RIVADAVITE, Na$_6$MgB$_{24}$O$_{40}$·22H$_2$O, A NEW BORATE FROM ARGENTINA[1]

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Abstract

The new mineral, rivadavite, is a hydrous sodium magnesium borate from the Tincalayu borax deposit, province of Salta, Argentina. It occurs in nodular aggregates imbedded in borax.

Rivadavite is monoclinic, $2/m$; space group $P2_1/m$; $a=14.779$, $b=8.010$, $c=11.128$ Å, $\beta=105°57'$; $a:b:c=1.8452:1:1.3895$; volume 1266.9 Å^3; cell contents: 3Na$_2$O·MgO·12B$_2$O$_3$·22H$_2$O. Colorless well-formed crystals of 3 mm maximum length are elongated on [010]. Faces of eleven forms are present on all crystals; those best developed are: $a\{100\}$, $O\{\bar{1}01\}$, $p\{011\}$ and $Z\{\bar{1}11\}$. Strongest lines in the X-ray powder photographs are, in Å: 14.2 (100); 7.59 (100); 2.950 (66); 3.246 (64); 6.23 (51); 4.740 (51).

The new mineral is optically biaxial (+); $\alpha=1.470$, $\beta=1.481$, $\gamma=1.497$; $2V=80°$; $r>v$; $Y=b$; $c\wedge Z-32°$. The hardness is $3\frac{1}{2}$; density 1.905 (meas), 1.910 (calc). Cleavage: $\{100\}$, $\{\bar{1}01\}$ excellent; $\{010\}$ poor. The chemical analyses recalculated to 100 percent: Na$_2$O 12.7, K$_2$O 0.03, MgO 2.69, FeO 0.05, B$_2$O$_3$ 57.98, H$_2$O 26.6. DTA shows endothermic peaks at 218°, 632°, 797°C and an exothermic peak at 672°C. Rivadavite is named in honor of Bernardino Rivadavia (1780–1845), first President of the Argentine Republic and promoter of mineralogical and mining studies in his country.

Introduction

Rivadavite, a new borate mineral was found in the Tincalayu borax deposit located in Salar del Hombre Meurto (Salt Pan of the Dead Man), province of Salta, Argentine Republic. As described by Catalano (1930, 1964) this is a nearly circular salt pan with the lowest point at an elevation of 3,700 meters above sea level. It extends from 25° 10′ to 25° 35′ S and 66° 45′ to 67° 15′ W. There are two types of borate deposits in the area: one, associated with the present playa where ulexite has recently formed and may still be forming; and the other in older rocks but now standing at an elevation above the salt pan. This second type is a tabular plug-like body of massive borax in folded and faulted siltstones and sandstones probably of late Cenozoic age (Muessig and Allen, 1957). The Tincalayu mine is located in these older rocks in the north central part of the salt pan area at an elevation of 4000 meters above sea level. In the same sedimentary rocks but outside the main deposit are found lenses of borax, ulexite and inderite. The mine can be reached by car from Pocitos Station on the G. M. Belgrano Railway, 146 km to the north. For a discussion of the geology of the area one is referred to the papers by Catalano (1930, 1964) and Muessig and Allen (1937).

Rivadavite is named in honor of Bernardino Rivadavia[2] (1780–1845), first President of the Argentine Republic. In addition to being a great statesman he was founder of, among many other institutions, Museo de Historia Natural, today Museo Argentino de Ciencias Naturales Bernardino Rivadavia (Palcos, 1960). He was instrumental in promoting research in mineralogy and mining in Argentina (Puccirilli, 1960).

The specimens of rivadavite were obtained through the courtesy of Dr. Luis Conti, geologist of the Banco Industrial de la República Argentina and Dr. Peter H. Grimley, geologist for the company, Boroquímica Limitada, that owns the deposit.

OCCURRENCE

The principal mineral constituent of the Tincalayu deposit is borax but associated with it are minor amounts of halite and rare borates. These include kernite noted by Ahlfeld and Angelelli (1948), ezcurrite described by Muessig and Allen (1957), and macallisterite. Macallisterite, described by Schaller, *et al* (1965) as a new mineral from Death Valley, California, here is found in crystals more than ten mm across. This is the third reported occurrence of macallisterite. Rivadavite occurs in this association completely surrounded by massive borax in nearly spherical aggregates measuring from 1–9 cm in diameter (Fig. 1). The subparallel arrangement of many of the small crystals gives the nodules a silky appearance.

MORPHOLOGY

The nodular masses of rivadavite are composed entirely of aggregates of single crystals with individuals attaining a maximum length of three mm. The crystals elongated on the *b* axis, flattened on {100} have in general a length:width:thickness = 12:2:1 (Fig. 2).

Fifteen crystals were measured on the two-circle optical goniometer; twelve oriented with [010] the rotation axis and three with [001] the rotation axis. The faces of the {h0l} forms gave good signals but more than half of the other faces, seen only as points of light, gave fair to poor signals or none at all. For this reason the axial ratios and angles given in the Angle Table are calculated from X-ray measurements rather than from morphological measurements. In no instance, however, did the ϕ and ρ angles obtained from morphological measurements differ by more than fifteen minutes from the calculated.

Faces of the forms listed in the body of Table 1 were present on all crystals measured but those best developed are *a* {100}, *O* {$\bar{1}$01}, *p*

[2] The name rivadavite has been approved by the Commission of New Minerals and New Mineral Names of the International Mineralogical Association.
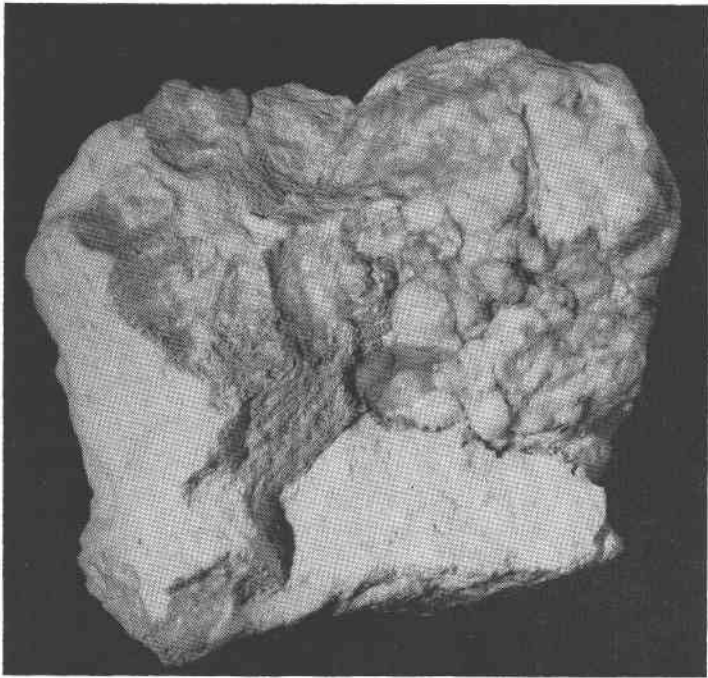
Fig. 1. Rivadavite nodule in borax altering to tincalconite (white). Note casts of smaller nodules. $\frac{2}{3}$ actual size.

$\{011\}$ and Z $\{\bar{1}11\}$. On most of the crystals the faces at the negative end of the b axis were better developed than those at the positive end, and several of the minor forms had no representatives at the positive end. For this reason it was at first felt that the crystals might belong to crystal class -2. However, etch test indicated the higher symmetry $2/m$.

PHYSICAL AND OPTICAL PROPERTIES

Rivadavite shows three cleavages: $\{100\}$ and $\{\bar{1}01\}$ excellent and $\{010\}$ poor. The crystals are extremely brittle and tend to break in splintery fragments elongated on the b axis. Although the nodules of crystal aggregates are white, the individual crystals are quite colorless and transparent with a vitreous luster. The hardness is $3\frac{1}{2}$. The specific gravity measured by suspension in a mixture of bromoform and acetone was determined as 1.905 ± 0.002. The calculated specific gravity is 1.910.

Optical properties in Na light:

$$\left.\begin{array}{l} \alpha = 1.470 \\ \beta = 1.481 \\ \gamma = 1.497 \end{array}\right\} \pm 0.0001 \qquad \begin{array}{l} \text{Opt. } (+) \\ 2V = 80° \\ r > V \end{array} \qquad \begin{array}{l} c \wedge Z - 32° \\ Y = b \end{array}$$
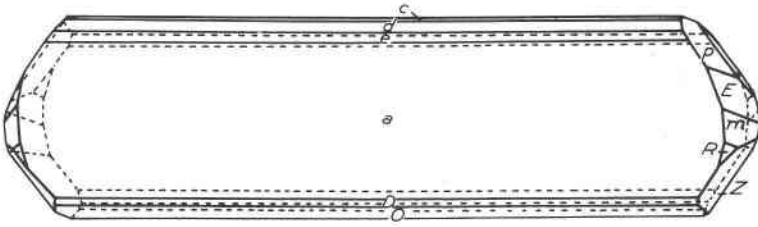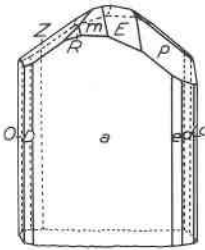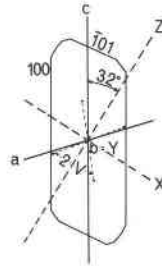
FIG. 2

FIG. 3

FIG. 4

FIG. 2. Rivadavite crystal idealized to show symmetry $-2/m$.

FIG. 3. Rivadavite crystal b axis vertical showing the form development at the negative end of the b axis.

FIG. 4. Optical orientation of rivadavite on (010).

From X-ray and morphological study rivadavite is definitely monoclinic and crystals elongated on b and lying on the dominant form $\{100\}$ should show extinction parallel to the length. However, under these conditions a 2°–3° extinction angle is observed, a fact that could not be reconciled with other observations. The optical orientation is shown in Figure 4 assuming $Y = b$.

X-ray Study

The unit cell dimensions of rivadavite given in Table 2 were determined from Weissenberg photographs taken with copper radiation and nickel filter with b the rotation axis; and precession photographs taken with molybdenum radiation and zirconium filter with a and b the precessing axes. Extinctions in $0k0$ with $k = 2n$ lead to the space groups $P2_1/m$ or $P2_1$. However, crystals immersed for 10–20 seconds in slightly acid (HCl) water at 60° C show characteristic etch patterns or $\{100\}$ and $\{\bar{1}01\}$ indicating that [010] is nonpolar. The similarities of corresponding spots on the precession photographs also suggest the higher symmetry (Wilson 1949). For these reasons, and negative pyroelectric tests, the space group is given as $P2_1/m$.

TABLE 1. RIVADAVITE ANGLE TABLE
Monoclinic; prismatic—2/m

$a:b:c = 1.8452:1:1.3895$; $\beta = 105°57'$; $p_0:q_0:r_0 = 0.7530:1.3895:1$; $r_2:p_2:q_2$
$= 0.7485:0.5635:1$; $\mu = 74°03'$; p_0' 0.7829, q_0' 1.3895; x_0' 0.2858

	Forms	ϕ		ρ		ϕ_2		$p_2 = B$		C		A	
c	001	90°	00′	15°	57′	74°	03′	90°	00′	—		74°	03′
a	100	90	00	90	00	0	00	90	00	74	03	—	
m	110	29	24	90	00	0	00	29	24	82	15	60	36
p	011	11	37	54	50	74	03	36	49	53	11	80	32
d	101	90	00	46	54	43	06	90	00	30	57	43	06
e	201	90	00	61	38	28	23	56	33	45	41	28	22
O	$\overline{1}$01	−90	00	26	26	116	26	90	00	42	23	116	26
D	$\overline{2}$01	−90	00	52	00	142	02	90	00	67	57	142	02
Z	$\overline{1}$11	−19	41	55	57	116	26	38	47	65	01	106	12
E	121	21	02	71	26	43	06	27	46	66	27	70	07
R	$\overline{3}$21	−36	37	73	52	154	17	39	32	83	48	124	57

Other less common forms: 304, 807, $\overline{1}$04, $\overline{6}$01, 311.

CHEMICAL COMPOSITION

The nodular aggregates of rivadavite crystals on optical examination appear to be entirely free from impurities and thus no sample preparation was necessary for chemical analysis. Before the wet analysis was undertaken, a spectrochemical analysis revealed, in addition to the major elements, Si, Ca, Mn, Pb (0.001%–0.01%) and Al, Ti, Cu, Zn (0.0001%–0.001%). The finely ground mineral quickly dissolves in warm water (80°C) yielding a solution with pH 8–9. After standing for a short while, the solution becomes yellow; finally a pale brown flocculent precipitate of ferric hydroxide is formed. The chemical analysis, Table 4, was made by Dr. Jun Ito.

TABLE 2. UNIT-CELL DATA FOR RIVADAVITE*

$a = 14.779$⎫
$b = 0.010$⎬ ± 0.003Å   Space group $P2_1/m$
$c = 11.128$⎭   Density:
                                      measured 1.905 g/cm³
                                      calculated 1.910 g/cm³
$\beta = 105°57'$ for cell content $Na_6MgB_{24}O_{40} \cdot 22H_2O$
$a:b:c = 1.8452:1:1.3895$
Cell vol. 1266.9 Å³

* Values refined using powder photograph data (Table 3).

TABLE 3. X-RAY POWDER DATA FOR RIVADAVITE

$(CuK\alpha = 1.54178; CuK\alpha_1 = 1.54051; Ni filter)$

Camera diameter 114.59 mm

I[1]	d (obs)	d (calc)[2]	hkl	I[1]	d (obs)	d (calc)[2]	hkl
100	14.2	14.211	100	66	2.950	2.956	$\bar{4}03$
11	10.7	10.702	001			2.956	$\bar{5}01$
4	9.93	9.965	$\bar{1}01$	2	2.882	2.886	203
100	7.59	7.603	101			2.885	$\bar{3}22$
13	7.11	7.105	200	49	2.849	2.856	$\bar{5}02$
10	6.99	6.978	110			2.842	500
38	6.85	6.850	$\bar{2}01$	1	2.813	2.812	321
2	6.42	6.413	011	9	2.760	2.767	$\bar{2}04$
51	6.23	6.243	$\bar{1}11$			2.757	222
33	5.533	5.534	$\bar{1}02$	2	2.713	2.715	213
49	5.340	5.351	002			2.713	$\bar{4}21$
		5.316	210	15	2.657	2.658	420
7	5.069	4.983	$\bar{2}02$	9	2.576	2.579	$\bar{1}31$
51	4.740	4.737	300			2.577	501
2	4.438	4.449	012	13	2.508	2.507	104
9	4.230	4.231	$\bar{2}12$	7	2.486	2.487	$\bar{2}31$
8	4.005	4.005	020	29	2.454	2.453	511
35	3.946	3.949	301	2	2.392	2.392	114
2	3.857	3.855	120			2.389	032
1	3.816	3.802	202	24	2.369	2.369	600
1	3.682	3.688	$\bar{4}01$	11	2.316	2.318	520
13	3.625	3.611	$\bar{2}03$			2.310	132
38	3.550	3.553	400	7	2.277	2.279	$\bar{1}24$
		3.543	121			2.277	$\bar{2}24$
		3.542	311	1	2.248	2.247	$\bar{3}32$
44	3.490	3.489	220	9	2.213	2.214	214
12	3.337	3.366	$\bar{1}13$			2.212	331
		3.350	$\bar{4}11$	1	2.184	2.185	232
		3.322	$\bar{3}03$	24	2.150	2.148	413
64	3.246	3.245	$\bar{1}22$	11	2.102	2.103	$\bar{1}01$
		3.144	302			2.099	702
46	3.135	3.125	401	1	2.068	2.068	015
		3.122	$\bar{2}22$	13	2.029	2.030	700
13	3.063	3.068	$\bar{3}13$			2.030	431
		3.058	320	1	1.998	1.997	224
11	3.012	3.016	113	4	1.986	1.986	$\bar{5}24$

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

[2] The calculated d values were obtained on an IBM 7094 Computer using a program for calculations of all possible spacings. Computer time was obtained on N.F.S. Grant No. GP-2723, Harvard University.

TABLE 3—(Continued)

I[1]	d (obs)	d (calc)[2]	hkl	I[1]	d (obs)	d (calc)[2]	hkl
7	1.945	1.946	530	1	1.399		
		1.945	$\bar{2}$25	1	1.383		
1	1.921	1.921	$\bar{3}$25	1	1.362		
		1.921	621	1	1.338		
9	1.874	1.875	042	1	1.308		
		1.873	241	1	1.296		
9	1.856	1.857	324	1	1.272		
1	1.833	1.833	$\bar{1}$06	1	1.260		
1	1.811	1.811	720	1	1.244		
1	1.796	1.796	$\bar{6}$32	1	1.229		
1	1.761	1.761	$\bar{4}$16	1	1.201		
1	1.745	1.746	702	1	1.188		
		1.744	440	1	1.172		
1	1.729	1.729	$\bar{7}$05	1	1.159		
		1.729	$\bar{4}$42	1	1.127		
1	1.712	1.712	$\bar{8}$04	1	1.110		
			106	1	1.093		
1	1.699	1.701	$\bar{1}$35	1	1.084		
7	1.650	1.650	$\bar{7}$32	1	1.075		
1	1.620			1	1.063		
7	1.585			1	1.045		
4	1.560			1	1.035		
1	1.525			1	1.017		
1	1.501			1	0.989		
4	1.479			1	0.951		
1	1.463			1	0.926		
1	1.446			1	0.907		
1	1.433			1	0.898		
1	1.420			1	0.881		
1	1.407						

On the basis of forty oxygens, the chemical analysis in Table 4 can be recast to yield the formula: $Na_{5.90}Mg_{0.94}B_{24.05}O_{40} \cdot 21.4\ H_2O$. This is including potassium with sodium and iron with magnesium, and assuming all the water to be essential. This seems to be a reasonable assumption, for, during a 24-hour period 45 percent of the water was lost at 110°C. If on the other hand the $H_2O(-)$ is considered nonessential, the formula would have $20.2H_2O$. Since the ratio of $Na^+:Mg^{++}=1:6$, we prefer to consider sodium and magnesium as occupying different structural sites; and the ideal formula as: $Na_6MgB_{24}O_{40} \cdot 22H_2O$ with $Z=1$. Moreover, using this formula, the calculated specific gravity, 1.910, agrees well with the measured specific gravity, 1.905. Assuming $20H_2O$ the calculated specific gravity is 1.862.

TABLE 4. CHEMICAL ANALYSIS OF RIVADAVITE

	Wt. percent	Wt. percent recalculated	Mol. prop.
Na_2O	12.7	12.65	0.20409
K_2O	0.03	0.03	0.00031
MgO	2.70	2.69	0.06671
FeO	0.05	0.05	0.00069
B_2O_3	58.2	57.98	0.83256
$H_2O(+)$	25.3	25.20	1.47646
$H_2O(-)$[1]	1.4	1.40	
Total	100.38	100.00	

[1] $H_2O(-)$ determined by heating at 95°C for 24 hours.

DIFFERENTIAL THERMAL ANALYSIS

A differential thermal analysis of rivadavite yielded the curve of Figure 5 in which are shown major endothermic peaks at 218°, 632°,
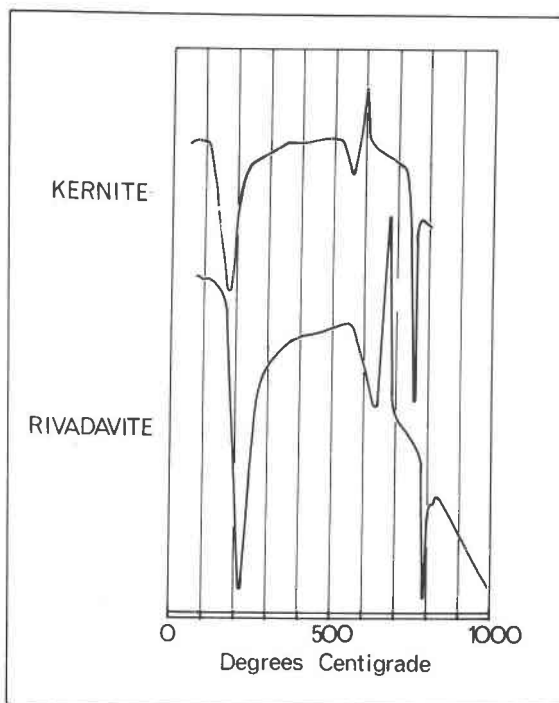
FIG. 5. DTA curves of rivadavite and kernite. Rate of heating 20°/min.; reference junction 0°C; thermocouple Pt/Pt+13% Rh; reference material, Al_2O_3.

797°C and an exothermic peak at 672°C. A minor endothermic peak appears at 97°C that may represent the loss of adsorbed water. The first major endothermic is fairly broad and is interpreted as the loss of structural water and the material becomes amorphous. The second major endothermic peak is also fairly broad and is attributed to the loss of OH. If, however, the mineral is held at a temperature of 300° for 30 minutes
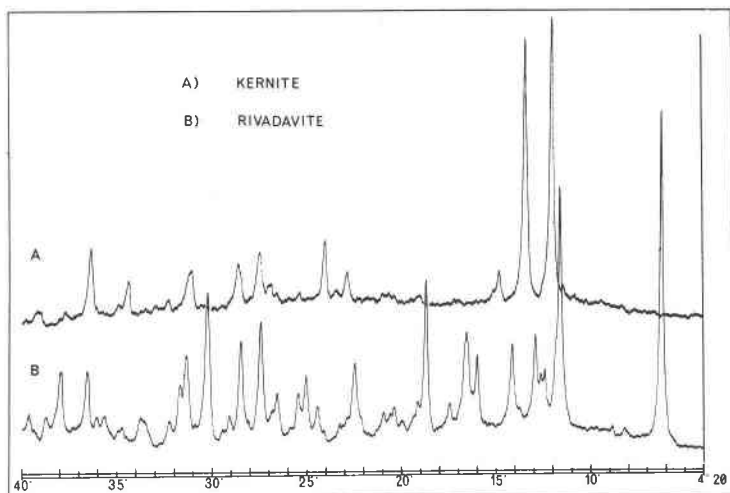

FIG. 6. Diffractometer charts of rivadavite and kernite. Cu radiation, Ni filter. Preferred orientation because of cleavage alters the relative intensities of the rivadavite peaks compared to data in Table 3.

nearly all the water is lost. The final endothermic peak results from fusion of the sample. If the heating is continuous beyond the exothermic peak but to less than the melting temperature, a crystalline substance results. This compound has the following optical properties: $\alpha = 1.498$, $\beta = 1.540$, $\gamma = 1.590$ (± 0.001 Na light) optical ($+$), $2V = 80°$. The strongest peaks on the X-ray diffractometer chart correspond to the following spacings given in order to decreasing intensity: $d = 3.20, 3.01, 3.37, 3.72, 2.93$ Å.

Although the DTA curve is reproducible under the rapid heating conditions (20°C per minute), 45 percent of the water is given off in 24 hours at 110°C and 90 percent of the water is lost in 30 minutes at 300°C. The differential thermal behavior of kernite is very similar to that of rivadavite as shown by a comparison of the curves of Figure 5. However, a comparison of the diffractometer charts (Fig. 6) of these two minerals shows them to be crystallographically quite dissimilar.

In the blowpipe flame rivadavite reacts much as does borax and kernite; it intumesces and then fuses to a white cauliflower-like mass that

on further heating forms a clear colorless glass. Heated in the closed tube
it gives off water and turns white.

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