THE EMPIRICAL UNIT-CELL CONTENTS OF THE FRIEDELITE FAMILY

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Frondel and Bauer (1953) have shown that the friedelite family of minerals can be divided into three sections: pyrosmalite and manganpyrosmalite, with $c = 7.15$ Å; schallerite, with $c \approx 14.3$ Å (both Type I with $As_2O_3 \approx 12\%$ and Type II with $As_2O_3 \approx 6$ to 8%); and friedelite and ferroschallerite with $c = 21.43$ Å. Taking one analysis of manganpyrosmalite, they calculated the empirical unit-cell contents included (with a small correction) in Table 1 below (column 1); these clearly indicate a unit-cell formula $[(Mn, Fe, Mg, Zn)_{16}Si_{12}O_{30}(OH, Cl)_{20}]$, neglecting the As, too small in amount to locate. Noting the simple multiple relation in their cell-dimensions, they concluded that the unit-cell contents of pyrosmalite, schallerite, and friedelite (including ferroschallerite, regarded as an arseniferous variety of friedelite) are respectively: $2[(Mn, Fe)_8Si_6O_{15}(OH, Cl)_{10}]$, $4[(Mn, Fe)_8(Si, As)_6O_{15}(OH, Cl)_{10}]$, and $6[(Mn, Fe)_8(Si, As)_6O_{15}(OH, Cl)_{10}]$.

McConnell (1954) made an independent study of schallerite; for Type II material with As_2O_3 6.37% he found a unit-cell 0.5% smaller along both a- and c-axes than Frondel and Bauer had found, probably for Type I schallerite. From Frondel and Bauer's cell-dimensions and the density and chemical analysis of Bauer and Berman (1928), he calculated a unit-cell content of 105.2 (O, OH, Cl), and taking this as an approximation to an integral 104 (supported by the fact that the absence of odd orders of $(000l)$ diffractions indicates that the space-group contains only even numbers of lattice positions), he recalculated the analysis to a basis of 104 (O, OH, Cl). This gave $(Mn, Fe, Mg, Ca)_{32.5}As_{5.5}Si_{23.5}O_{71.4}(OH)_{32.6}$ or nearly $4[(Mn, Mg, Fe)_8As_{1\frac{1}{3}}Si_6O_{18}(OH)_8]$ for schallerite. McConnell further concluded that the formulae of pyrosmalite and friedelite are probably $2[(Mn, Mg, Fe)_8Si_6O_{14}(OH, Cl)_{12}]$ and $6[(Mn, Fe, Mg)_8Si_6O_{14}(OH, Cl)_{12}]$ respectively.

Though Frondel and Bauer only considered one analysis of pyrosmalite, their deduction of the formula of pyrosmalite is perfectly sound; but their assumption that, because schallerite and friedelite have respectively twice and three times the cell-volume of pyrosmalite, their formulae must be simply twice and three times the pyrosmalite formula (apart from some replacement of Si by As in schallerite) is quite unsound; and equally, McConnell's reverse assumption that the formulae of pyrosmalite and friedelite may be deduced from that of schallerite is unsound.

The only strictly reliable and convincing evidence of true unit-cell

TABLE 1. EMPIRICAL UNIT-CELL CONTENTS OF MANGANPYROSMALITE,
PYROSMALITE, SCHALLERITE, FRIEDELITE, AND FERROSCHALLERITE

	1*	2	3	4	5	6*	7*	8*
Si	11.9	12.6	12.0	12.0	12.1	24.1	23.5	23.9
As	0.02	—	—	—	—	5.6	5.6	3.4
(Mn, Fe, etc.)	16.0	15.5	15.8	16.1	17.3	32.3	32.6	33.2
(OH, Cl)	21.2	20.7	22.0	18.7	22.4	35.6	32.7	36.4
O	29.3	30.4	27.8	30.7	30.3	71.1	71.6	69.1
Σ(cations)	27.9	28.1	27.8	28.1	29.4	62.0	61.7	60.5
Σ(O, OH, Cl)	50.5	51.0	50.8	49.4	52.8	106.6	104.3	105.5

	6a	7a	8a	9	10	11	12
Si	23.7	23.1	24.3	35.4	33.8	35.4	33.8
As	5.5	5.5	3.4	—	—	—	—
(Mn, Fe, etc.)	31.8	32.1	33.8	47.1	48.1	47.8	50.8
(OH, Cl)	35.0	32.2	36.9	71.6	64.2	64.7	56.7
O	70.0	70.5	70.2	82.1	83.5	86.3	90.1
Σ(cations)	61.0	60.7	61.5	82.5	81.9	83.2	84.6
Σ(O, OH, Cl)	105.0	102.7	107.1	153.7	147.7	151.0	146.8

	13	14	14a	15*	16*	17*	17a
Si	33.5	37.7	35.7	34.7	35.1	35.7	23.8
As	—	—	—	0.7	—	8.7	5.8
(Mn, Fe, etc.)	52.6	48.5	45.8	47.1	45.3	48.1	32.1
(OH, Cl)	54.4	69.6	65.8	68.0	67.1	49.2	32.8
O	92.5	89.1	84.2	83.6	81.9	108.1	72.0
Σ(cations)	86.2	86.2	81.5	82.6	80.4	92.6	61.7
Σ(O, OH, Cl)	146.9	158.7	[150]	151.7	149.0	157.3	104.8

* Material studied by Frondel and Bauer by X-ray methods.

Manganpyrosmalite:
1. Sterling Hill, N.J. C. Frondel and L. H. Bauer, *Am. Mineral.*, 1953, **38,** 755; the oxygen value of 2.3591 cited in table 2, p. 757 is incorrect, as the oxygen equivalent of the chlorine has not been subtracted, nor the oxygen of the As_2O_3 added in; with these corrections, Frondel and Bauer's data yield the figures tabulated here.

Pyrosmalite:
2. Nordmark, Sweden. J. Lang, *Jour. prakt. Chem.*, **83,** 424 (1861).
3. Nordmark, Sweden. E. Ludwig, *Tscherm. Min. Mitt.*, 211 (1875).
4. Dannemora, Sweden. N. Engström, *Geol. För. Förhandl., Stockholm*, **3,** 116 (1876).
5. Dannemora, Sweden. A. Gorgeu, *Bull. Soc. Min. France*, **7,** 58 (1884); the cited density (3.19) is probably too high; the mineral was closely associated with hedenbergite.

TABLE 1—*(continued)*

Schallerite:

6. Franklin, N.J.; (type I). R. B. Gage, E. S. Larsen, and H. E. Vasser, *Am. Mineral.*, **10**, 9 (1925); re-calculated assuming the As is all trivalent, and with Frondel and Bauer's cell-dimensions.

7. Franklin, N.J.; (type I). L. H. Bauer and H. Berman, *Am. Mineral.*, **13**, 342 (1928), table 1, No. 7, and table 2*a*, No. 4; re-analysis of type material; calculated using Frondel and Bauer's cell-dimensions.

8. Franklin, N.J.; (type II). L. H. Bauer and H. Berman, *Am. Mineral.*, **13**, 342 (1928), table 1, No. 9, and table 2*a*, No. 3; calculated using McConnell's cell-dimensions.

6*a*.⎫
7*a*.⎬ Re-calculation of analysis 6, 7, and 8, using McConnell's cell-dimensions for
8*a*.⎭ analyses 6 and 7, and Frondel and Bauer's for analysis 8.

Friedelite:

9. Adervielle, Neste de Louron, Hautes Pyrénées. E. Bertrand (A. Gorgeu, analyst), *Bull. Soc. Min. France*, **7**, 3 (1884).

10. Harstig mine, Wermland, Sweden. G. Lindström, *Geol. För. Förhandl., Stockholm*, **13**, 127 (1891).

11. Harstig mine, Wermland, Sweden. G. Flink, *Bihang. Sver. Vet.-Akad. Handl.*, **16**, part 2, No. 4 (1890).

12.⎫ Veitsch, Styria. A. Hofmann and F. Slavík (F. Kovář, analyst), *Rozpr. České*
13.⎭ *Akad.*, Ser. II, **18**, No. 27 (1909).

14. Vielle-Aure, Neste d'Aure, Hautes Pyrénées. H. Lienau, [*Chem.-Zeitung*, **1**, 362 (1905)] quoted by C. Doelter, *Handb. Min. Chem.*, **2**, part I, 749 (1914) with an incorrect locality; correct locality see Dana, *Syst. Min.*, 6th edn, App II, p. 43; the cited density (3.21) is probably too high.

14*a*. Analysis 14 re-calculated on a basis of 150 (O, OH, Cl).

15. Franklin, N.J. C. Palache (W. T. Schaller, analyst), *Am. Jour. Sci.*, ser. 3, **29**, 177 (1910); *Zeits. Kryst.*, **47**, 582 (1910); L. H. Bauer and H. Berman, *Am. Mineral.*, **13**, 341 (1928), table 1, No. 3, and table 2*a*, No. 1.

16. Franklin, N.J. L. H. Bauer and H. Berman, *Am. Mineral.*, **13**, 341 (1928), table 1, No. 4, and table 2*a*, No. 2.

Ferroschallerite:

17. Franklin, N.J. L. H. Bauer and H. Berman, *Am. Mineral.*, **15**, 340 (1930).

17*a*. Two-thirds the unit-cell contents of analysis 17, for comparison with analyses 6, 7, and 8.

NOTE: There are several analyses of members of the friedelite family in the literature which, being without density determinations, are useless for the calculation of empirical cell-contents.

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contents comes from chemical analysis, density, and unit-cell dimensions, all determined on the same specimen. From these data the unit-cell contents and chemical formula may be derived by several procedures, including Frondel and Bauer's, McConnell's, and Hey's (1939, 1954); compare also Nicholls and Zussman (1955) and Francis and Hey (1956). Strictly, then, only analyses for which the unit-cell dimensions and the density were determined on the analysed material are valid data for the

calculation of empirical unit-cell contents; but in many minerals, there is evidence that the range of variation of the unit-cell dimensions is limited, and it may then be reasonable to accept and use unit-cell dimensions determined on a different specimen, while allowing an increased assessment of probable error. Frondel and Bauer's x-ray data were obtained on material which included type specimens of schallerite, ferroschallerite, and manganpyrosmalite, and pyrosmalite from the original locality, Nordmark, Sweden. The difference in cell-dimensions between pyrosmalite and manganpyrosmalite is very small (0.01 Å in both a and c), and we may therefore reasonably use these cell-dimensions to calculate empirical unit-cell contents for all pyrosmalites for which densities and chemical analyses are available. Frondel and Bauer examined both Type I and Type II schallerite, but do not note any difference in lattice dimensions. McConnell's x-ray data were obtained on Type II schallerite and indicate a distinctly smaller cell. Empirical unit-cell contents based both on Frondel and Bauer's measurements and on McConnell's are therefore included in Table 1. For friedelite and ferroschallerite, Frondel and Bauer's work suggests that there is little or no variation in cell-dimensions. In view of the usually preponderant effect of errors in the physical data on the empirical unit-cell contents (Hey, 1954), it is probably safe to assume that the figures given in Table 1 are within about 2% of the truth, except as mentioned below.

It will be seen from Table 1 that the evidence probably indicates a unit-cell content of $2[(Mn, Fe)_8Si_6O_{15}(OH, Cl)_{10}]$ for pyrosmalite and manganpyrosmalite, as found by Frondel and Bauer.

For schallerite, the unit-cell probably contains $104(OH, Cl)$, as found by McConnell; the arsenic-poor Type II material probably has the distinctly smaller cell found by McConnell; As does not appear to substitute for Si, and the repeat is perhaps best written $4[(Mn, Fe)_8As_{2-x}Si_6(O, OH, Cl)_{26}]$, where x is about 0.6 and $O:(OH, Cl)$ varies, perhaps from about 2.2 to about 1.9; but more analyses, with x-ray and density data, will be necessary before the nature of the substitutions in this mineral is clear.

Eight analyses of friedelite are available, including two of material examined by x-ray methods by Frondel and Bauer (Table 1, columns 15 and 16); assuming that the cell-dimensions are constant, and using Frondel and Bauer's values, the unit-cell contents included in Table 1 are derived. One analysis (column 16) includes 1.94% H_2O-, but if this is assumed to be impurity, deducted from the analysis, and the density adjusted accordingly, the empirical unit-cell contents fall out of line with the other seven analyes, so it has been assumed that all the water in this analysis is essential. It seems fairly clear that the total (O, OH, Cl) is

150 atoms per unit cell in friedelite, and that the high value for analysis 14 is simply due to a high (and incorrect) density. Analyses 12 and 13, which combine low (O, OH, Cl) with low (OH, Cl) and low Si, but high total cations, are probably analyses of impure material. The remaining analyses indicate a formula

$$6[(Mn, Fe, Mg, Zn, Ca)_{8-x}Si_{6-y}(O, OH)_{15}(OH, Cl)_{10}],$$
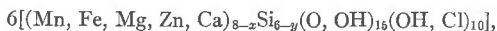
where x and y can each reach about 0.3 and the deficit in valency is balanced by OH replacing O up to nearly 10(OH) per unit cell.

Ferroschallerite presents a difficult problem; Frondel and Bauer, noting that it has the 21 Å basal spacing and gives an x-ray powder photograph like that of friedelite, concluded that it is merely an arsenic-rich variety of friedelite; it cannot be classed as a variety of schallerite, which gives a distinct x-ray powder pattern and has a 14 Å basal spacing, yet its empirical unit-cell contents (Table 1, columns 17 and 17a) are quite distinct from those of friedelite and approximate to $1\frac{1}{2}$ times the unit-cell contents of schallerite. For the present, it seems best to regard ferroschallerite as a distinct species, with a unit-cell formula near

$$[(Mn, Fe)_{48}As_9Si_{36}O_{111}(OH, Cl)_{45}] \text{ or } 6[(Mn, Fe)_8As_{1.5}Si_6O_{18}(OH, Cl, O)_8].$$
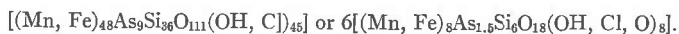
The apparent identity of the x-ray powder photographs is against ferroschallerite being a separate species, but there does not appear to be any authenticated example of a species showing a variation in unit-cell content comparable to that between friedelite and ferroschallerite, while examples on non-isostructural species whose x-ray powder photographs are extremely similar are known (for example, gonnardite and natrolite; M. H. Hey, H. Meixner, and A. A. Moss, unpublished data).

The true relations of these four species remain somewhat obscure. The increase in oxygen atoms per unit-cell does not seem to bear any simple relation to the arsenic content. Indeed, both the arsenic-rich Type I schallerite and the arsenic-poor Type II appear to have the same total of anions (O, OH, Cl) per unit cell, which suggests that the relation is not an isomorphous replacement such as OH′ by AsO₂′, as might seem possible.

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