X-RAY STUDY OF HOLDENITE, MOOREITE AND TORREYITE

JOAN PREWITT-HOPKINS,
*Radcliffe College, Cambridge, Massachusetts.**

ABSTRACT

The following data have been obtained by the Weissenberg and powder diffraction methods:

Holdenite. Unit cell dimensions: $a_0=11.97$kX, $b_0=31.15$, $c_0=8.58$. Space group *Bmam*. Cell contents $2[(Mn, Ca)_{25}(Zn, Mg, Fe)_{15}(AsO_4)_7(OH)_{33}O_{13}]$. Specific gravity 4.118 (calc.), 4.11 (meas.).

Mooreite. Unit cell dimensions: $a_0=11.18$ kX, $b_0=20.25$, $c_0=19.52$. Space group $P2_1/m$. Cell contents $13[(Mg, Mn, Zn)_8(SO_4)4H_2O]$. Specific gravity 2.543 (calc.), 2.47 (meas.).

Delta-mooreite, originally thought to be a chemical variant of mooreite, is a distinct species. The new name *torreyite* is proposed for the mineral.

HOLDENITE

Holdenite was first described by Palache and Shannon[1] in 1927, as an arsenate of manganese and zinc with the probable formula: $Mn_8Zn_4(AsO_4)_2(OH)_{10}O_4$. The only specimen on which the mineral was found is a slab of massive franklinite apparently from the wall of a veinlet as indicated by a slickensided surface. Also on the specimen were small amounts of calcite, willemite, barite, galena, and pyrochroite.

The orthorhombic crystals are all well developed with many forms, and conform to dipyramidal symmetry. The crystals are tabular parallel to the macropinacoid and have a poor brachypinacoidal cleavage. The color varies slightly but is mostly a clear pink with either a yellowish or purplish tinge. Crystals from the original specimen have been studied by the Weissenberg method. 0-layer photographs were taken in copper radiation about [001], [010], and [100], and 1- and 2-layer photographs were taken around [001]. The following data were obtained:

(a) from rotation photographs	(b) from Weissenberg photographs
$a_0=11.84\pm0.2$ kX	$a_0=11.97\pm0.08$ kX
$b_0=31.15\pm0.3$	$b_0=31.15\pm0.08$
$c_0=\ 8.58\pm0.3$	$c_0=\ 8.58\pm0.1$

The original morphological cell selected by Palache coincides with the structure cell here found. Using the values from Weissenberg photographs the axial ratio of the structure cell is: $a_0:b_0:c_0=.3842:1:.2754$ as compared with $a:b:c=.3802:1:.2755$ in the morphological cell. The cell of holdenite as determined from the Weissenberg projections is

* Contribution from the Department of Mineralogy and Petrography, Harvard University, No. 305.

[1] Palache, C., and Shannon, E. V., Holdenite, a new arsenate of manganese and zinc, from Franklin, New Jersey: *Am. Mineral.*, **12**, 144–148 (1927).

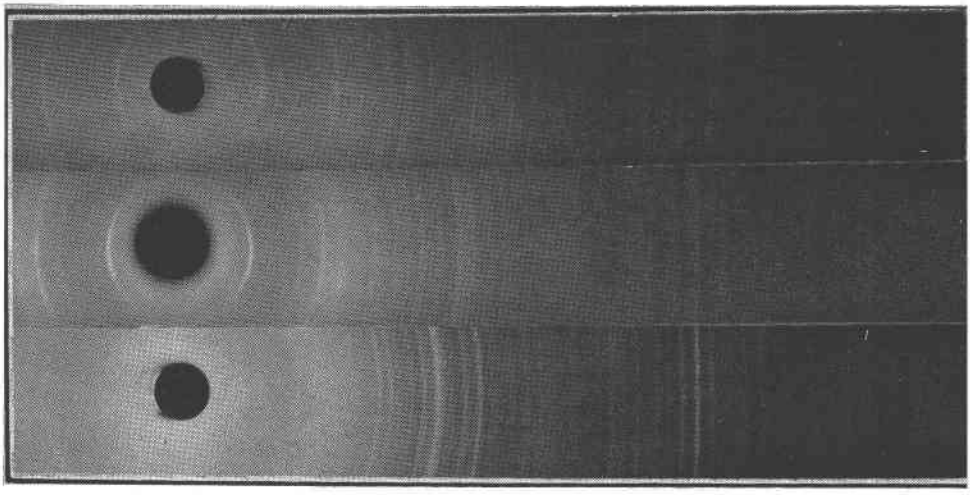

FIG. 1. Powder Photographs
Top: mooreite
Middle: torreyite
Bottom: holdenite

B-centered with a glide along [100]. Assuming that the mineral is holohedral as indicated by its morphology, the space group is *Bmam*. The spacing data obtained from powder photographs is summarized in Table 4, and the pattern is shown in Fig. 1.

The specific gravity was originally given as 4.07, which was determined by floating in Clerici solution. By measurement on the Berman microbalance it has been redetermined as $4.11 \pm .01$. Using this data and the original analysis of Shannon the following cell contents have been obtained:

The simplest formula is thus: $(Mn, Ca)_{25}(Zn, Mg, Fe)_{15}(AsO_4)_7(OH)_{33}O_{13}$ with Mn:Ca = 46:4, and Zn:Mg:Fe = 25:3:2.

The calculated specific gravity is 4.118, which compares closely to the measured specific gravity of 4.11. The formula is complex and can not be regarded as entirely certain due to the unsatisfactory nature of the analysis. The original sample, obtained after great difficulty, weighed only 0.42 gram, and was shown to contain impurities in unknown amounts. Almost 10 per cent of the sample was assumed to be impurities, but there is no tangible evidence to that effect. Perhaps some of the silica is present substituting for arsenic, rather than all in the form of willemite. Further, more calcium may be substituting for manganese than is indicated, since the actual amount of carbon dioxide present is uncertain.

TABLE 1. CELL CONTENTS OF HOLDENITE

	1	2	3	4	5	6		7	8
CaO	3.80	.268	.0478	.0478	.0478	3.81	50.93	50	2.81
MnO	37.75	41.92	.5910	.5910	.5910	47.12			40.84
ZnO	28.08	25.12	.3087	.3087	.3087	24.61	30.00	30	25.46
MgO	1.45	1.61	.0399	.0399	.0399	3.18			1.51
FeO	1.80	2.00	.0278	.0278	.0278	2.21			1.80
As_2O_5	17.40	19.32	.0846	.4230	.1692	13.49			20.14
H_2O	6.62	7.35	.4079	.4079	.8158	65.04		66	7.44
PbO	Trace					O=147.18		148	
SiO_2	2.01								
CO_2	[1.09]								
	[100.00]	100.00		1.846					100.00

1. It was shown that the analyzed sample was impure and contained calcite and willemite. From this it has been assumed that the silica, carbon dioxide, and their combining proportions of zinc and calcium are due to such impurities. CO_2 was shown to be present by qualitative test and is here given by difference.

2. Analysis 1 recalculated to 100 per cent after the deduction of CaO and SiO_2 as calcite and willemite.

3. Molecular quotients.

4. Atomic quotient of oxygen.

5. Atomic quotient of the metals.

6. Measured unit cell contents. Molecular weight of cell = 7973.

7. Ideal unit cell contents.

8. The ideal analysis for the formula: $2[(Mn,Ca)_{25}(Zn,Mg,Fe)_{15}(AsO_4)_7(OH)_{33}O_{13}]$ with Mn:Ca = 46:4, and Zn:Mg:Fe = 25:3:2.

MOOREITE

The original description of this mineral was made by Bauer and Berman[2] in 1929 using material from Sterling Hill, New Jersey. The mooreite is associated with altered pyrochroite, rhodochrosite, zincite, and fluoborite in veinlets of calcite-franklinite-willemite ore. Two varieties of mooreite were recognized. One, mooreite proper, occurs in cavities in the pyrochroite in well developed tabular crystals; here the association is with fluffy fluoborite, which resembles fibrous willemite. The other type is massive and occurs in veins cutting the pyrochroite; here the fluoborite is lacking and willemite is in very close association. This latter

[2] Bauer, L. H., and Berman, Harry, Mooreite, a new mineral, and fluoborite from Sterling Hill, N. J.: *Am. Mineral.*, **14,** 165–172 (1929).

TABLE 2. CELL CONTENTS OF MOOREITE

	1	2	3	4	5	6	7	8
MgO	25.41	25.38	.629	.629	.629	57.98		25.26
MnO	11.46	11.93	.168	.168	.168	15.49	104	11.11
ZnO	24.57	24.58	.302	.302	.302	27.84		25.19
SO_3	11.11	10.99	.137	.412	.137	12.63	13	10.72
H_2O	27.20	27.12	1.505	1.505	3.01	277.46	286	27.17
B_2O_3	present					O=278.38	286	
	99.75	100.00		3.02				

1. Original analysis of L. H. Bauer, 1929. B_2O_3 found present but not determined.
2. Analysis 1 recalculated to 100 percent after deducting $CaCO_3$ 0.89 and SiO_2 0.06 per cent.
3. Molecular quotients.
4. Atomic quotient of oxygen.
5. Atomic quotient of the metal.
6. Measured number of atoms in the unit cell. Molecular weight of the cell=9217.92.
7. Theoretical number of atoms in the unit cell.
8. Calculated analysis from the formula:
   $13[(Mg, Mn, Zn)_8(SO_4)(OH)_{14} \cdot 4H_2O]$ where Mg:Mn:Zn=59:16:29.

variety has been called delta-mooreite and is re-described on a following page.

The crystals of mooreite are white with a pearly luster and are tabular parallel to the cleavage, which is perfect and clinopinacoidal. Though no mention of twinning was made in the earlier description, effects seen optically and on x-ray patterns show that many of the crystals are twinned. An attempt to define the twinning law has proved unsuccessful; all evidence indicates twinning on {100}, but this is not certain.

Material was used from the type analyzed specimen from Sterling Hill. Rotation, 0-, 1-, 2-layer Weissenberg photographs were taken about [100], [010], [001]. The unit cell dimensions using the average obtained from 0-layer Weissenberg films are:

$$a_0=11.18 \text{ kX}, b_0=20.25, c_0=19.52.$$

The powder photograph is illustrated in Fig. 1 and the data summarized in Table 4. The space group is defined by the observed systematic extinctions,

hkl present all orders
$h0l$ present all orders
$0k0$ present only when $k=2n$,

as $P2_1$ or $P2_1/m$. Since the morphology is monoclinic holohedral the

space group is $P2_1/m$. The elements and projection constants in the cell are:[3]

$p_0=1.743$	$a=0.551$
$q_0=0.812$	$c=0.961$
$\mu=57°37'$	$\beta=122°23'$

The ratio of the x-ray cell is: $a_0:b_0:c_0=0.552:1:0.964$.

The specific gravity was originally given as 2.470, as measured on the pycnometer, and this was confirmed by several new measurements on the Berman microbalance. Using this specific gravity and the observed cell dimensions, the cell contents are as follows:

The simplest formula is thus: $13[(Mg,Mn,Zn)_8(SO_4)(OH)_{14}\cdot 4H_2O]$ where Mg:Mn:Zn=59:16:29. (Berman gives: Mg:Mn:Zn=4:1:2.) The specific gravity calculated from this is 2.543, as compared with the experimental value of 2.470.

The formula found here is identical with that given by Berman. The agreement between the actual number of atoms in the unit cell and the theoretical number and between the calculated and measured specific gravities is satisfactory in view of the large size of the cell and the presence of impurities in unknown amounts in the analyzed sample.

TABLE 3. A COMPARISON OF THE PROPERTIES OF MOOREITE AND TORREYITE (DELTA-MOOREITE)

Mooreite	Torreyite (delta-mooreite)
$(Mn, Mg, Zn)_8(SO_4)(OH)_{14}\cdot 4H_2O$	$(Mg, Mn, Zn)_7(SO_4)(OH)_{12}\cdot 4H_2O$
where Mg:Mn:Zn=4:1:2	where Mg:Mn:Zn=5:3:4
nX=1.533	nX=1.570
nY=1.545	nY=1.584
nZ=1.547	nZ=1.585
2V=50°±	2V=40°±
G=2.47	G=2.665
Perfect clinopinacoidal cleavage.	Perfect clinopinacoidal cleavage.
Monoclinic holohedral.	Monoclinic.
Powder data in Table 4 and Fig. 1.	Powder data in Table 4 and Fig. 1.

TORREYITE (formerly delta-mooreite)

Delta-mooreite was first described by Bauer and Berman[2] as a very basic, hydrous sulfate of magnesium, manganese and zinc, differing somewhat from mooreite in ratios. It also was observed to be formed

[3] The elements given in Berman's paper were calculated from selected angles. LaForge (priv. comm., 1936) recomputed the elements in 1936 using all of the measured angles and his values are used here.

TABLE 4. X-RAY POWDER DATA. Fe RADIATION, Mn FILTER

Holdenite		*Mooreite*		*Torreyite*	
d	*I*	*d*	*I*	*d*	*I*
5.83	6	10.37	10	13.06	10
4.69	2	8.29	9	8.17	4
4.15	1	7.66	1	7.20	3
3.93	1	6.66	3	6.18	7
3.76	1	6.22	3	5.35	9
3.61	9	5.98	4	4.71	6
3.43	2	5.14	10	4.54	6
3.31	1	4.61	5	4.13	2
3.14	1	4.38	7	3.85	8
2.99	10	4.14	5	3.72	4
2.72	1	3.82	6	3.47	5
2.60	2	3.45	7	3.29	5
2.47	8	3.41	1	3.13	5
2.38	4	3.32	3	2.91	5
2.34	2	3.16	6	2.81	3
2.25	1	3.02	1	2.76	7
2.20	1	2.93	4	2.61	5
2.09	2	2.84	2	2.47	3
2.04	1	2.79	2	2.37	3
2.01	1	2.68	6	2.29	2
1.79	2	2.62	5	2.23	1
1.77	1	2.56	4	2.15	1
1.75	1	2.49	1	2.09	1
1.63	2	2.45	4	2.04	1
1.60	1	2.39	7	1.97	1
1.56	1	2.32	5	1.85	2
1.53	3	2.29	4	1.79	2
1.49	1	2.20	1	1.76	1
1.43	1	2.15	2	1.73	2
1.40	2	2.12	3	1.70	3
1.31	1	2.04	2	1.62	3
1.27	1	1.98	2	1.58	2
1.25	2	1.96	3	1.56	3
1.23	2	1.91	3	1.53	1
1.14	1	1.88	3	1.50	2
1.08	1	1.86	2	1.41	1
1.05	1	1.83	2		
1.04	1	1.79	3		
		1.76	1		
		1.74	7		

earlier than mooreite. The formula was given as $(Mg,Mn,Zn)_7(SO_4)(OH)_{12}\cdot 4H_2O$, with Mg:Mn:Zn = 5:3:4. It occurs only at Sterling Hill, N. J. No crystals have been found but an optical study indicated that it is monoclinic. There is a good {010} cleavage.

When a powder photograph of delta-mooreite was taken it was found to be quite different from that of mooreite. The powder data is given in Table 4 and the photographs are reproduced in Fig. 1. Thus, the two minerals are structurally unlike and are distinct species. A comparison of their properties is given in Table 3. A new name, *torreyite,* is proposed to replace the name delta-mooreite. Torreyite is in honor of John Torrey[4] (1796–1873), who was a natural scientist with special interests in botany, chemistry, and mineralogy. He received his early training in chemistry and mineralogy from Amos Eaton. Naming the mineral for him seems appropriate as he was one of the earliest workers at Franklin, publishing a paper on franklinite, willemite, and rhodonite in 1822.[5]

The material used for *x*-ray work was from the type specimen and was checked optically, by its specific gravity and spectrographically. The chemical analysis by Bauer follows:

MgO	17.27
MnO	17.98
ZnO	26.30
SO_3	11.64
H_2O	26.39
B_2O_3	present
SiO_2	0.08
	99.66

No mention of twinning was made by Berman but intricate polysynthetic twinning was observed in the present study. Using the universal stage the twin plane was identified as perpendicular to the {010} cleavage.

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[4] Encyclopedia Britannica, 14th ed., 1929, vol. 22, p. 305. John Torrey: A biographical notice, *Am. Jour. Sci.*, 3rd series, **5,** 411–421.

[5] Torrey, John, *Am. Jour. Sci.*, Ser 1, **5,** 399–403 (1822).