MANGANPYROSMALITE AND ITS POLYMORPHIC RELATION TO FRIEDELITE AND SCHALLERITE*

CLIFFORD FRONDEL AND L. H. BAUER,
Harvard University, Cambridge, Massachusetts, and New Jersey Zinc Company, Franklin, New Jersey

ABSTRACT

Manganpyrosmalite, $(Mn, Fe)_8(Si_6O_{15})(OH, Cl)_{10}$, is a new species isostructural with pyrosmalite. It occurs at Sterling Hill, New Jersey, as granular veinlets in franklinite ore. Hexagonal, with a_0 13.36 Å, c_0 7.16; Z=2; G=3.13 (meas.), 3.14 (calc.). Uniaxial negative, with ω 1.669, ϵ 1.631 (Na). Hardness $4\frac{1}{2}$. Perfect cleavage (0001). Color pure brown.

Manganpyrosmalite, schallerite and friedelite are polymorphs representing multiple stacking variants along [0001] of layer-structures, analogous to the micas. Cell dimensions (new data):

	a_0	c_0	Lattice type	Z
Manganpyrosmalite	13.36 Å	7.16	Hexagonal	2
Pyrosmalite	13.35	7.15		
Schallerite	13.43	14.31	Hexagonal	4
Friedelite	13.40	21.43	Rhombohedral	6

All of these species show serial variation in composition by substitution of (Mn^2, Fe^2), (OH, Cl) and (Si, As^3). Ferroschallerite is discredited; it is a variety of friedelite. Zeophylite, gyrolite, truscottite, okenite and centrallassite are not related to the minerals at hand.

MANGANPYROSMALITE

Pyrosmalite, $(Fe, Mn)_8(Si_6O_{15})(OH, Cl)_{10}$, is known only from the magnetite deposits of Nordmark and Dannemora, Sweden. The manganese-rich analogue of pyrosmalite recently has been found in the franklinite deposit at Sterling Hill, New Jersey. The mineral occurs in massive granular form with friedelite, bementite and willemite as veinlets. Individual grains range up to about 0.3 mm. in size and show a perfect basal cleavage. The cleavage surfaces are warped, and the aggregates have a somewhat schistose structure. The specific gravity is 3.13 and the hardness is $4\frac{1}{2}$. Optically, the mineral is uniaxial negative and the indices of refraction, measured in sodium light, are ω 1.669, ϵ 1.631.

An x-ray powder pattern taken in filtered iron radiation was indexed in terms of a hexagonal cell with $a_0=13.36$, $c_0=7.16$ Å, as shown in Table 1. Gossner and Mussgnug (1931) reported a hexagonal cell with $a_0=13.44$, $c_0=7.20$ kX from an x-ray rotation study of the isostructural mineral pyrosmalite, and the values $a_0=13.35$, $c_0=7.15$ Å were obtained here from rotation photographs taken in iron radiation of pyrosmalite

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TABLE 1. *X*-RAY POWDER SPACING DATA FOR MANGANPYROSMALITE
Iron radiation, manganese filter. Indexing for hexagonal cell with $a_0 = 13.36$ Å, $c_0 = 7.16$.

I	*d* meas.	*d* calc.	*hkil*	*I*	*d* meas.	*d* calc.	*hkil*
3	11.60	11.57	$10\bar{1}0$	1	1.768	1.769	$10\bar{1}4$
10	7.16	7.16	0001	1*	1.733	1.729	$11\bar{2}4$
1	6.71	6.68	$11\bar{2}0$	5	1.672	1.670	$44\bar{8}0$
3	6.09	6.09	$10\bar{1}1$	4	1.627	1.626	$30\bar{3}4$
1	5.77	5.78	$20\bar{2}0$	5	1.523	1.523	$40\bar{4}4$
2	4.886	4.885	$11\bar{2}1$	1	1.432	1.432	0005
1	4.509	4.500	$20\bar{2}1$	2	1.419	1.421	$10\bar{1}5$
1	4.376	4.373	$21\bar{3}0$			1.416	$50\bar{5}4$
2	3.736	3.732	$21\bar{3}1$	2	1.371	1.385	$42\bar{6}4$
8	3.583	3.580	0002			1.390	$20\bar{2}5$
4	3.419	3.421	$10\bar{1}2$	2	1.342	1.342	$30\bar{3}5$
3	3.338	3.340	$22\bar{4}0$	2	1.285	1.283	$40\bar{4}5$
2	3.035	3.028	$22\bar{4}1$	1	1.266	1.262	$8.2.\bar{1}0.0$
		3.040	$20\bar{2}2$	1	1.238	1.244	$63\bar{9}3$
2	2.882	2.892	$40\bar{4}0$	1	1.194	1.195	0006
2	2.770	2.770	$21\bar{3}2$	1**	1.790		
9	2.683	2.682	$40\bar{4}1$	1**	1.406		
2	2.549	2.525	$41\bar{5}0$	2*	1.126	1.124	$22\bar{4}6$
2	2.385	2.386	0003	1**	1.106		
1	2.334	2.337	$10\bar{1}3$	2**	1.089		
7	2.251	2.250	$40\bar{4}2$	2**	1.082		
		2.247	$11\bar{2}3$	1**	1.063		
1*	2.102	2.095	$21\bar{3}3$	1**	1.047		
4	1.843	1.840	$40\bar{4}3$				

*=diffuse line; **=very diffuse line.

crystals from Nordmark. The observed *x*-ray unit for pyrosmalite conforms to the accepted morphological unit for this species.

A chemical analysis of the manganpyrosmalite from Sterling Hill is cited in Table 2, together with the unit cell contents calculated therefrom. Assuming the crystal structure to be based on a sheet-framework (phyllosilicate), with an Si:O ratio of 2:5, the formula may be written:

$$(Mn, Fe)_8(Si_6O_{15})(OH, Cl)_{10}.$$

This interpretation corresponds to that taken of pyrosmalite by Berman (1937), Strunz (1949) and Winchell (1951). Two formula-units are contained in the unit cell. The specific gravity calculated from the measured cell contents is 3.14. The structure also can be assumed to be based on a three- or six-fold ring grouping for the silica framework, giving the formula:

$$(Mn, Fe)_8(Si_3O_9)_2(OH, Cl)_4 \cdot 3H_2O$$

This formula corresponds to that derived by Bauer and Berman (1928) for the composition of pyrosmalite. According to Zambonini (1908), pyrosmalite gives off only about 1.3 weight per cent H_2O below 345° C. Other formulae, differing but slightly in weight percentages, can be written depending on the way in which the O and H are arbitrarily assigned to Si, OH or H_2O (see Gossner and Mussgnug (1931) and Zambonini (1901, 1908)). The phyllosilicate interpretation seems likely in view of the micaceous habit and cleavage and particularly in view of the dimensional relations to the polymorphs friedelite and schallerite described beyond.

TABLE 2. CHEMICAL ANALYSIS AND UNIT CELL CONTENTS OF MANGANPYROSMALITE

Analysis (L. H. Bauer)		Molecular quotient	Atomic quotient	Unit cell contents (Exper. M.W.=2086)		Theory
MnO	39.09	.5511	.5511	Mn=11.50	15.99	16
FeO	12.43	.1730	.1730	Fe = 3.61		
MgO	0.74	.0184	.0184	Mg= .38		
ZnO	1.94	.0238	.0238	Zn = .50		
CaO	nil					
SiO_2	34.13	.5683	.5683	Si =11.86	11.89	12
As_2O_5	0.13	.00066	.0013	As = .03		
Cl	3.80	.1072	.1072	Cl = 2.24 2.24 Cl	21.2	20
H_2O	8.18	.4542	.9084	H =18.95 18.95 OH		
	100.44		2.3591 (O)	O =49.22 30.27 O for Si		30
O=Cl	0.86					
	99.58					

The six reported chemical analyses of pyrosmalite, summarized by Hintze (1891), Dana (1892) and Zambonini (1901), and the present analysis of manganpyrosmalite indicate that a continuous solid solution series extends from at least Fe:Mn$\sim$1.5:1 to Fe:Mn$\sim$1:3.2. The names pyrosmalite and manganpyrosmalite are here applied to the halves of the series with Fe>Mn and Mn>Fe in atomic per cent, respectively.

RELATIONS TO OTHER MINERALS

The relations of pyrosmalite to other minerals of similar chemical, crystallographic and optical properties have been discussed by a number of investigators. Among these studies, Berman in his 1937 paper on the classification of the silicates placed pyrosmalite in a group with schallerite, friedelite, ferroschallerite and the calcium-bearing silicates zeophyllite, truscottite, gyrolite and centrallassite. All were interpreted as

TABLE 3. SPECIMENS EXAMINED BY X-RAYS IN THE PRESENT STUDY

Friedelite Pattern

Friedelite. Franklin, N. J. No. 87123. Material analyzed by Schaller, cited by Palache (1910), and cited by Bauer and Berman (1928). The original discovery specimen of friedelite at Franklin.

Friedelite. Franklin, N. J. No. 89854. Sharply developed hemimorphic crystals comprising the material described by Palache (1935) and shown in Fig. 133 and Plate 14, Fig. *C* in his publication. The massive friedelite lining the specimen was analyzed by Gage, cited by Bauer and Berman (1928).

Friedelite. Franklin, N. J. No. 89432. The material analyzed by Bauer and cited by Bauer and Berman (1928). A vein of pale reddish brown material.

Friedelite. Sterling Hill, N. J. No. 89865. A low-chlorine type analyzed by L. H. Bauer in 1927 (unpublished).

Friedelite. Sterling Hill, N. J. No. 89868. Dense, dark flesh-colored vein. A partial analysis made in 1927 by L. H. Bauer, hitherto unpublished, gave Cl 2.96, As_2O_3 0.11, H_2O 9.91 $\omega = 1.648$.

Friedelite. Franklin, N. J. No. 90351. Bright flesh-pink vein material.

Friedelite. Franklin, N. J. No. 89859. Brown type with massive green willemite.

Friedelite. Franklin, N. J. No. 92249.

Friedelite. Franklin, N. J. No. 90341. Dark red-brown dense material resembling serpentine.

Friedelite. Franklin, N. J. No. 91190. Crust of platy reddish brown crystals.

Friedelite. Adervielle, Hautes Pyrénées, France. No. 85643, Dense pink material.

Friedelite. Pajsberg, Sweden. No. 87122. Crystals in cavities of a magnetite-amphibole rock.

Ferroschallerite. Franklin, N. J. No. 89999. Type analyzed material of Bauer and Berman (1930). Coarse cleavable grains associated with a zinc- and manganese-bearing cummingtonite described by the same authors.

Ferroschallerite. Franklin, N. J. No. 92791. Three additional specimens which, with the foregoing, represent the three types of occurrence described by Palache (1935).

Schallerite Pattern

Schallerite. Franklin, N. J. No. 87106. The type analyzed material of Gage, Larsen and Vassar (1925), later re-analyzed by Bauer and Berman (1928). Termed by Bauer and Berman (1928) and by Palache (1935) as schallerite Type I.

Schallerite. Franklin, N. J. No. 89866. The material analyzed by Bauer and Berman (1928) and termed by them and by Palache (1935) as schallerite Type II.

Schallerite. Franklin, N. J. No. 101106. Dense reddish brown type associated with bementite. An unpublished analysis of this material made in 1950 by Mrs. Marie L. Lindberg of the U. S. Geological Survey shows it to be close in composition to the original schallerite (Type I) of Gage, Larsen and Vassar (1925).

Schallerite. Franklin, N. J. No. 90000. Dense vein. Not analyzed.

Pyrosmalite Pattern

Pyrosmalite. Nordmark, Sweden. No. 85651. Blackish brown crystals on magnetite.

Pyrosmalite. Nordmark, Sweden. No. 85650. Pale brown translucent crystals with calcite and fibrous green amphibole.

Pyrosmalite. Dannemora, Sweden. No. 96422. Brown, foliated vein-mass in magnetite-pyroxene rock. Duplicate specimen from Riksmuseets Mineralogiska Avdelning, Stockholm.

Manganpyrosmalite. Sterling Hill, N. J. No. 104001. Material described in the present study.

sheet structures. It was suggested by Berman that solid solution series involving (Fe, Mn), (OH, Cl) and (Si, As[3]) probably extended between friedelite, schallerite and pyrosmalite. All three species were referred to the same formula-type, the names friedelite and pyrosmalite being applied to material high in Mn and Fe, respectively, and the name schallerite to material containing much As[3] in substitution for Si. Strunz (1949) has accepted the formula and the grouping advanced by Berman (1937), but has put the calcium-bearing species into a separate group. He remarks that the minerals of the Friedelite Group probably are homotypes, and points out a dimensional relationship to mica. Winchell (1951) treats pyrosmalite and friedelite as a solid solution series, the names being applied to the Fe and Mn ends of the series, respectively. Schallerite and ferroschallerite are classed separately, as are the calcium-bearing species.

New Data

The mutual relations of the minerals mentioned above have been investigated here by *x*-ray single-crystal and powder methods. The study material, which included a number of analyzed specimens, is described in Table 3. The results of this work may be briefly summed as follows. Pyrosmalite and manganpyrosmalite give identical *x*-ray powder patterns and unit cell dimensions and constitute an isostructural series. Friedelite has a different and distinctive *x*-ray pattern and unit cell, and so does schallerite. The dimensional relations between these minerals prove to be of special interest. The value of a_0 of the unit cell in hexagonal coordinates for all these species is virtually identical, and the values of c_0 are almost exact multiples, as shown in Table 4. The *x*-ray powder data are tabulated in Tables 1 and 5. Manganpyrosmalite, friedelite and schallerite are polymorphs, and represent stacking variants along [0001] of layer structures analogous to the polymorphs found, for example, in the mica group.

It may be noted that type ferroschallerite is found by *x*-ray study to have the pattern and cell dimensions of friedelite. This mineral is only a

Table 4. Unit Cell Dimensions

	a_0	c_0	Lattice type	Unit cell contents
Pyrosmalite	13.35 Å	7.15	Hexagonal	2 $(Fe, Mn)_8(Si_6O_{15})(OH, Cl)_{10}$
Mangan-pyrosmalite	13.36	7.16 (=1)	Hexagonal	2 $(Mn, Fe)_8(Si_6O_{15})(OH, Cl)_{10}$
Schallerite	13.43	14.31 (=2)	Hexagonal	4 $(Mn, Fe)_8(Si_6O_{15})(OH, Cl)_{10}$
Friedelite	13.40	21.43 (=3)	Rhombohedral	6 $(Mn, Fe)_8(Si_6O_{15})(OH, Cl)_{10}$

TABLE 5. *X*-RAY POWDER SPACING DATA FOR FRIEDELITE AND SCHALLERITE
Iron radiation, manganese filter, in Å

Friedelite				Schallerite			
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
1	11.4	1	1.449	9	7.37	2	2.109
9	7.17	1	1.439	10	3.59	5	2.037
7	3.60	2	1.402	2	3.45	3	1.842
6	2.88	1	1.374	1	3.30	2	1.727
10	2.56	3	1.359	1	3.11	9	1.674
3	2.408	1	1.313	5	2.848	3	1.631
4	2.115	2	1.204	7	2.687	4	1.521
2	1.974	1	1.200	3	2.546	1	1.422
3	1.731	1	1.167	6	2.478	3	1.394
6	1.676	1	1.093	1	2.395	2	1.373
2	1.632	1	1.090	1	2.321	1	1.294
1	1.625	1	1.065	3	2.253	1	1.286
1	1.520			1	2.208	2	1.185

variety of friedelite relatively high in Fe and As, and it is not a variety of schallerite or a separate species as originally described by Bauer and Berman (1930). The name should be abandoned. *X*-ray powder study of centrallasite, truscottite, okenite, gyrolite and zeophyllite indicates that these minerals are not related to friedelite, schallerite or pyrosmalite-manganpyrosmalite.

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