CRYSTAL CHEMISTRY OF SCHALLERITE

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ABSTRACT

Crystallographic data obtained from precession and powder diffraction photographs indicate that schallerite is hexagonal. For a specimen containing 6.37 per cent As_2O_3, $a_0 = 13.36$ and $c_0 = 14.24$ Å.

If the combining ratio with oxygen is known for each oxide, the number of oxygen atoms in the unit cell can be calculated from the chemical analysis, specific gravity and dimensions of the unit cell. Knowledge of the number of oxygen atoms, in turn, permits calculation of the number of positively charged atoms, thus leading to the structural formula. The method is illustrated by calculations on schallerite.

A fundamental difficulty arises from the recent assumption of a phyllosilicate structure for schallerite: either the number of tetrahedral cations is significantly deficient or the number of oxygen atoms is excessive or both.

INTRODUCTION

Investigations on schallerite were carried out without knowledge of concurrent studies on manganpyrosmalite, friedelite and schallerite by Frondel and Bauer (1953). These authors concluded that these three minerals are phyllosilicates in which arsenic occurs in tetrahedral coordination in isomorphic substitution for silicon. However, the only mineral that they considered in detail chemically contained merely 0.13 per cent As_2O_5. Thus the question of the manner of occurrence of arsenic in the structure does not appear to have been conclusively resolved by their results.

Whereas the writer's crystallographic measurements essentially confirm the measurements reported by Frondel and Bauer (1953), their conclusion concerning the phyllosilicate structure of schallerite contains a fundamental incompatibility which they did not adequately consider.

Gossner and Mussgnug (1931) investigated pyrosmalite by Laue and rotation methods, and although they discuss the dimensional relation to mica and chlorite, they do not indicate a structural relation to phyllosilicates. These authors were unable to obtain a complete structural analysis, but they concluded that the structural formula for pyrosmalite is $4[(Mn, Fe)_4(OH, Cl)_6Si_3O_7]$, and obtained $a_0 = 13.44$ and $c_0 = 7.20$ for the hexagonal unit cell of space group $C\bar{3}m$.

Although the present work will not further resolve the structure of schallerite, a novel method for deriving the structural formula of such complex silicates will be demonstrated.

ACKNOWLEDGMENTS

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Samples of pyrosmalite (*R 3555*) and friedelite (*R 9080*) from the type localities were supplied by the U. S. National Museum through the kindness of Dr. George Switzer. The sample of schallerite was supplied by the late L. H. Bauer who was Chief Chemist of the New Jersey Zinc Company.

CRYSTALLOGRAPHIC MEASUREMENTS

Powder diffraction data are given in Table 1 for schallerite which contains 6.37 per cent As_2O_3 (analysis by D. J. Demorest). Table 2 contains the summary information from a precession photograph that was used to index the powder photograph.

The dimensions for the hexagonal unit cell compare with those obtained by Frondel and Bauer (1953), as follows:

	Present Results	*Results of F. & B.*
a_0	13.36	13.43
c_0	14.24	14.31

The differences probably are to be attributed to differences in the arsenic contents of the samples. Inasmuch as their sample probably more closely corresponded with the type 1 (high arsenic) schallerite for which Bauer and Berman (1928) reported physical and chemical data, the unit cell dimensions obtained by Frondel and Bauer (1953) will be used in subsequent crystal chemical calculations in preference to the measurements obtained by the writer. The agreement is sufficiently good to eliminate the existence of any significant differences.

CALCULATION OF THE STRUCTURAL FORMULA

Before proceeding with a calculation of the structural formula of schallerite, it is necessary to demonstrate that the formula for manganpyrosmalite proposed by Frondel and Bauer, i.e. $2[(Mn, Fe)_8(Si_6O_{15}) (OH, Cl)_{10}]$, is not compatible with the silicate sheet proposed by Strunz (1949) and apparently accepted by them. Although the periodicity of the sheet, when taken as [210] of the mica structure, is approximately correct, it is clearly indicated in Fig. 1 that this layer unit contains 14 silicon atoms

TABLE 1. POWDER DIFFRACTION PATTERN OF SCHALLERITE

(Radiation: $\lambda FeK_{\alpha}=1.937$ Å; Camera radius = 57.3 mm.)

Line Number	Estimated Intensity	Interplanar Spacing	Experimental $\sin^2\theta$	*hk.l*	Calculated $\sin^2\theta$
1	1	7.025	.0190	00.2	.0185
2	4	3.547	.0743	00.4	.0740
3	½	3.411	.0802	10.4	.0810
4	½	3.313	.0855	22.0	.0841
5	3	2.825	.1175	40.1	.1166
6	6	2.673	.1311	40.2	.1305
7	5	2.466	.1540	40.3	.1537
8	½	2.370	.1668	00.6	.1664
9	½	2.309	.1759	32.3	.1748
10	1	2.222	.1901	33.0	.1892
11	½	2.105	.2109	33.2	.2078
12	½	2.087	.2146	42.2	.2148
13	5	2.022	.2291	40.5	.2277
14	4	1.975	.2789	40.6	.2785
15	10	1.688	.3364	44.0	.3362
16	2	1.6275	.3535	44.2	.3547
17	6	1.5108	.4063	40.8	.4079
18	½	1.4420	.4512	44.5	.4518
				80.1	.4521
19	1	1.4256	.4616	00.10	.4622
20	1	1.4176	.4669	80.2	.4668
21	3	1.3906	.4852	33.8	.4850
				40.9	.4865
22	2	1.3687	.5000	54.4	.5013
				44.6	.5026
23	½	1.3546	.5113	72.3	.5109
				21.10	.5113
24	½	1.3432	.5288	61.7	.5279
				81.2	.5299
				55.1	.5300
25	2	1.2913	.5453	55.2	.5439
				22.10	.5463
26	2	1.2796	.5557	81.3	.5530
				43.8	.5551
				73.1	.5580
27	½	1.2580	.5928	82.1	.5930

rather than 12. Thus the supposition of Gossner and Mussgnug (1931), that pyrosmalite is not structurally related to mica, is valid if it is assumed that manganpyrosmalite and pyrosmalite are isostructural. Frondel and Bauer (1953) state that the powder patterns are identical so there is no reason to question this isostructural relation.

TABLE 2. RELATIVE INTENSITIES (UNCORRECTED) FROM PRECESSION PHOTOGRAPH ($h0.l$)

(Radiation MoK_α)

l \ h	0	1	4	8	9	12
0	—				v. wk	str.
1	—		med.*	med.*	v. wk.	abs.
2	med.*	v. wk.	str.*	str.*		med.
3	abs.		med.*	str.		abs.
4	str.*	wk.*	wk.	wk.		med.
5	abs.		med.*	med.		abs.
6	med.*		wk.*	wk.		wk.
7	abs.		med.	med.		abs.
8	wk.		med.*	wk.		abs.?
9	abs.		med.*	med.		abs.
10	med.*		wk.	v. wk.		med.
11	abs.		v. wk.	v. wk.		abs.
12	wk.		wk.	wk.		med.
14	med.					med.

* Starred reflections were identified on the powder diffraction pattern (Table 1).

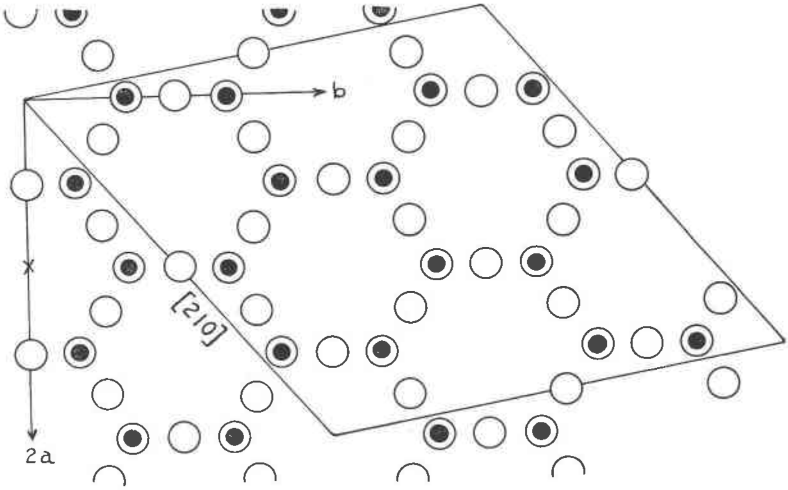

FIG. 1. Tetrahedral silicate layer of phyllosilicates showing a hexagonal periodicity of about 13.4 Å in the orthogonal direction [210] (Strunz, 1949). Any hexagonal sheet with such dimensions will contain 14 silicon atoms (solid circles) rather than 12. The a and b periodicities are for the unit cell of muscovite, assuming that $b_0 = a_0\sqrt{3}$.

Table 3. Calculation of the Number of Oxygen Atoms

Oxides*	Weight Per cents	Weight Ratios $\Sigma=4535$	Oxygen Ratios	Weights of Oxygen Atoms
SiO_2	31.44	1423.8	.5328	758.6
MnO	44.70	2024.2	.2256	456.7
MgO	2.19	99.2	.3968	39.4
FeO	2.12	96.1	.2227	21.4
CaO	.36	16.3	.2853	4.7
ZnO	.54	24.5	.1966	4.8
As_2O_3	12.24	554.3	.2426	134.5
H_2O	6.55	296.6	.8879	263.4
	100.14	4535.0		1683.5

* Analysis by L. H. Bauer (Bauer and Berman, 1928). The analysis includes 0.08 per cent of Cl which has been disregarded for the purpose of these calculations.

From the writer's investigation of schallerite and the data provided by Gossner and Mussgnug (1931) and by Frondel and Bauer (1953), the interpretations contained in the latter work are quite acceptable with respect to the stacking of structural units in the *c* direction. Nevertheless, if this premise is correct, it follows that none of these polymorphs are phyllosilicates if pyrosmalite is not.

In order to resolve the problem further it is necessary to make an assumption which has almost universal applicability, that is, the number of oxygen atoms (including hydroxyl, chlorine and fluorine) within the unit cell is an integer. The particular integer may be known from pertinent structural analogies or may require determination in situations where the structural information is inadequate, as is the case with schallerite.

Assuming that the lattice dimensions, specific gravity and chemical composition are known, it is possible to calculate the number of oxygen atoms in the unit cell by means of the following equation:

$$n_0 = \frac{D \cdot V(C_1p_1 + C_2p_2 + C_3p_3 + \cdots)}{26.56\Sigma_c}$$

where

n_0 = number of oxygens per unit cell
D = experimental specific gravity
V = volume of the unit cell in cubic Å
Σ_c = summation of weight percentages of oxides
$C_1, C_2 \cdots$ weight percentages of oxides
$p_1, p_2 \cdots$ atomic weight ratios of oxygen to molecular weights of oxides, i.e. 32/60.06 for SiO_2.

The detailed calculations are given in Table 3 in conformity with lattice dimensions given by Frondel and Bauer, and the specific gravity and analysis given by Berman and Bauer (1928). The molecular weight for the unit cell was computed in the usual manner as

$$(MW\cdot Z) = \frac{3.368\cdot \sin 60^\circ\cdot 13.43^2\cdot 14.31}{1.66} = 4535.$$

This calculation yields a total oxygen weight of 1683.5 atomic units or 105.2 oxygen atoms, whereas Frondel and Bauer (1953) assumed 30 oxygens on the basis of a Si:O ratio of 2:5 and calculated an additional 21.2 hydroxyl and chlorine ions. They calculate a total for large anions as 51.2 but conclude that the correct number is 50 (their Table 2, p. 757) for the unit cell of manganpyrosmalite which is approximately half as large as schallerite.

Because odd orders of 00.*l* are absent (Table 1) the number of oxygens must contain the factor 2. Table 2 demonstrates a pronounced pseudo-symmetry tending toward a quartering in the *a* direction, that is, $h=4n$ for all except a few weak reflections. Were this smaller a_0 dimension real, the number of oxygens would necessarily contain the factor 32 but more likely a factor of 8 is indicated for reasons which will appear subsequently. The integer 104 is within about one per cent of the calculated value and tentatively can be accepted as correct, at the same time noting that this is twice the value obtained by Gossner and Mussgnug (1931) for the unit cell of pyrosmalite.

On the basis of 104 oxygen atoms, the number of cations (including hydrogen atoms of hydroxyl ions) in the unit cell can be calculated by methods previously described in detail (McConnell, 1951). The calculations are given in Table 4 and are summarized as follows:

	Si	(Mn, Mg, Fe, etc.)	As	H	O
Analytical	23.5	32.5	5.5	32.6	105.2
Theoretical	24	40		32	104

and for pyrosmalite (Gossner and Mussgnug, 1931):

	Si	(Mn, Mg, Fe, etc.)	As	H	O
Theoretical	12	16		24	52

An obvious ambiguity arises concerning the arsenic. If added to the silicon the total becomes 29, which is reasonably close to the 28 required for the phyllosilicate structure (Strunz, 1949). It must be recalled, however, that manganpyrosmalite and pyrosmalite contain a number of silicon atoms which is inconsistent with Strunz's proposal.

Although the sum of the metallic cations is exactly 38 (rather than 40) this number is highly improbable because it does not contain the factor

TABLE 4. CALCULATION OF THE NUMBER OF CATIONS IN THE UNIT CELL

Oxides*	Weight Per cents	Molecular Ratios	Cation Ratios	Ratios of Charges	Charges of Cations $\Sigma=208$	Cations in Unit Cell	
SiO_2	31.44	.5235	.5235	2.094	93.8	23.5	
MnO	44.70	.6302	.6302	1.261	56.5	28.2	38.0
MgO	2.19	.0543	.0543	.109	4.9	2.5	
FeO	2.12	.0295	.0295	.059	2.6	1.3	
CaO	.36	.0064	.0064	.013	0.6	0.3	
ZnO	.54	.0048	.0048	.010	0.4	0.2	
As_2O_3	12.24	.0619	.1238	.371	16.6	5.5	
H_2O	6.55	.3637	.7274	.727	32.6	32.6	
	100.14				208.0		

* See note for Table 3.

8. Pyrosmalite contains only 16 rather than 20 metallic cations and the vacancies are compensated by 24 rather than 16 hydrogen atoms. The structural formula for type 1 schallerite therefore becomes

$$8[((Mn, Mg, Fe)_{4.0}As_{0.7})Si_3O_9(OH)_4]$$

which simplifies to $8[R''_5Si_3O_9(OH)_4]$ when trivalent atoms are absent.

It remains necessary to consider Bauer's analysis of type 2 schallerite (Bauer and Berman, 1928). If the total number of oxygen atoms (including 0.60 per cent of chlorine) is taken as 104, similar calculations yield the following results:

	Analytical		*Theoretical*
Si	23.8		24
Mn, Fe, Mg	31.7	36.4	
As	3.3		40
Al	1.4		
H	35.3		32

Again it is necessary to conclude that the number of hydroxyl ions is not fixed but exceeds 32 when the number of divalent and trivalent metallic cations is insufficient to produce electrical neutrality. Here, as was the case for type 1 schallerite, the calculated number of silicon atoms is slightly less than the theoretical requirement. In light of the suggestion of Wickman (1951) that arsenic with valences of both 3 and 5 occurs in dixenite, it is possible that a very small amount of arsenic occurs in tetrahedral coordination.

The general structural formula for schallerite must account for more than 32 hydroxyl ions as well as less than 40 metallic cations, thus:

$$8[[R^{\cdot\cdot}_{(5-x-y)}R^{\cdot\cdot\cdot}_{x}]Si_3O_9[O_4H_{(4+2y-x)}]].$$

In conclusion it must be commented that the mutual consistency of these calculations indicates the excellence of the experimental data given by Bauer, Berman and Frondel. While the writer obtained the conclusion that schallerite is not consistent with a phyllosilicate structure prior to the appearance of the published results on schallerite (Frondel and Bauer, 1953), all of the crystal chemical calculations have been revised in order to obtain a greater consistency by using unit cell dimensions made on material more nearly comparable to that on which the chemical analysis and specific gravity had been determined.

There is a major discrepancy between Strunz's proposal and the crystal chemical calculations for manganpyrosmalite which Frondel and Bauer (1953) did not recognize. However, the stacking of structural units, as postulated by these authors, is confirmed by the writer's independent investigations of schallerite.

An alternative explanation is obtained by assuming that the two missing silicon atoms required for the phyllosilicate sheet of pyrosmalite and manganpyrosmalite are compensated by statistical substitution of H_4, as proposed by the writer for the tetrahedral layer of the montmorillonite structure (McConnell, 1950) and for ortho-antigorite (McConnell, 1954). Under these circumstances it would presumably follow that the arsenic (and aluminum in type 2) occurs in tetrahedral coordination in schallerite. Contrary evidence exists, however. It is highly improbable that both pyrosmalite and manganpyrosmalite should be deficient by two silicon atoms, whereas schallerite shows a very small deficiency, if any. Under any circumstances, it is concluded that the structure contains 104 rather than 100 large anions (O+OH+Cl).

REFERENCES

BAUER, L. H., AND BERMAN, HARRY (1928), Friedelite, schallerite, and related minerals: *Am. Mineral.*, **13,** 341–348.

FRONDEL, CLIFFORD, AND BAUER, L. H. (1953), Manganpyrosmalite and its polymorphic relation to friedelite and schallerite: *Am. Mineral.*, **38,** 755–760.

GOSSNER, B., AND MUSSGNUG, F. (1931), Die molekulare Einheit von Pyrosmalith: *Zeits. Krist.*, **76A,** 525–528.

McCONNELL, DUNCAN (1950), The crystal chemistry of montmorillonite: *Am. Mineral.*, **35,** 166–172.

——— (1951), The crystal chemistry of montmorillonite. II—Calculation of the structural formula: *Clay Minerals Bull.* (London) **1,** 179–188.

——— (1954), Ortho-antigorite and the tetrahedral configuration of hydroxyl ions: *Am. Mineral.*, **39,** 830–831.

STRUNZ, H. (1949), Mineralogische Tabellen, p. 222.

WICKMAN, F. E. (1951), From the notes of the late K. Johansson. VII—A revised chemical analysis of dixenite from Långban: *Geol. Fören. Förhandl.*, **73,** 637–638.

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