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AMEGHINITE, Na₂O·3B₂O₃·4H₂O, A NEW BORATE FROM ARGENTINA¹

L. F. Aristarain and C. S. Hurlbut, Jr., Department of Geological Sciences, Harvard University.

Abstract

Ameghinite is a new hydrous sodium borate found at the Tincalayu borax deposit Salta, Argentina. It occurs in small nodules embedded in borax associated with ezcurrite and rivadavite.

The new mineral is monoclinic, 2/m or m; space group C2/c or Cc; a=18.454 Å, b=9.895 Å, c=6.322 Å ± 0.005 Å, $\beta=104^{\circ}20'$; a:b:c=1.8650:1:0.6389; cell volume 1118.1 ų; cell contents: $4[\text{Na}_2\text{O}\cdot 3\text{B}_2\text{O}_3\cdot 4\text{H}_2\text{O}]$. Crystals elongated on [010] with a maximum length of 5 mm are frequently bent. Faces of eight forms were observed; those best developed are: $c\{001\}$, $a\{100\}$, $p\{011\}$, and $m\{110\}$. The strongest lines in the X-ray powder photograph in Å are: 3.065 (100), 3.147 (76), 2.548 (29), 3.352 (17), 2.914 (17).

Ameghinite is colorless but under ultraviolet light shows a strong pale blue fluorescence and phosphorescence. The hardness is $2\frac{1}{2}$; the specific gravity 2.030 ± 0.006 (meas.) 2.037 (calc.). Cleavage: {100} good, {010} and {001} poor. Optically biaxial (-), α =1.429, β =1.528, γ =1.538; 2V=33°; r<r; Z=b, $X \land c$ =9°.

The chemical analysis recalculated to 100 percent: B₂O₃ 59.60, Na₂O 19.60, H₂O 20.80. The mineral is soluble in cold water. DTA shows major endothermic peaks at 245° (strong) and 780°C and an exothermic peak at 635°C.

The new mineral is named in honor of Florentino and Carlos Ameghino, Argentine geologists of late 19th and early 20th centuries.

Introduction

The Tincalayu borax deposit in the province of Salta, Argentina has already been the source of two new minerals. Ezcurrite, $2\mathrm{Na_2O} \cdot 5\mathrm{B_2O_3} \cdot 7\mathrm{H_2O}$, described by Muessig and Allen (1957) and later restudied by Hurlbut and Aristarain (1967), and rivadavite, $3\mathrm{Na_2O} \cdot \mathrm{MgO} \cdot 12\mathrm{B_2O_3} \cdot 22\mathrm{H_2O}$ described by Hurlbut and Aristarain (1967). The present paper is a description of a third new mineral, ameghinite, $\mathrm{Na_2O} \cdot 3\mathrm{B_2O_3} \cdot 4\mathrm{H_2O}$, from the same mine. These minerals, unknown elsewhere, undoubtedly owe their origin to the unusual type of occurrence. Original borate playa

¹ Mineralogical contribution No. 435, Harvard University.

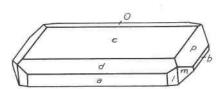
deposits were buried and subsequently folded and faulted forming a plug-like body composed essentially of massive borax. The other uncommon borates, kernite and macallisterite, are also present. For the geology of the deposit and the adjacent area one is referred to Catalano (1930, 1964) and Muessig and Allen (1957).

Ameghinite is found in nodular masses embedded in the massive borax. Of the several nodules that have been observed, most of them are nearly spherical and about a centimeter in diameter, but one is larger and pipelike in shape—3 centimeters in diameter and 5 centimeters long. The manner of occurrence of ameghinite is identical with that of ezcurrite and rivadavite with which it is closely associated. In fact a single study specimen $25 \times 15 \times 12$ centimeters contains nodules of all these minerals. However, unlike the other two minerals that are found in contact with the surrounding borax, the nodules of ameghinite are in every case separated from the borax by tincalconite. The crystals at the centers of the nodules are intergrown with one another giving a massive appearance but near the periphery project outward as single individuals surrounded by tincalconite (Fig. 1).

Ameghinite is named in honor of two great Argentine geologists; the brothers Florentino and Carlos Ameghino. Florentino (1854–1911) was a man of great genius who published nearly 200 memoirs and monographs



Fig. 1. Ameghinite crystals (gray) embedded in tincalconite (white). Note the bent crystal with sharp boundaries near the center of the photograph. Magnification ×7.



Y a 100 2v 33

Fig. 2. Ameghinite crystal showing all the observed forms.

Fig. 3. Optical orientation of ameghinite.

in paleontology, stratigraphy and anthropology. Carlos (1865–1936) was a field geologist with exceptional abilities as an observer and collector. George Gaylord Simpson (1948) writes of them, "The partnership of the Ameghino brothers was an outstanding example of teamwork and their achievement was one of the most remarkable in scientific history."

MORPHOLOGY

Crystals of ameghinite are characteristically elongated on [010] and flattened on $\{001\}$ (Fig. 2). On the largest crystals, about 5 millimeters long, the $\{001\}$ faces are frequently curved as though bent around the a axis. The smaller crystals, one millimeter or less in length, lack the pronounced curvature but even they show some bending and give a series of signals from the $\{001\}$ faces. Otherwise the smaller crystals give good reflections with consistent goniometric measurements. The relative dimensions along c, a and b axes are approximately 1:2:4.

Twelve crystals were measured on the reflecting goniometer with [010] the axis of rotation. The forms listed in Table 1. were present on all crystals with the exception of $\{310\}$ which was found on only two crystals. The axial ratios derived from the morphology differ only slightly from those obtained from the X-ray measurements. The latter ratios were used in calculations of the values given in the Angle Table, but in no case do the ϕ and ρ angles differ more than 10 minutes from the measured.

PHYSICAL AND OPTICAL PROPERTIES

Ameghinite has three cleavages— $\{100\}$ very good, and $\{001\}$ and $\{010\}$ poor. It is extremely brittle and where cleavage is not developed on crushing, breaks with a conchoidal fracture. The crystals are quite colorless and transparent with a vitreous luster. A most characteristic feature is its fluorescence and phosphorescence when exposed to ultraviolet light. Under both long- and short-wave lengths it fluorescess a pale blue very similar to the fluorescence of scheelite, and continues to glow for many seconds after removal of the exciting rays. The hardness is $2\frac{1}{2}$.

The specific gravity of ameghinite was measured by the modified

Table 1. Ameghinite Angle Table Monoclinic; Prismatic—2/m*

 $a:b:c=1.8650:1:0.6389; \beta=104^{\circ}20'; p_0:q_0:r_0=0.3426:0.6190:1$ $r_2:p_2:q_2=1.6155:0.5534:1; \mu=75^{\circ}40'; p_0' 0.3539, q_0' 0.63890, x_0' 0.2555$

		9	6	f)	¢	12	$\rho_2 =$	= B	(A	1
с	001	90°	00′	14°	20′	75°	40′	90°	00′	0°	00′	75°	40
b	010	0	00	90	00	_	_	0	00	90	00	90	00
a	100	90	00	90	00	0	00	90	00	75	40	0	00
m	110	28	58	90	00	0	00	28	58	83	10	61	02
l	310	59	01	90	00	0	00	59	01	78	01	30	59
Þ	011	21	48	34	32	75	40	58	14	31	46	77	51
d	101	90	00	31	21	58	39	90	00	17	01	58	39
0	101	-90	00	5	36	95	36	90	00	19	56	95	36

^{*} Although the morphology points to the crystal class 2/m, X-ray study indicates the possibility of class m.

pycnometer method suggested by Fahey (1961) and by the Berman balance. The respective values obtained were 2.024 and 2.036. An average of these two values, 2.030 ± 0.006 , is taken as the measured specific gravity. The difference in the measurements may be attributed to small amounts of tincalconite (sp. g. 1.88) adhering to the surface of some of the crystal fragments used in the pycnometer method.

The optical properties of ameghinite are given in Table 2. In Figure 3 one can see that the X optical direction is almost perpendicular to $\{001\}$; thus crystals lying on this dominant form yield a nearly centered acute bisectrix interference figure. The axial angle was measured using a spindle stage. The high birefringence, 0.109, seems to be unique among the borate minerals.

X-RAY STUDY

The unit-cell dimensions were determined from precession photographs (Mo/Zr) with a, b and c as precessing axes; and Weissenberg photographs

TABLE 2. OPTICAL PROPERTIES OF AMEGHINITE

Na		
$\alpha = 1.429$	Opt. (-)	Z = b
$\beta = 1.528 \pm 0.001$	$2V = 33^{\circ}$	$X \land \epsilon = 9^{\circ}$
$\gamma = 1.538$	r < v weak	

(Cu/Ni) with b the rotation axis. The values given in Table 3 were refined with data derived from X-ray powder photographs. Extinctions in the single crystal photographs lead to the space groups C2/c or Cc. Because of the nature of the crystals, pyroelectric and piezoelectric tests were not performed and etch tests were indecisive in determining the crystal class. However, the morphology suggests that the crystals belong to the class 2/m.

The spacings given in Table 4 were derived from powder photographs (Cu/Ni) but with intensities obtained from diffractometer charts. The calculated d values were determined with an IBM 7094 Computer.

TABLE 3. UNIT CELL DATA FOR AMEGHINITE

a = 18.454 Å b = 9.895 Å c = 6.322 Å	Monoclinic C_2/c or (Cc) $\mu = 75^{\circ}40'$; $\beta = 104^{\circ}20'$
a:b:c=1.8650:1:0.6389 Cell volume 1118.1ų	Z = 4

Specific gravity: meas. 2.030 ± 0.006 ; calc. 2.037 for $Na_2O \cdot 3B_2O_3 \cdot 4H_2O$

CHEMICAL COMPOSITION

The small crystals of ameghinite occur either partially or completely surrounded by tincalconite (Fig. 1). Thus the problem of purification of a sample for chemical analysis involved chiefly the separation of these two minerals. Microscopic examination of ameghinite fragments separated by heavy liquids showed small amounts of tincalconite adhering to most of them. Treatment in a supersonic device, liberated most but not all of these adhering particles. An attempt was made to differentially dissolve the tincalconite in water but, since ameghinite was found to be only slightly less soluble, the method proved to be impracticable. Thus the sample on which the chemical analysis was made contained a small amount (estimated optically at two percent) of tincalconite.

Table 5 gives the chemical analysis of ameghinite from which is derived the ratios of the oxides Na₂O:B₂O₃:H₂O=1.11:3:4.05. From this we believe the theoretical formula to be Na₂O·3B₂O₃·4H₂O. A close similarity exists between the chemical analysis of the new mineral and analyses of ezcurrite and nasinite (Table 6). However, optical and X-ray study shows them to be completely different. See Figure 4 for a comparison of the diffractometer charts of ameghinite and ezcurrite. The assumed theoretical composition of ameghinite (Table 6, column 5) shows a considerable departure from the reported chemical analysis. For this reason many

TABLE 4. X-RAY POWDER DATA FOR AMEGHINITE

hkl	$d({ m obs})^{\scriptscriptstyle 1}$	$d({ m calc})^2$	I^3	hkl	d (obs)	d (calc)	I
200	8.935	8.940	1	733	1,600	1.601	<1
Ī11	5.315	5.309	6	842	1.585	1,585	<1
310	5.110	5.105	<1	333	1.579	1.580	<1
	4 051	3.103	<1 13		1.319	1.300	
020	4.951 4.741	4.948	13	352	1.548	1.548	<1
111	4.741	4.740	7	841)	1,531	1.531	<1
400	4.466	4.470	7	400		1.531 1.531	
220	4.322	4.329	7	243	1.503	1.503	1
021	3.845 3.749	3.849	7 7 7 3 3	752	1.487	1.488	<1
$\frac{3}{2}$ 21	3 749	3.754	3	062	1.453	1.452	<1
311	3.564	3.567	6	353	1.439	1.439	<1
221	3.352	3.351	17	534)		1,406	<1
	2 242	2 244	7		1.405	1 404	1
130	3.242 3.147	3.244		443)		1.404 1.375	
202	3.14/	3.146	76	370	1.375	1.375	<1
002	3.064	3.063	100	842	1.357	1.358	<1
600	2.984	2.980	7	860	1.325	1.327	< 1
312	2.914	2.913 2.815 2.700	17	371		1.326	
131	2.811 2.701	2.815	3	571	1.309	1.310	<1
202	2.701	2.700	10	424	1.302	1.302	<1
$\frac{1}{2}$ 22	2 655	2.655	11	172	1.290	1.290	<1
022	2.655 2.603 2.548	2.604	<1	112	1.274	1.200	<1
620	2.548	2.553	29		1 263		<1
602	2.346	2.333	11		1.263 1.226 1.218		<1
222	2.465 2.373	2.462 2.370	1	1	1 210		
	2.313	2.370			1 200		<1
340	2.283	2.285	1		1.209		<1
800	2.232	2.235 2.204	4		1.196		<1
622\ 712}	2.200	2.204	3		1.182 1.161		<1
440´	2,166	2.164	2		1,129		<1
T13	2 047	2.043	$\begin{bmatrix} 2\\7\\3 \end{bmatrix}$		1.095		<1
730	2 013	2.019	3		1.071		<1
150	1 066	1,967	<1		1.055		<1
113	1 037	1 036	3		1.031		<1
602	2.013 1.966 1.937 1.913	1 012	1		1.022		<1
		1.936 1.912 1.878	3		1.022		1
$\frac{350}{442}$	1.878	1.877			1.001		<1 <1
151	1.859	1.858	3		0.991		<1
242	1.826	1.824	1		0.987		<1
821	1.814	1.814	1		0.980		<1
223	1.768	1.767	<1		0.972		<1
641	1.740	1.741	<1		0.941		<1
551	1.720	1.721	<1		0.926		<1
442	1.720	1.675	1		0.830		>1
	1.675		1 2		0.830 0.794		<1 <1
323 260	1.638 1.621	1.639 1.622	3 <1		0.794		< 1

¹ Observed value obtained using CuK α =1.54178Å; CuK α 1=1.54051Å; Ni filter; camera diameter 114.59 mm.
² The calculated d values were obtained and indexed by means of an I.B.M. 7094 Computer. Computer time was obtained on N.S.F. Grant No. GP-2372, Harvard Univer-

sity.

The line intensities were derived from a diffractometer chart obtained with Cu radiation. For this purpose ameghinite was ground with about 30 volume percent glass to minimize preferred orientation.

	1 Wt. %	2 Wt. %	3 Mol.	4 Formula
	Wt. 70	recalculated	proportions	content
$\mathrm{B_2O_3}$	59.3	59.60	0.8558	3
Na_2O	19.5	19,60	0.3162	1.11
H_2O	20.7	20.80	1.1545	4.05
$\mathrm{H_2O}(-)$	0.6			
Total	100.1	100.00		

TABLE 5. CHEMICAL ANALYSIS OF AMEGHINITE

possible ratios of the molecular proportions were considered. From these calculations two theoretical formulas were found to agree approximately with the chemical analysis and the molecular weight calculated using the unit-cell dimensions and measured specific gravity. The ratios Na_2O : B_2O_3 : H_2O for these formulas are 1:3:4 and 4:11:15.

Column 6, Table 6, gives the chemical composition of the theoretical compound $4Na_2O \cdot 11B_2O_3 \cdot 15H_2O$ which agrees very well with the chemi-

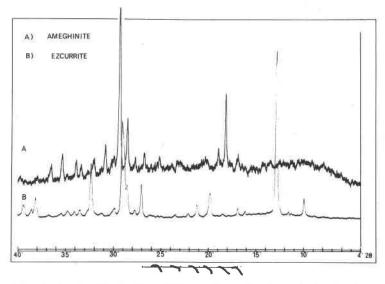


Fig. 4. Diffractometer charts of ameghinite and ezcurrite. Cu radiation, Ni filter. The preferred orientation because of cleavage affects the relative intensity of ezcurrite peaks.

^{1.} Jun Ito, Analyst.

^{2.} Analysis recalculated to 100% disregarding $H_2O-(90^{\circ}C)$ considered as essentially adsorbed water.

^{4.} Formula content assuming 3(B₂O₃).

cal analysis reported for ameghinite. However, using the measured cell dimensions, the molecular weight for such a compound would be 1284.2 with a calculated specific gravity of 1.90. The theoretical formula Na₂O $/3B_2O_3\cdot4H_2O$ leads to a molecular weight of 343.0 and a calculated specific gravity of 2.037 with Z=4 the molecular weight of the unit-cell content is 1372. As previously indicated the molecular weight calculated using the measured specific gravity (2.03) and cell volume (1118.1ų) is

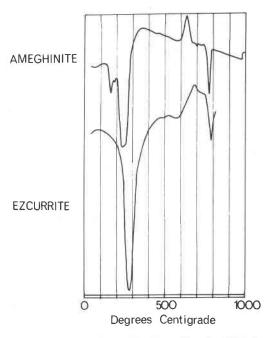


Fig. 5. DTA curves of ameghinite and ezcurrite. Rate of heating $25^{\circ}/\text{mi}$; reference junction 0°C ; thermocouple Pt/Pt+13% Rh; reference material Al_2O_3 .

1367.4. This close agreement clearly indicates that the formula for ameghinite is $Na_2O \cdot 3B_2O_3 \cdot 4H_2O$.

Ameghinite is soluble in cold water. In the blowpipe flame it intumesces and then fuses to a clear colorless glass in a manner similar to borax.

DIFFERENTIAL THERMAL ANALYSIS

A differential thermal analysis of ameghinite was made in air at one atmosphere from 40°–1000°C. The resulting pattern is shown in Figure 5. The first major endothermic peak at 245°C is interpreted as resulting

	1	2	3 Ezcurrite	4	5	6
	Ezcurrite	Nasinite	& nasinite theoretical		Ameghinite theoretical	4Na ₂ O · 11B ₂ O ₃ · 15H ₂ O
$\mathrm{B_2O_3}$	59.53	58,14	58.20	59.60	60.92	59.65
Na_2O	19.84	20.84	20.72	19.60	18.07	19.31
K_2O	0.18	19.15				-
H_2O	20.45	21.02	21.08	20.80	21.01	21.04
	100.00	100.00	100.00	100,00	100.00	100.00

Table 6. Comparison of Ameghinite with Other Borates of Similar Chemical Composition

- 1. Ezcurrite recalculated to 100%. Analysis by Ito of material from Tincalayu Mine; Hurlbut and Aristarain (1967).
 - 2. Nasinite recalculated to 100%. Analysis in Cipriani and Vannuccini (1961).
 - 4. This study from column 2, table 5.

from the loss of water. Following this reaction the material became amorphous and the resulting glass has an index of refraction of 1.50. The loss of water may take place in two or three steps as indicated by the small endothermic peaks at 165°C and 190°C. However, the X-ray powder patterns of samples heated at these temperatures show only minor changes in the intensity of a few lines.

The exothermic peak at 635°C results from the formation of a crystal-line phase. The crystals are platy with the X optical direction perpendicular or nearly perpendicular to the plates. The optical properties are: $\alpha = 1.458$, $\beta = 1.517$, $\gamma = 1.531 \pm 0.001$ (Na light); optically (-), $2V = 55^{\circ}$. This is the same phase that is formed on slow cooling of an ezcurrite melt form 780°C (Hurlbut and Aristarain, 1967). The spacings in Å and the relative intensities of strongest peaks as obtained on an X-ray diffractometer chart are: 4.43 (100), 2.97 (87), 3.31 (80), 3.88 (47), 8.69 (36), 3.44 (31).

This phase must have the composition Na₂O·3B₂O₃, although the refractive indices do not agree closely with those reported for the compound synthesized by Morey and Merwin (1936). It was this phase that Cipriani and Vannuccini (1961) produced on heating nasinite and biringuccite (hoeferite) and called "borate E".

The small endothermic peak at 700°C may be related to the formation of another crystalline phase reported by Jenckel (1936). However, this phase was not found in experiments performed during the present study.

The strong endothermic peak at 780°C (starting at 740°C and ending at 790°C) results from melting of the sample. Ponomareff (1914) reports

this melting point at 694°C; Cole, Taylor and Schales (1935) at 720°C; and Morey and Merwin (1936) at 766°C. These last authors report the melting to be incongruent, a fact confirmed in the present study.

A sample of ameghinite heated to 850°C for 12 hours and air quenched contains two crystalline phases, embedded in a glass (n=1.494). Because of the small size of the crystals and their small volume relative to the glass it was impossible to take X-ray photographs or obtain complete optical data. Both are birefringent. Crystals of one are equidimensional with refractive indices considerably greater than the index of refraction of the glass. The other occurs in radiating, bladed crystals of low birefringence and indices only slightly greater than the glass. It is optically (+) with Y parallel to the longest dimension and Z parallel to the shortest dimension, and appears to be orthorhombic. The first of these phases may be interpreted as Na₂O·4B₂O₃, the compound reported by Morey and Merwin (1936) formed on the incongruent melting of Na₂O·3B₂O₃. The second could be a polymorph of Na₂O·4B₂O₃ or the crystalline phase of Na₂O·3B₂O₃ reported by Jenckel (1936).

In Figure 5 the DTA pattern of ezcurrite is given to show the similarity with that of ameghinite.

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