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BERMANITE, AND ITS OCCURRENCE IN CÓRDOBA, ARGENTINA[1]

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ABSTRACT

In Argentina bermanite was found in thin crusts as an alteration product of triplite in a pegmatite near Tanti, Córdoba. The crystallographic and physical properties are similar to those described in the literature except for conspicuous twinning, also seen in a restudy of the type material. Because of this twinning and the nonorthorhombic orientation of the optical indicatrix, bermanite, previously described as orthorhombic, is considered monoclinic. Four major types of rotation twins were observed optically. They are, with composition plane and twin axis, as follow: 1. $\{\bar{1}01\}$, $[101]$; 2. $\{101\}$, $[\bar{1}01]$; 3. $\{001\}$, $[100]$; 4. $\{\bar{3}01\}$, $[100]$. Twinning of types 1 and 2 could not be observed optically in orthorhombic crystals. X-ray study of crystals from Argentina and Arizona coupled with a positive pyroelectric response, yields the space group, $P2_1$; or, if considered orthorhombic, the space group, $C222_1$. Monoclinic symmetry yields a pseudo-orthorhombic cell: $a=c=5.426$ Å, $b=19.206$ Å, $\beta=110°30'$ (Argentina); and the optical orientation $X=b$, $Y\wedge c=-36\frac{1}{2}°$. The transformation formula, orthorhombic to monoclinic, is: $110/002/1\bar{1}0$.

A new chemical analysis of the mineral from Arizona yielded: Al_2O_3 0.19, Fe_2O_3 3.20, Mn_2O_3 30.6, MnO 12.8, MgO 1.05, CaO 0.75, H_2O 20.2, P_2O_5 31.4. Total 100.19. These values result in the empirical formula:

$$\overset{2+}{Mn}_{0.82}Mg_{0.12}Ca_{0.06}\overset{3+}{Mn}_{1.75}\overset{3+}{Fe}_{0.18}Al_{0.02}P_2O_{13.99}H_{10.14}$$

which idealized is: $Mn^{2+}Mn_2^{3+}(PO_4)_2(OH)_2\cdot 4H_2O$. A microprobe analysis of Argentine bermanite indicates the following weight percentages: Fe_2O_3 8.0, Mn_2O_3 26.5, MnO 11.6. A DTA curve shows three major endothermic peaks with maxima at 270°, 430°, 1110°C, two minor exothermic peaks with maxima at 695° and 985°C and a strong exothermic peak at 610°C.

INTRODUCTION

Bermanite was originally described from the 7-U-7 Ranch near Hillside, Arizona as an alteration product of triplite (Hurlbut, 1936). It was considered to be orthorhombic, dipyramidal, and the suggested chemical formula was given as:

$$(Mn^{2+}, Mg)_5Mn_8^{3+}(PO_4)_8(OH)_{10}\cdot 15H_2O.$$

In the process of studying pegmatite minerals from Argentina, this rare phosphate was found in the Province of Córdoba. Since bermanite from this locality presents extensive twinning that is not in accord with the described symmetry, it was felt that it deserved a detailed study. This feeling was reinforced when a reexamination of the type material also showed similar, though less common, twinning. Furthermore, since

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the chemical formula was questioned by Ginzburg (1954) and Leavens (1967), and since only one chemical analysis was available, it seemed desirable while studying the Argentine mineral to review some aspects of the description of the original material from Arizona.

OCCURRENCE IN ARGENTINA

On the eastern slope of the Sierra Grande, 45 kilometers due west from the City of Córdoba (see Fig. 1) in the Tanti district, is a group of pegmatites called Cerro Blanco (Arias, 1960). The country rock to which the pegmatites appear to be genetically related is a pink granite, part of the large igneous mass known as the Achala batholith. The age of these rocks has been discussed by many workers; some consider them lower Paleozoic (Pastore, 1932), others as preCambrian (Linares, 1959). This last author, by using Pb/U ratios in uraninite, determined the age of the pegmatites of the region as ranging from 455 to 520 million years.

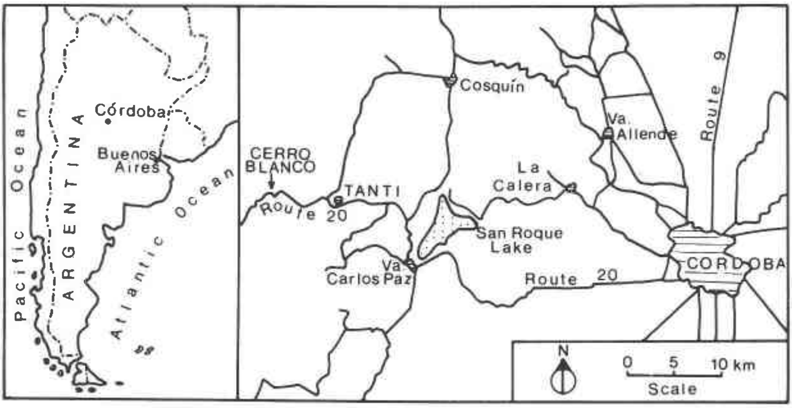


FIG. 1. Location of Cerro Blanco, Córdoba, Argentina.

Bermanite was found by the present authors in one of the Cerro Blanco pegmatites called El Criollo, that is located 7 kilometers west of the small town of Tanti following Route 20 (kilometer marker 764). This pegmatite is worked principally for feldspar, quartz and beryl but minor amounts of columbite are recovered. Crystals of apatite and nodular masses of chalcocite and hematite are also present. Nodules of triplite are common throughout the Cerro Blanco pegmatites but at El Criollo is one of gigantic size, approximately 4 meters in diameter (see Fig. 2). Around its altered periphery and in fractures through it are thin crusts of secondary bermanite associated with metastringite, eosphorite, and a black manganese oxide. X-ray powder photographs and electron probe analysis

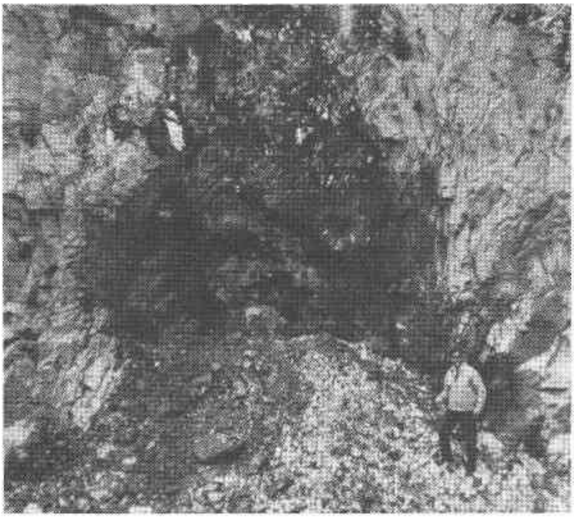


FIG. 2. Large triplite nodule in pegmatite at El Criollo mine, Córdoba, from which bermanite has formed as a secondary mineral.

show that this mineral closely resembles the oxide, manganous manganite, as described by Samson and Wadsley (1948). In addition to the alteration minerals of triplite mentioned, pachnolite, $NaCaAlF_6 \cdot H_2O$ was also observed. This rare mineral is present in white crusts and as colorless crystals on bermanite.

The origin of the bermanite at El Criollo is similar to that reported by Hurlbut (1936), Correia Neves (1958a) and Behier (1960); that is, as a surface alteration of triplite. The mineral also has been reported by Correia Neves (1958a, 1958b, 1960a) as an alteration product of lithiophilite. Association with other secondary phosphates has been found by Lindberg and Pecora (1958), Correia Neves (1960b), and Leavens (1967).

MORPHOLOGY AND PHYSICAL PROPERTIES

The Argentine bermanite forms thin crusts deposited directly on and partially embedded in the black manganese oxide. On some specimens the bermanite is in subparallel aggregates of a dull reddish-brown color, very similar to the type material from Arizona. On others, small crystals, rarely attaining 0.5 millimeter in maximum dimension, coat the surface. Some of these crystals have a submetallic luster that may result from a thin film of the manganese oxide; but most of them are a pale red showing red internal reflections.

Many single crystals of the Argentine bermanite were observed but they were so tenaciously held that it was difficult to extract them intact from the underlying material. The few that were removed, although well formed, were small (<0.5 mm) for normal optical goniometric work. However, the angular measurements obtained were well within the range of those observed on the type material.

The specific gravity of bermanite from Argentina was determined by suspension in a mixture of bromoform and acetone as 2.850 ± 0.005. See Table 2 for a comparison with other observed values. The hardness, $3\frac{1}{2}$, and the cleavage are both similar to those observed in the type material.

From optical evidence given below it appears that bermanite is not orthorhombic as originally described but monoclinic, pseudo-orthorhombic. In the orthorhombic orientation the habit and major forms ({001}, {010}, {110} and {111}) of the Argentine material are identical to those described and figured by Hurlbut (1936), (see Fig. 3). In addition three new forms, {100}, {032}, and {034}, were observed on Argentine crystals. If the orthorhombic symmetry is preserved, attention should be called to the fact that X-ray study (see below) shows the point group to be 222 not $\frac{2}{m}\frac{2}{m}\frac{2}{m}$ as originally given. The dipyramidal forms as given by Hurlbut (1936) must, therefore, be subdivided in accordance with this lower symmetry.

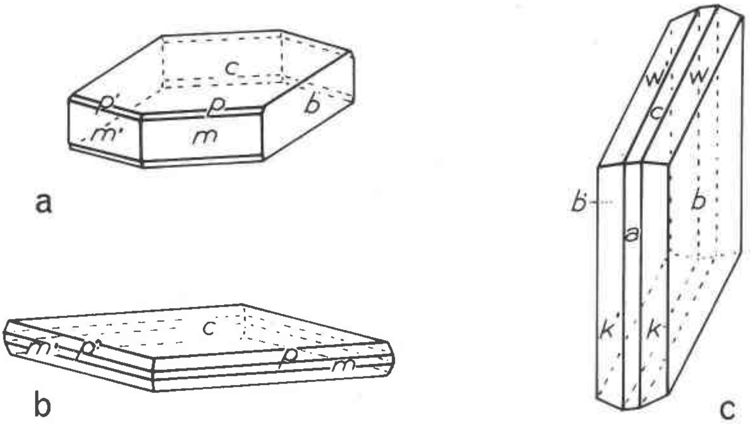


FIG 3. Crystal drawings of bermanite. **a.** and **b.** Orthorhombic orientation reproduced from Hurlbut (1936) with form lettering adjusted to conform to symmetry of point group 222. **c.** Crystal drawing of b in monoclinic orientation. Orthorhombic forms *c, m, m', p, p'* become respectively monoclinic *b* and *b'*, *a*, *c*, *k* and *k'*, *w* and *w'*.

BERMANITE AS A MONOCLINIC CRYSTAL

Oriented as a monoclinic crystal the orthorhombic axial planes (100), (010) and (001) became respectively (101), (10$\bar{1}$) and (010). The transformation formulas are: orthorhombic to monoclinic 110/002/1$\bar{1}$0; monoclinic to orthorhombic 101/10$\bar{1}$/010. Thus as a monoclinic crystal belonging to point group 2, the dominant forms are {001}, {010}, {0$\bar{1}$0}, {100}, {110}, {1$\bar{1}$0}, {011}, {0$\bar{1}$1} and {$\bar{1}$01} (See Fig. 3c).

The orthorhombic axial ratios given by Hurlbut (1936) from morphological measurements are: $a{:}b{:}c = 0.6890{:}1{:}2.2018$. Transformed to monoclinic the ratios are:

$$a{:}b{:}c = 0.2758{:}1{:}0.2758; \beta = 110°52'.$$

The monoclinic polar elements are:

$$p_0{:}q_0{:}r_0 = 1{:}0.2577{:}1; \quad r_2{:}p_2{:}q_2 = 3.8805{:}3.8805{:}1; \mu = 69°08';$$
$$p_0' = 1.0701; \quad q_0' = 0.2758; \quad x_0' = 0.3812$$

OPTICAL PROPERTIES

Although bermanite has been reported previously from seven localities (Leavens, 1967) the optical properties have been given for only three. These, and the optical properties of the Argentine mineral, summarized in Table 1, are in essential agreement. The only significant difference is in

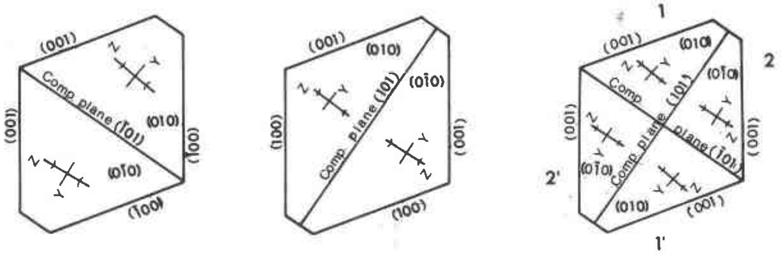
TABLE 1. OPTICAL PROPERTIES OF BERMANITE

Locality	(1) 7-U-7 Ranch Arizona, U.S.A.	(2) Mangualde, Portugal	(3) Coosa Co. Alabama,. U.S.A.	(4) Tanti, Córdoba Argentina
α	1.687	1.685	1.687	1.690
β	1.725 ±0.003	<1.744	1.729	1.729 ±0.001 Na light
γ	1.748	>1.744	1.751	1.750
Birefringence	0.061	>0.059	—	0.060
2V	74°	—	75° about	72°
Optic Sign	neg.	neg.	neg.	neg.
Dispersion	$r<v$	$r<v$ strong	$r<v$ strong	$r<v$
Pleochroism	—	$Z>X>Y$	—	$Z>X>Y$
X	light red	brown	light red	light red
Y	pale yellow	light brown	pale yellow	pale yellow
Z	deep red	dark brown	red	deep red
Orientation	$X=c$	$X=c$	$X=c$	Ortho $X=c$
	[a]$Z=a$	$Z=a$	—	$Z\wedge a=2°$
				Mon $X=b$
				$Y\wedge c=-36\frac{1}{2}°$

(1) C. S. Hurlbut, Jr. (1936).
(2) J. M. Correia Neves (1958, a).
(3) P. B. Leavens (1967).
(4) This study.
[a] Reexamination showed $Z\wedge a=2°$.

the extinction angle, $Z\wedge a$(orth) = 2°, as observed in the Argentine material. On reexamination, the Arizona bermanite showed the same extinction angle. This departure from the normal orientation of the optical indicatrix in orthorhombic crystals can be accounted for by assuming the crystals to be monoclinic.

Because of the equivalence of the monoclinic *a* and *c* axes, two orientations are possible but each gives rise to a different position of the optical indicatrix. We have chosen *c* as the axis having an extinction angle of $-36\frac{1}{2}°$ with *Y*. The transformation formula was determined according to this selection. Then, as a monoclinic crystal the optical orientation of bermanite is: $X=b$, $Y\wedge c=-36\frac{1}{2}°$ and $Y\wedge a=32\frac{1}{2}°$.



(a) (b) (c)

FIG. 4. Illustrations of the most common twin laws in bermanite drawn as seen lying on faces perpendicular to [010]. **a.** Type 1: twin axis [101]; composition plane, {1̄01}. **b.** Type 2: twin axis [1̄01]; composition plane {101}. **c.** Composite twin of Types 1 and 2.

TWINNING

Of the earlier workers on bermanite, Correia Neves (1960a) is the only one who makes any mention of twinning. He reports twinning on orthorhombic {010} and in drippings ("em goteira") with crystals "symmetric with respect to (100)". From his description and illustration (1958a, Fig. 1) this is interpreted by us as twinning on orthorhombic {001} (monoclinic {010}).

The present study revealed several types of twinning all of which are assumed to be twinning by rotation with twin axes parallel or normal to the composition planes. They are described, as are the pertinent figures, in the monoclinic orientation.

Type 1. One of the two most frequently observed is twinning about [101] with this axis lying in the composition plane, {1̄01}. The *Z* optical direction makes an angle of 2° with the trace of this plane on (010). Occasional crystals are observed as shown in Figure 4a, but most frequently this twinning is seen in combination with Type 2, (Fig. 4c) or Types 3 and

4. Crystals are commonly twinned polysynthetically according to this law, with extremely thin individuals, see Figure 5.

Type 2. This type of twin is equally common to Type 1; the twin axis $[\bar{1}01]$ is parallel to the composition plane, $\{101\}$, (Fig. 4b). The Y optical direction makes an angle of 2° with the trace of this plane on (010). Only a few crystals were observed with this twin alone; in general they are seen in combination with other types. Polysynthetic twins according to this law were observed; they have a similar appearance but are less common than those of Type 1.

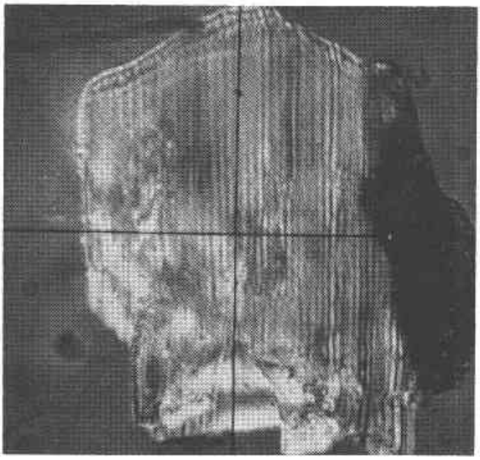
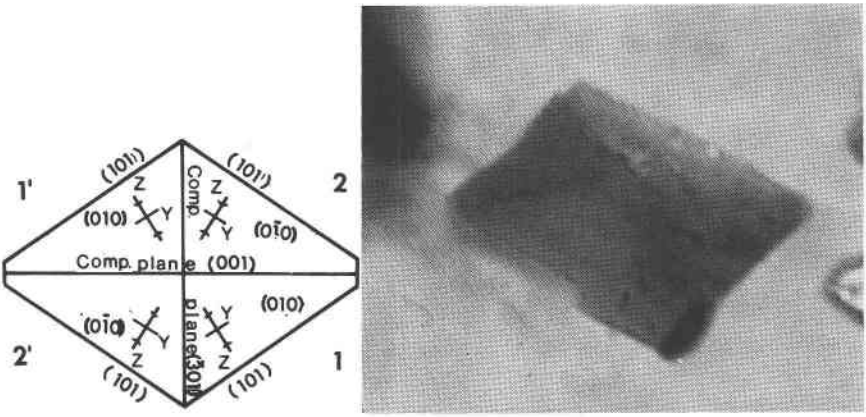


FIG. 5. Photomicrograph of bermanite showing polysynthetic twinning of Type 1. Crossed polars, 250×.

Type 3. The composition plane of this type is $\{001\}$ with twin axis [100] lying in this plane. In Type 3 the Y optical direction of the two individuals makes an extinction angle of $32\frac{1}{2}^\circ$ with the trace of the composition plane on (010). Because of the great difference in absorption between the Y (pale yellow) and Z (deep red) directions this type is easily seen in plane polarized light. This twinning is less frequently observed than Types 1 and 2 and is usually in combination with Type 4 (Fig. 6), or Types 1 and 2, (Fig. 7). Type 3 can also be described as a reflection twin.

Type 4. This type of twinning is never observed except in combination with Type 3 producing a fourling bounded by faces (101). See Figure 6a. The individuals are joined on an (*h0l*) plane that form the extinction angle, $Z\wedge 33\frac{1}{2}^\circ$ with the trace of this plane on (010) was determined as $\{\bar{3}01\}$ with the twin axis, [100], normal to this plane. This type can be



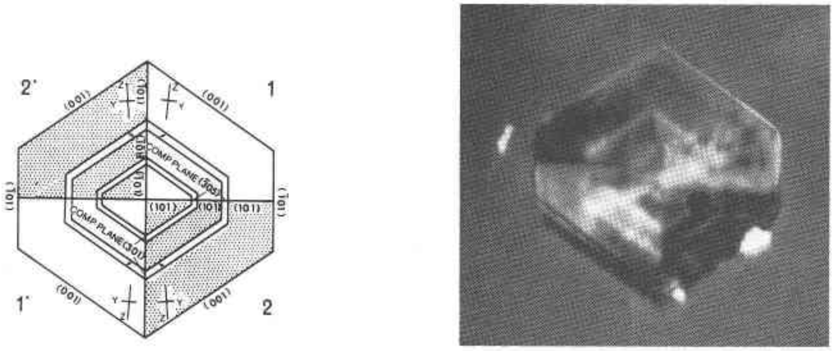
(a) (b)

FIG. 6. Bermanite showing twins of Types 3 and 4 as seen on crystals lying on faces perpendicular to [010]. **a.** Drawing showing the relationship of the four individuals of the composite twin as distinguished by different optical orientations. Individuals 1 & 2, and 1′ & 2′ are twinned on [100] with composition plane {001}; doublets 1–2 and 1′–2′ are twinned on [100] with composition plane {3̄01}. **b.** Photomicrograph showing differential absorption in differently oriented individuals. Plane polarized light, 300×.

equally well explained as a reflection twin on {3̄01}. From the geometry of the four individuals this plane should be at 90° to the other composition plane {001}. Using the dimensions of the unit cell $(\bar{3}01)\wedge(001)=89°$.

There are several other types of twins in addition to the four described although twin laws could not be deduced for all of them. However, twinning on {301} and {503}, was determined. Many of the twinned crystals are not as regular as those shown in the drawings. Frequently diamond-shaped plates are composed of many twin types arranged in a highly irregular manner. In other plates of similar shape, combinations of several types of twinning result in a regular pattern. Thus Figure 7 shows a plate composed basically of twin Types 1 and 2 but in each of the four individuals, bands of Type 3 can be observed. Twinning, once observed, appears to be the rule rather than the exception in the Argentine material.

All the types of twinning that have been described are possible in orthorhombic crystals of class 222, with the major composition planes {010}, {100}, {110} and {120}. However, twinning on orthorhombic {010} and {100} equivalent to monoclinic {1̄01}, type 1, and {101}, type 2, can not be detected optically. Neither can one detect twinning on orthorhombic {001}, Correia Neves (1958a, 1960a).



(a) (b)

FIG. 7. Composite twin of bermanite. **a.** Drawing showing four major units forming a composite twin of Types 1 and 2. Each unit shows thin bands resulting from twinning of Type 3. A twin relation exists between the adjacent thin bands of quadrants 1 & 2′ and 1′ and 2 with composition plane {301}; the plane separating the same bands between 1 & 2 and 1′ & 2′ is composition plane {3̄05}. Since {301} of the thin bands is parallel to {1̄01} of the thicker bands, no twin relation exists along this contact. **b.** Photomicrograph of twin crystals illustrated in **a.** Crossed nicols, 250×.

X-RAY STUDY AND SYMMETRY

Because several of the observed types of twinning and the orientation of the optical indicatrix are incompatable with orthorhombic symmetry, single crystal X-ray studies were carried out. Precession photographs were taken using material from both Argentina and the type locality. All crystals used showed no optical evidence of twinning and they were thus assumed to be single individuals, although twinning on {010} could exist for it cannot be detected optically.

Photographs of the 0, 1st and 2nd layers taken with monoclinic [010] (orthorhombic c axis) as precession axis were identical as to the position of the spots. Photographs with the orthorhombic *a* and *b* as precession axes were also taken. On all photographs are two sets of rows intersecting at 90°. Assuming orthorhombic symmetry the extinctions lead to the non-centro-symmetric space group $C222_1$, the space group determined by Leavens (1967).

Considered as monoclinic the distribution of spots on the photographs can be interpreted resulting from a crystal in which $a=c$, and the extinctions indicate either the space group $P2_1/m$ or $P2_1$. With the positive pyroelectric effect reported by Leavens (1967) and also observed in the present study, the mineral would fall in the space group $P2_1$.

The intensities of the spots on the precession photographs suggest orthorhombic symmetry. However, monoclinic twinned crystals would yield photographs of similar appearance. For this reason and because twinning is so abundant, it is uncertain that single crystals have been used for X-ray studies. Furthermore, because of the optically observed twins, impossible to detect in orthorhombic crystals, we prefer to consider bermanite monoclinic.

The unit cell dimensions of bermanite are summarized in Table 2. The values obtained in the present study for material from Argentina and type material from Arizona were refined using X-ray powder photographs and are presented for both orthorhombic and monoclinic orientations.

Table 3 gives the X-ray powder photograph data for bermanite from Arizona and Córdoba. Because of compositional zoning, the *d* spacings and cell dimension data determined must be considered average values for the bulk samples.

CHEMISTRY

The original chemical analysis of bermanite (see Table 4, column 1) yielded the formula:

$$R_5^{2+}R_8^{3+}(PO_4)_8(OH)_{10}\cdot 15H_2O$$

where $R^{3+} = Mn$, Fe; $R^{2+} = Mn$, Mg, Ca, Na. (Hurlbut, 1936). This formula was questioned by Palache, Berman and Frondel (1951) but they placed it in their classification with hydrous phosphates in which $R^{2+} + R^{3+}:P = 3:2$. Ginzburg (1954) using the same chemical analysis proposed the formula:

$$(Mn, Mg, Ca)_5(Mn, Fe)_7(PO_4)_8(OH)_7\cdot 16H_2O.$$

In his reexamination of bermanite, Leavens (1967) using the same chemical data arrived at the ideal formula:

$$Mn_4^{2+}Mn_8^{3+}(PO_4)_8(OH)_8\cdot 16H_2O \quad \text{or} \quad Mn^{2+}Mn_2^{3+}(PO_4)_2(OH)_2\cdot 4H_2O.$$

To obtain this formula he disregarded the small amounts of calcium and sodium as impurities and transferred 16% of the reported Mn^{2+} to Mn^{3+}. Leavens pointed out that his formula fitted the space group requirements.

During the present study an unsuccessful effort was made to separate bermanite from Argentina pure enough for a wet chemical analysis. Because of the questions already mentioned regarding the formula, and since a relatively large amount of bermanite from Arizona is now available a new chemical analysis of the type material seemed desirable. Such an analysis was made by Dr. Jun Ito and is given in Table 4, column 3. The molecular proportions calculated from the new chemical data are

TABLE 2. UNIT CELL DATA FOR BERMANITE

	As orthorhombic:				As monoclinic:	
Locality	Mangualde, Portugal	Coosa County Alabama, U.S.A.	7-U-7 Ranch Arizona, U.S.A.	Tanti, Córdoba Argentina	7-U-7 Ranch Arizona, U.S.A.	Tanti, Córdoba Argentina
Reference	(1)	(2)	(3)	(4)	(5)	(6)
a (Å)	6.1	6.200	6.192	6.186	5.425	5.426
b (Å)	8.93	8.925	8.906	8.916	19.210	19.206
c (Å)	19.26	19.206	19.210	19.206	5.425	5.426
β	—	—	—	—	110°24′	110°30′
a:*b*:*c*	0.683:1:2.157*	0.695:1:2.152*	0.695:1:2.157	0.694:1:2.154	0.282:1:0.282	0.283:1:0.283
Cell Vol. (Å^3)	—	—	1059.4	1059.2	529.7	529.6
Sp. g.: meas.	—	2.85	2.84	2.850	2.84	2.850
calc.	—	—	2.840	—	2.840	—
Wt. cell content	—	—	1812	1818	906	909
Z	—	4	4	4	2	2
Space group	—	$C222_1$	$C222_1$	$C222_1$	$P2_1$	$P2_1$

(1) J. M. Correia Neves, (1958a).
(2) P. B. Leavens (1967).
(3) to (6) This paper.
* Calculated from cell data.

TABLE 3. X-RAY POWDER DATA FOR BERMANITE

(1)		(2)		(3)	(4)
7-U-7 Ranch Arizona, U.S.A.		Tanti, Cordoba Argentina		Monoclinic	Ortho-rhombic
I/I_0	d (Å) obs.	I/I_0	d (Å) obs.	*hkl*	*hkl*
100	9.63	100	9.68	020	002
16	5.10	65	5.08	100	110
28	4.82	65	4.81	040	004
6	4.49	8	4.48	$\bar{1}01$	020
4	4.34	17	4.33	$\bar{1}11$	021
3	4.02	10	4.06	$\bar{1}21$	022
19	3.673	26	3.668	$\bar{1}31$	023
4	3.511	—	—	140, 041	114
23	3.263	33	3.252	$\bar{1}41$	024
10	3.202	10	3.201	060	006
11	3.062	12	3.056	111 150, 051	201 115
36	2.905	39	2.912	$\bar{1}51$	025
7	2.787	26	2.785	$\bar{1}31$	203
10	2.710	5	2.705	160, 061	116
2	2.665	6	2.657	$\bar{2}01$	130
4	2.591	10	2.591	$\bar{1}61$	026
7	2.529	22	2.526	200	220
3	2.463	24	2.454	$\bar{2}31$ 220, 022	133 222
10	2.337	24	2.335	$\bar{2}41$	134
3	2.240	12	2.233	$\bar{2}02$ 240, 042	040 224
3	2.168	10	2.160	$\bar{2}22$ 180, 081	042 118
11	2.112	24	2.112	$\bar{1}81$	028
3	2.051	—	—	$\bar{2}61$ 171	136 207
10	1.925	20	1.920	$\bar{1}91$	029
1	1.871	5	1.855	181	208
11	1.828	15	1.829	$\bar{2}62$	046
2	1.694	8	1.684		
1	1.636	1	1.635		
1	1.604	1	1.601		
1	1.544	1	1.543		
1	1.465	1	1.464		
1	1.457	1	1.454		
6 additional lines		8 additional lines			

(1) and (2) Observed values obtained using Fe Kα = 1.9373 Å, Fe Kα = 1.93597 Å, Mn filter. Camera diameter = 114.59 mm. Line intensities were derived from diffractometer charts obtained with Fe radiation.

(3) Indices of equivalent spacings, with k negative are omitted.

(4) Indices of spacings in orthorhombic orientation are included for comparison.

given in the same table. The atomic proportions (column 6) calculated assuming $P=2$, yield the empirical formula:

$$\overset{2+}{\mathrm{Mn}}_{0.82}\mathrm{Mg}_{0.12}\mathrm{Ca}_{0.06}\overset{3+}{\mathrm{Mn}}_{1.75}\overset{3+}{\mathrm{Fe}}_{0.18}\mathrm{Al}_{0.02}\mathrm{P}_2\mathrm{O}_{13.99}\mathrm{H}_{10.14}$$

TABLE 4. CHEMICAL ANALYSES OF BERMANITE FROM 7-U-7 RANCH, ARIZONA, WEIGHT PERCENT

	1	2	3				
	Theoretical composition	Type material	Type[a] material	Recalculated to 100%	Atomic proportions with $P=2$		
Al_2O_3	—	—	0.19	0.19	Al	0.0169	
Fe_2O_3	—	3.03	3.20	3.19	Fe^{3+}	0.1811	1.95
Mn_2O_3	34.26	28.76	30.6	30.54	Mn^{3+}	1.7524	
MnO	15.39	13.79	12.8	12.78	Mn^{2+}	0.8157	
MgO	—	2.39	1.05	1.05	Mg	0.1177	0.99
CaO	—	0.72	0.75	0.75	Ca	0.0604	
Na_2O	—	0.32	—	—	H	10.1374	
H_2O	19.55	19.33	20.2	20.16	P	2.0000	
P_2O_5	30.80	31.39	31.4	31.34	O	13.9882	
Total	100.00	99.73	100.19	100.00			

(1) For formula $Mn^{2+}Mn_2^{3+}(PO_4)_2(OH)_24H_2O$.
(2) C. S. Hurlbut, Jr. (1936), analysis by F. A. Gonyer.
(3) This study, analysis by J. Ito.

[a] Spectrochemical analysis shows: traces of Ti and Sr; faint traces of Na, Si, Cu, Zn, Sn, Ba and Pb; very faint traces of V, Cr, Mo, Ag, and Bi.

which can be expressed as:

$$(Mn^{2+}, Mg, Ca)_{1.00}(Mn^{3+}, Fe,^{3+}, Al)_{1.95}(PO_4)_2(OH)_2 \cdot 3.99H_2O$$

plus a small amount of hydrogen. The resulting ideal formula:

$$Mn^{2+}Mn_2^{3+}(PO_4)_2(OH)_2 \cdot 4H_2O,$$

agrees with that proposed by Leavens and is in conformity with that intimated by Palache, *et al.*, (1951).

The volume of the monoclinic unit cell of the Arizona bermanite is 529.7 Å^3 and the weight of the cell content, using the measured specific gravity (2.84) is 906. The molecular weight calculated from the empirical formula is 226.5 which, with $Z=2$, gives the weight of the cell content as 906. (See Table 2).

Optical and electron probe examination of bermanite from both Arizona and Argentina shows zoning representing chemical variations. Thus the empirical formula represents an average of the bulk composition of the analyzed sample.

A microprobe analysis was carried out on the Argentina bermanite by Dr. C. Klein. His average values in percent were: MnO_2 43.4 and FeO 7.2. He also noted in the different zones an antithetic relation of iron and manganese; the higher the MnO_2 the lower the FeO and visa versa. The reported Fe0 is equivalent to 8.0 percent Fe_2O_3, indicating a higher iron content than the Arizona mineral. If the manganese content given as MnO_2 is allocated to Mn_2O_3 and MnO, in the same ratio as Mn^{3+} to Mn^{2+} (2.15:1) in Ito's analysis (Table 4), the resulting percentages are Mn_2O_3 26.5, Mn0 11.6.

A differential thermal analysis of bermanite from Arizona yielded the curve shown in Figure 8. The first endothermic peak with maximum at 270°C begins at room temperature and at 375°C coalesces with a second endothermic peak. The first peak results from a loss of water amounting to 9.59 percent of the total weight, equivalent to approximately $2\frac{1}{2}$ of the 4 molecules of the bermanite formula. The sample becomes dark brown with the following optical properties: $\alpha=1.765$, $\beta=1.805$ (?), $\gamma=1.835$, opt (−), $2V\approx70°$. The spacings of the strongest lines of the X-ray powder photograph are: 7.24(100), 2.51(50), 2.82(30), 3.30(20) Å. These spacings are similar to those reported by Leavens (1967). The second endothermic peak with a maximum at 430°C and extending to 590°C is interpreted as indicating loss of the remaining H_2O and possibly some (OH). The color is dark brown to black. The resulting phase is poorly

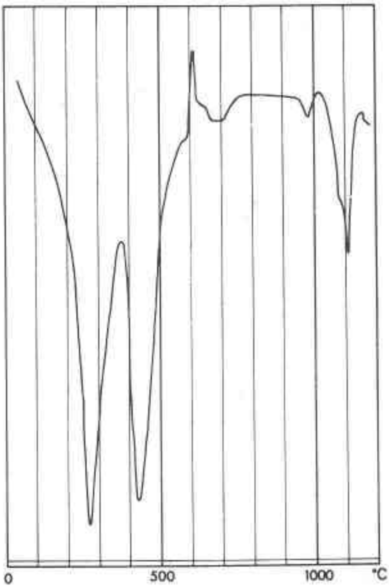


FIG. 8. Differential thermal analysis curve of bermanite from 7-U-7 Ranch, Arizona. Rate of heating 25°C/min.; reference junction 0°C; thermocouple Pt/Pt+13% Rh; reference material Al_2O_3.

crystalline with a mean index of refraction of 1.810 and yields only broad ill-defined lines on an X-ray powder photograph.

The exothermic peak with maximum at 610°C is produced by a transformation to a microcrystalline aggregate apparently composed of a single phase with surprisingly low mean index of refraction, 1.620. The spacings of the principal lines in the X-ray powder photograph are: 2.71(100), 3.01(80), 2.81(70), 3.41(60) Å.

The exothermic peak is followed by two small endothermic peaks with maxima at 695° and 985°C. Bermanite heated in the range 800°–1000°C produces invariably, whether cooled slowly or rapidly, a microcrystalline phase with mean index of refraction of 1.705. It yields an excellent powder photograph whose principal lines have the following spacings: 2.26(100), 2.75(82), 2.15(80), 2.34(64) Å. Its color is gray in contrast to the dark-browns of the heating products formed at lower temperatures.

The final endothermic peak at 1110°C is a consequence of fusion of the sample. A dark red glass with an index of refraction of 1.695 results.

All the heating products of bermanite are magnetic.

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