-feldspar when water is lost above about 370° C. At lower temperatures and normal water vapor pressures, the mineral most closely resembles orthoclase, but the associated water is zeolitic.

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Stewart determined the lattice type and refined the unit-cell parameters from the x-ray powder data; Malcolm Ross determined the space group from x-ray single-crystal pictures, and he and Stewart constructively reviewed the manuscript; Harry Bastron, Robert E. Mays, and Chris Heropoulos spectrographically analyzed samples of buddingtonite; Edward J. Young ran dehydration experiments; and Harry C. Starkey determined the ion exchange capacities. Leonice Beatty and Lois M. Jones made a partial analysis of acid-treated buddingtonite; George T. Faust obtained the DTA data on these samples. All of the above are colleagues with the U. S. Geological Survey. We are also indebted to Dr. Ron J. P. Lyon of the Stanford Research Institute for the infrared absorption curves and for valuable discussions. We are especially grateful to Dr. Daniel S. Barker for the exchange of ideas and manuscripts prior to publication.

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