

## REEXAMINATION OF BERMANITE

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## ABSTRACT

The space group of bermanite, determined from X-ray precession and Weissenburg photographs of crystals from the type locality, is  $C222_1 = D_2^3$ ;  $a = 6.20_0$ ,  $b = 8.92_3$ ,  $c = 19.20_6$  Å. Indexed X-ray powder data are included. Space group restrictions and microprobe analysis of type material show that the ideal formula of bermanite is  $Mn^{2+}Mn_2^{3+}(PO_4)_2(OH)_2 \cdot 4H_2O$ ,  $Z = 4$ . Microprobe examination showed that crystals from the type locality contain iron only in the rims; bermanite from the Fletcher Quarry, North Groton, N. H., is homogeneous and contains less than 0.25 percent iron. Available physical data for bermanite are summarized and thermogravimetric and infrared analyses added. The known occurrences for the mineral are reviewed. Bermanite is common in small amounts as one of the last phosphates to form during the weathering of primary pegmatitic iron-manganese phosphates.

## INTRODUCTION

Bermanite was originally described by Hurlbut (1936) as an alteration product of triplite in a pegmatite on the 7-U-7 Ranch, west of Hillside, Bagdad district, Arizona. The formula was determined to be  $Mn_5Mn_8(PO_4)_8(OH)_{10} \cdot 15H_2O$ . Since then, bermanite has been reported from the Sapucaia pegmatite, Brazil (Lindberg and Pecora, 1958), and from pegmatites in Portugal (Correia Neves, 1958a, b, 1960a, b) and Madagascar (Behier, 1958, 1960).

This paper presents findings on the space group and the proposed new formula of bermanite as well as a summary of the physical properties and occurrence of the mineral.

*Space Group.* The largest and best-formed crystals of bermanite are from the type locality. Even these are small, being one or two mm. in size at most, and are usually in sheaf-like aggregates, with curved, composite faces. After a number of trials a crystal from the type locality was selected for X-ray study. Even this crystal gave some weak doubling of diffraction spots because of composite crystallinity. However, the results were entirely suitable for space-group determination.

Zero-first- and second-level precession photographs were made about the  $c$  and  $a$  axes using Mo/Zr radiation. These indicated an orthorhombic,  $c$ -centered cell with a screw axis in the  $c$  direction. A 0-level photograph, about  $a$ , using a very long exposure, showed no diffraction spots incompatible with the screw axis. The second level about  $a$  showed that 0-level extinctions were caused by a screw axis and not by a  $b$  glide plane. A 0-level  $b$  axis Weissenburg photograph gave the same results; in addition, symmetrically placed spots showed the same intensities, indicating that bermanite is orthorhombic, not monoclinic with  $\beta = 90^\circ$ .

These symmetry restrictions are compatible only with the space group

$C222_1 = D_2^5$ . Hence the crystal class of bermanite is orthorhombic disphenoidal, a noncentrosymmetric class.

Several minute crystals of bermanite from the type locality were sent to J. W. Davisson of the U. S. Naval Research Laboratory, Beltsville, Md., for determination of centrosymmetry. Dr. Davisson reported that:

"The crystals appear to be non-centrosymmetric. When the glass phial containing the specimens is immersed in liquid nitrogen (cork removed), the specimens tend to separate and cling to the wall. If the specimens are then dislodged from the wall by tapping, they cling at a different position. When specimens of NaCl of equivalent size are similarly treated, there is no clinging action. When both bermanite and NaCl specimens are placed together in the phial, the bermanite clings and the NaCl does not.

The clinging action is not due to ice formation, since the clinging action of bermanite persists after dislodgement. It is inferred that the clinging action is due to the formation of electrostatic charge produced by the pyroelectric effect. This can be taken as strong evidence that the crystal lacks a symmetry center."

TABLE 1. X-RAY POWDER DATA FOR BERMANITE  
WILLIAMS PROSPECT, COOSA COUNTY, ALABAMA

<i>I</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>
10	9.62	9.60	002	2b	2.783	2.790	203
6	5.09	5.09	110	1	2.669	2.682	130
5	4.81	4.80	004	1	2.600	2.601	026
1	4.47	4.46	020	2	2.538	2.546	220
2	4.35	4.35	021	1	2.475	2.474	133
1	4.03	4.05	022	1b	2.446	2.461	222?
3	3.65	3.66	023	3	2.340	2.342	134
1	3.50	3.49	114	1	2.167	2.171	042, 118
4	3.266	3.269	024	3	2.114	2.114	028
1-	3.196	3.201	006	1	2.057	2.056	136, 207
2	3.066	3.066	115	2	1.926	1.925	029
1-	3.061	3.060	201	1-	1.854	1.857	3, 14
5	2.909	2.911	025	1	1.830	1.830	046

FeK $\alpha$  radiation, 114.59 mm. camera.

X-ray powder film data for bermanite from the Williams property, Coosa County, Alabama, was used to refine the unit cell dimensions (Table 1). The computer program used was that of Evans *et al.* (1963). Refinement yielded  $a = 6.20_0$ ,  $b = 8.92_5$ ,  $c = 19.20_6$  Å, with a standard error of 0.028 Å.

Although bermanite is noncentrosymmetric, crystals from the type locality, the only ones suitable for goniometric study, appear holohedral, with symmetrical development of the *hkl* faces.

*Chemistry.* The space group  $C222_1$  contains only four- and eight-fold

positions, and the formula originally proposed for bermanite,  $\text{Mn}_5^{2+}\text{Mn}_8^{3+}(\text{PO}_4)_8(\text{OH})_{10}\cdot 15\text{H}_2\text{O}$ , with  $Z=1$ , is incompatible with this space group. However, the similar formula  $\text{Mn}_4^{2+}\text{Mn}_8^{3+}(\text{PO}_4)_8(\text{OH})_8\cdot 16\text{H}_2\text{O}$ , with four  $\text{Mn}^{2+}\text{Mn}_2^{3+}(\text{PO}_4)_2(\text{OH})_2\cdot 4\text{H}_2\text{O}$  per unit cell fits the space group requirements.

A sample of the type material was analyzed with the ARL electron microprobe, and the results were used to interpret the original wet analysis. Microprobe analysis gave essentially no Na and less than 0.1 percent Ca, and MgO between 2.2 percent and 2.5 percent in the type bermanite. Iron is strongly concentrated in the rims of type bermanite crystals, as described at the end of this section. In the absence of other evidence it is assumed that the bulk  $\text{Fe}_2\text{O}_3$  value of the original analysis is correct.

The original analysis of bermanite (Gonyer in Hurlbut, 1936), is given in Table 2, column 1. Below the oxide analysis are the elemental propor-

TABLE 2. RECALCULATION OF THE FORMULA OF BERMANITE  
CALCULATED ON BASIS OF 8 P PER UNIT CELL

	1	2	3
$\text{Fe}_2\text{O}_3$	3.04	3.06	3.03
$\text{Mn}_2\text{O}_3$	28.84	29.15	31.71
MnO	13.82	13.97	11.62
MgO	2.40	2.42	2.42
CaO	0.72		
$\text{Na}_2\text{O}$	0.32		
$\text{H}_2\text{O}$	19.38	19.59	19.53
$\text{P}_2\text{O}_5$	31.48	31.81	31.79
	100.00	100.00	100.00
$\text{Fe}^{3+}$	.692	.678	.678
$\text{Mn}^{3+}$	6.596	6.596	7.182
$\text{Mn}^{2+}$	3.518	3.514	2.928
Mg	1.076	1.072	1.072
Ca	.230		
Na	.192		
H	38.86	38.80	38.80
P	8	8	8

1. Bermanite, 7-U-7 Ranch, Hillside, Arizona. Recalculated to 100%; original summation 99.73% (Hurlbut, 1936).

2. Same analysis recalculated to 100% after deducting  $\text{Na}_2\text{O}$  and CaO.

3. Same analysis with  $\text{Mn}^{2+} + \text{Mg}^{2+}$  set at 4 and balance of  $\text{Mn}^{2+}$  put with  $\text{Mn}^{3+}$ .

tions calculated from it in terms of eight P atoms. Column 2 shows this same analysis recalculated to 100 percent after the deduction of  $\text{Na}_2\text{O}$  and  $\text{CaO}$  as impurities, with the atomic proportions below. In the lower part of column 3 are the atomic proportions derived by taking divalent Mn in excess of  $\text{Mn}^{2+} + \text{Mg}^{2+} = 2$  and adding it to trivalent Mn, without changing any of the other atomic proportions. The whole is an excellent fit for the suggested formula,  $\text{MnMn}_2(\text{PO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ . The upper part of column 3 is the oxide analysis calculated from the lower part of the column. It is close to the original analysis, without  $\text{Na}_2\text{O}$  or  $\text{CaO}$ , except for the amounts of  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}$ .

Thus, a quite small error in the determination of the relative amounts of the two valence states of Mn would account for the difference between the formula originally proposed for bermanite and that suggested now. Total Mn is unchanged by this shift.

As mentioned above, microprobe examination showed that crystals of type bermanite are inhomogeneous; the inner parts of the crystals contain at most only a few tenths of 1 percent  $\text{Fe}_2\text{O}_3$ . The edges, a few tens of microns thick, contain approximately  $15 \pm 2$  percent  $\text{Fe}_2\text{O}_3$ . This means that the rims contain approximately equal amounts of trivalent Fe and Mn, although the cores contain almost no iron. The discontinuity between rim and core is sharp.

Microprobe examination of bermanite from the Fletcher Quarry, North Groton, New Hampshire, showed it to contain less than 0.25 percent iron, but slightly more than the cores of the type crystals. No Ca or Na was detected.

#### PHYSICAL DATA

Optical constants and specific gravity were measured for bermanite from the Williams pegmatite property, Coosa County, Alabama. Specific gravity was determined by suspension of grains in heavy liquids. These values and other data are summarized in Table 3.

Thermogravimetric and infrared absorption analyses were made on a 50 mg. sample of bermanite from the Williams prospect, Coosa County, Alabama. The infrared absorption spectra of bermanite at  $25^\circ\text{C}$  and  $100^\circ\text{C}$  are the same, and show absorption bands due to water and hydroxyl. On heating, bermanite gradually loses weight, presumably from water loss. At  $260^\circ\text{C}$  it has lost 10.52 weight percent; it then remains stable until heated to about  $290^\circ\text{C}$ . Infrared examination of this stable material shows that both water and hydroxyl are still present, but that water is much diminished. The X-ray diffraction pattern of this heated material (Table 4) is unlike that of bermanite.

Further heating is accompanied by continued weight loss, until, at

TABLE 3. OPTICAL DATA AND SPECIFIC GRAVITY OF BERMANITE

	7-U-7 Ranch Hurlbut, 1936	Coosa Co. Ala. This study	Mangualde, Port. Correia Neves, 1958a
$\alpha$	1.687	1.687	1.685
$\beta$	1.725	1.729	<1.744
$\gamma$	1.748	1.751	slightly >1.744
$2V$	(-) 74°	(-) about 75°	(-)
orientation	$X=c$ $Z=a$	$X=c$	$X=c$ $Z=a$
	$r < v$	$r < v$ , strong	$r < v$ , strong
pleochroism	$X$ light red $Y$ pale yellow $Z$ deep red	$X$ light red $Y$ pale yellow $Z$ red	$X$ brown $Y$ light brown $Z$ dark brown
S.G.	2.84	2.85 (calc. 2.88)	

350°C, the material has lost 16.67 weight percent and again forms a stable compound over a heating range of about 30°C. Infrared examination of the second stable heating product shows that all water is gone and that hydroxyl is largely depleted as well. The X-ray diffraction pattern of this material, given in Table 4, is somewhat like that of the first heating product. Neither of these patterns could be identified, in whole or part, in the ASTM file; both are weak and diffuse.

Continued heating caused additional weight loss, but no other stable compounds appear; when the run was ended at 1000°C, the specimen had lost 25.1 weight percent and was fused.

TABLE 4. X-RAY DATA FOR PRODUCTS OF HEATING BERMANITE

#1 (260°C)		#2 (350°C)	
$d$	$I$	$d$	$I$
8.93	3	7.05	2
7.26	10b	4.86	3
3.34	2	4.65	3
3.10	1	3.50	10
2.843	10	3.257	3
2.694	2	2.52	5b
2.519	6b		
1.545	1		
1.347	1b		

FeK $\alpha$  radiation, 114.59 mm. camera.

It was hoped that the thermogravimetric and infrared studies would elucidate the role of water in bermanite, but this did not prove to be the case, as bermanite recrystallizes on heating rather than dehydrating without structural change.

#### OCCURRENCE

Known occurrences of bermanite are given in Table 5, with a brief summary of associations. Bermanite is known only from pegmatites

TABLE 5. OCCURRENCES OF BERMANITE

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7-U-7 Ranch, Hillside, Arizona (Hurlbut, 1936). Coating seams in triplite, associated with metastrengite (Hurlbut's mineral #1), leucophosphite (#3), hureaulite (#6), and other phosphates.

Stewart Mine, Pala, Calif. With metastrengite, stewartite, and hureaulite on lithiophyllite and sicklerite. Schaller (1913) described the occurrences, but did not mention bermanite.

Tanti, Argentina (C. S. Hurlbut, Jr., pers. comm. 1965) (Pegmatite along rte 20, 5 mi. W of Tanti, Prov. Crodoba, Argentina. Crust on metastrengite coating triplite.

Fletcher quarry, North Groton, New Hampshire. Crusts on rockbridgeite; also an alteration of hureaulite with metastrengite and stewartite.

Madagascar (Behier, 1958). With metastrengite as an alteration of triplite.

Mangualde, Portugal (Correia Neves, 1958). Specimens of the USNM showed bermanite with metastrengite coating stewartite and weathered lithiophyllite.

Sapucaia pegmatite, Minas Gerais, Brazil (Lindberg & Pecora, 1958). Sparingly with metastrengite coating barbasalite-frondelite rock.

Williams prospect, Coosa County, Alabama (Leavens & Simpson, in prep.). Intimately intergrown with metastrengite and Mn oxides in rockbridgeite-lipscombite rock; in some specimens with stewartite and strunzite as an alteration of hureaulite.

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which contain oxidized and weathered masses of lithiophyllite, triphylite, triplite, or other primary manganese-iron phosphates. Bermanite is one of the last minerals to form during the weathering. It occurs lining seams and cavities and in small masses in the primary mineral or in such secondaries as rockbridgeite, hureaulite, or sicklerite. It may be a direct alteration of hureaulite, as at the Fletcher quarry; elsewhere, as at Pala, California, and the type locality, it is associated with fresh, late hureaulite crystals.

Metastrengite is usually associated with bermanite; stewartite is somewhat less common. Bermanite alters to Mn oxides; one Mn oxide altera-

tion of the bermanite from the Williams prospect gave an X-ray diffraction pattern like that of birnessite, but too diffuse to identify positively.

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