

Crystal-chemical data for schallerite, caryopilite and friedelite from Franklin and Sterling Hill, New Jersey

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Abstract

Five chemical analyses of schallerite from Franklin, New Jersey, yield the new formula, $Mn_{16}Si_{12}O_{30}(OH)_{14}[As_3^{3+}O_6(OH)_3]$. These data are consistent with arsenic present in stoichiometric quantities. The schallerite formula can be derived from that of friedelite by the substitution of two O for two (OH), coupled with the addition of $As^{3+}(OH)$. Schallerite is apparently not a true polytype of manganpyrosomalite. A second paragenesis of spherulitic schallerite in rhodonite is described in detail.

Caryopilite is reported from both Franklin and Sterling Hill. Both occurrences are arsenian; Franklin material containing from 1.2 to 1.4 percent As_2O_3 and Sterling Hill material containing 5.1 to 6.9 percent As_2O_3 . The limited As content is probably due to the presence of schallerite-like layers. Caryopilite occurs in rosette-like aggregates.

Friedelite from Franklin and Sterling Hill is shown to be the (OH) analog of mcGillite inasmuch as both phases have the same layer sequence, with $c = 86\text{\AA}$, but with considerable disorder in the sequence of tetrahedral layers. There appears to be a solid solution series between friedelite with compositions of $Mn_8Si_6O_{15}(OH)_9Cl$ and $Mn_8Si_6O_{15}(OH)_9(OH)$, but it is not represented by available analyses.

Introduction

Schallerite was discovered in early 1924 by R. B. Gage and was subsequently described as a new species from the Franklin mine, Franklin, Sussex Co., New Jersey, by Gage *et al.* (1925). It was later studied by Bauer and Berman (1928) who demonstrated a chemical relationship between schallerite and friedelite and, using type material, established that the arsenic reported as pentavalent in the original description was in fact trivalent. Bauer and Berman also noted a second occurrence of schallerite which

they termed *schallerite type II*, while giving the designation *schallerite type I* to the original material.

Fron del and Bauer (1953) suggested that friedelite, manganpyrosomalite and schallerite are polytypically related. All are hexagonal with $a \sim 13.4\text{\AA}$ and having values of c which are multiples of approximately 7.15\AA . McConnell (1954) discussed the possible nature of the layered structure in relation to the composition. Takéuchi *et al.* (1969) determined the structure of manganpyrosomalite, the simplest of the polytypically related structures, which has $c \sim 7.15\text{\AA}$, a value which is similar and apparently related to the

repeat of septechlorites. The structure was indeed shown to have a two-layer repeat, consisting of one brucite and one tetrahedral layer. The latter is unique, however, having half of the tetrahedral vertices pointing down to one brucite-like layer and half up to another brucite-like layer. It consists of 12-, 6- and 4-member rings. Takéuchi *et al.* (1969) showed how the schallerite and friedelite structures, as well as other variants, could be polytypically derived from the simpler manganpyrosomalite structure. Peacor and Essene (1980) subsequently presented data that imply that caryopilite is a member of the friedelite group, possibly possessing a structure with an irregular stacking sequence, while Donnay *et al.* (1980) showed that McGillite is a Cl-containing phase having $c = 85.7\text{\AA}$, four times that of friedelite.

Despite the numerous studies cited above, specific structural and compositional data for schallerite are quite limited. In particular, the role of As is not well defined, and there have been only two complete analyses, having 12.24 and 7.50 weight percent As_2O_3 , respectively. Berman (1937) suggested substitutions involving (OH-Cl) and (Si-As), a schallerite-friedelite solid solution series, and noted the presence of As in some friedelites. Hey (1956) noted that the formula of schallerite could be expressed as $(\text{Mn,Fe})_8\text{As}_{2-x}\text{Si}_6(\text{O,OH,Cl})_{26}$ where $0.6 \leq x \leq 1.2$, thus implying an addition solid solution mechanism for As rather than substitution. However, the limits and mechanism of As substitution remain unknown. Furthermore, although McConnell (1954) determined that schallerite is hexagonal with $a = 13.36$ and $c = 14.24\text{\AA}$ by means of precession photographs, details of its diffraction relations remained unclear, especially in view of schallerite's complex relation to other members of the friedelite group. These and other problems were brought to our attention when we noted the occurrence of a manganese layer silicate having a low As content (1.2–6.9 wt.% As_2O_3) and a unique powder pattern which is slightly similar to that of schallerite. We therefore initiated this study in order to clarify the crystal chemical relations of schallerite.

Schallerite description

Schallerite has been found in two parageneses in the Franklin Mine but has not been found at Sterling Hill or elsewhere. Samples from each of the two parageneses are unique, suggesting that they occurred only in two localized areas. The first occurrence was noted by Gage *et al.* (1925) who mentioned that it was found at approximately the 700 level of

the Franklin Mine, but that no attempt was made to deliberately collect schallerite samples and much of the material was crushed in the mining process. The type material, and that for analyses # 1–5 of this study (Table 1), consists of dense, dark, reddish-brown layers of schallerite which occur on banded willemite-franklinite ore devoid of calcite. On all the samples we examined, the ore matrix is identical and the schallerite is deposited on a fracture surface at nearly right angles to the banding of the ore. Another feature common to the samples is the presence of a coating of slightly pinkish-white, botryoidal calcite. These three features (the identical ore, the parallelism of the angle of the ore-bedding, and the identical calcite coating), further support the hypothesis that this was a very localized occurrence. The schallerite is 1.0 to 5.0 cm thick according to Gage *et al.* (1925), and the same is true of the samples of this study. The schallerite was deposited as a fine-grained massive material on the ore surface, followed by the deposition of a thin layer of calcite. Dissolution of this overlying calcite reveals a cellular corroded boxwork of schallerite at the schallerite-calcite interface. The dissolution, with dilute 1:1 hydrochloric acid, revealed schallerite crystals for the first time, only massive material having been previously described. The crystals are up to 2.0 mm in length and are markedly hemimorphic with dull {0001} and {000 $\bar{1}$ } pedions. Their morphology is similar to that of the related friedelite, but with a steeper pyramid. The schallerite crystals were positively identified using X-ray powder diffraction and Weissenberg and precession techniques. The schallerite crystals did not exhibit parallel growth but were randomly emplaced on the boxwork of fine-grained schallerite. This schallerite is the kind described as *schallerite type I* by Bauer and Berman (1928) and by Palache (1935), but we discard this terminology because we show later that it serves no useful purpose. A scanning electron photomicrograph of one of these schallerite crystals is shown in Figure 1.

The second distinct paragenesis of schallerite was noted by Bauer and Berman (1928) but undescribed by them except for chemical analysis. It was known to them and Palache (1935) as *schallerite type II*, (Samples C5834 and S-G 1017). This second occurrence is quite rare; few specimens exist. There are two in the Smithsonian collection, two in the Harvard University collection, and one in the Gerstmann Mineral Museum in Franklin, New Jersey. We have no knowledge of what part of the Franklin mine it came from, and there is little evidence of the mecha-

Table 1. Chemical analyses of schallerite. The number of cations computed from each weight percent is calculated on the basis of eight octahedrally coordinated cations.

Anal #	Sample #	SiO ₂	Fe ₂ O ₃ ^{††}	MgO	ZnO	MnO	As ₂ O ₃	Cl	H ₂ O	Other	O ≡ Cl	Total
	Theory	31.29				49.22	12.87		6.62			100.00
1.	Bauer (1928)	31.44	2.12***	2.19	0.54	44.70	12.24	0.08	6.55	0.36φ	0.02	100.20
2.	106769	32.0	2.4	2.6	1.7	42.6	13.10+	0.0	6.72*			101.1
3.	95118	31.5	1.7	2.2	1.3	43.1	12.71+	0.0	6.89*			99.4
4.	C6218	32.0	2.6	2.3	1.6	42.5	12.81+	0.0	6.82*			100.6
5.	SG-1016	31.8	1.8	2.0	1.4	43.8	12.5	0.1	6.60**			100.0
6.	C2873	32.0	1.8	2.9	1.6	42.2	12.87+	0.1	6.76*			100.2
7.	C5834	31.9	1.2	0.9	1.2	45.1	10.6	0.3			0.1	
8.	C5834	32.8	0.8	0.7	1.1	47.0	8.9	0.5			0.1	
9.	SG-1017	33.0	0.8	0.7	1.1	48.2	6.9	0.9			0.2	
10.	Bauer (1928)	32.42	0.62***	0.71	tr.	49.21	7.5	0.6	7.24	1.59φ	0.13	99.76
Ions per unit cell ψ												
1.	Bauer (1928)	5.83	0.30	0.61	0.07	7.02	1.38	0.03	8.11			
2.	106769	5.95	0.34	0.72	0.23	6.71	1.48		8.34			
3.	95118	6.00	0.24	0.62	0.18	6.95	1.47		8.75			
4.	C6218	6.01	0.37	0.64	0.22	6.76	1.46		8.55			
5.	SG-1016	5.99	0.26	0.56	0.19	6.99	1.43	0.03	8.29			
6.	C2873	6.01	0.25	0.81	0.22	6.71	1.47	0.03	8.47			
7.	C5834	6.18	0.17	0.26	0.17	7.40	1.25	0.10				
8.	C5834	6.21	0.11	0.20	0.15	7.53	1.02	0.16				
9.	SG-1017	6.10	0.11	0.19	0.15	7.55	0.77	0.28				
10.	Bauer (1928)	6.00	0.09	0.20		7.72	0.84	0.19	8.94			

* Penfield method; accuracy of data : ±2 percent of the amount present.

† Determined as As₂O₃ by wet chemistry; accuracy of data: ±2 percent of the amount present.

‡ Accuracy of microprobe analyses for Si, Fe, As, Mg, Zn, Mn, and Cl: ±3 percent of the amount present.

†† by microchemical test; φ CaO; φ Al₂O₃; tr.= trace; ψ on the basis of 8 octahedrally coordinated cations.

** - by difference

***- given as FeO

nism of emplacement due to the fact that little ore matrix is attached to the specimens.

In this assemblage, schallerite occurs as spherical to slightly rectangular aggregates resembling "augens" in a fine-grained matrix of light pink rhodonite. The overall appearance of the specimens vaguely resembles that of a mylonite, which we use only as a descriptive term without genetic implications. A photograph of a representative sample is shown in Figure 2. The samples are layered; the most obvious layered units are franklinite and non-contiguous layers of barite and schallerite (not shown in Figure 2). The bulk of the sample is composed of rhodonite and reddish-brown "augens" of schallerite, which are randomly distributed throughout the rhodonite. These "augens" are also found within the associated fine-grained, bedded franklinite, but they are quite small (1–2 mm). These schallerite spherules are actually aggregates of schallerite crystals and rhodonite. The majority of them are coatings over angular, small fragments of barite, calcite, willemite or franklinite.

In thin-section, the schallerite spherules are seen to

be composed of many discrete crystals, each similar in morphology to those shown in Figure 1. The individual crystals are oriented so that their apices point toward the center of the spherule and their bases

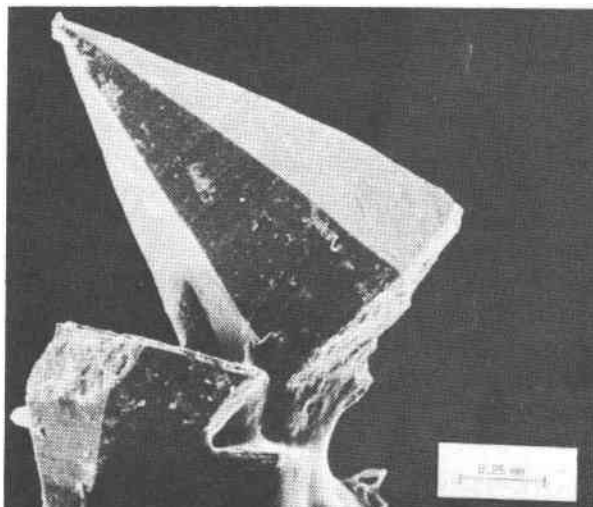


Fig. 1. Pyramidal hemimorphic crystal of schallerite (NMNH C2873). SEM photomicrograph.

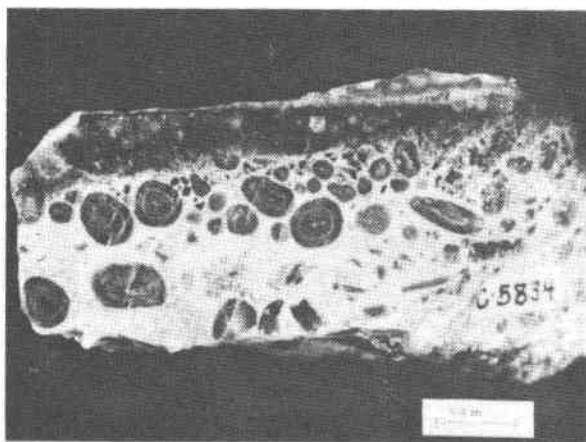


Fig. 2. Polished surface of schallerite-rhodonite specimen showing distribution and appearance of schallerite "augens."

(pedions) form the outside of the spherule (Figure 3). Rhodonite is moderately abundant as microcrystalline interstitial fillings between the schallerite crystals.

Chemical analyses

The samples described in this paper were chemically analyzed using an ARL-SEM-Q electron microprobe utilizing an operating voltage of 15 kV and a beam current of $0.15 \mu\text{A}$. The data were corrected using a modified version of the MAGIC-4 computer program. The standards used were synthetic olivenite for As; hornblende for Si, Al, Fe, Mg, and Ca; synthetic ZnO for Zn; and scapolite for Cl. Wavelength-dis-

persive microprobe scans indicated the absence of any other elements with atomic number greater than eight. Total water for four samples were determined wet-chemically by the Penfield method. The arsenic in schallerite was proven to be trivalent by Bauer (Bauer and Berman, 1928). However, owing to the complexity of the compound $\text{AsO}_3\text{-AsO}_4$ arsenosilicates found at Sterling Hill (Dunn and Nelen, 1980) and the difficulty in accurately determining the oxidation state of arsenic, we redetermined the oxidation state of the arsenic in four schallerite samples. Samples were dissolved in non-oxidizing acids, and total arsenic and trivalent arsenic were determined qualitatively by distillation and titration procedures; the full analytical procedure is given in Dunn and Nelen (1980). The water content was assigned to hydroxyl rather than H_2O on the basis of infrared spectroscopy (Paul Keller, personal communication) and the known crystal structure relations.

We consider analyses #1-6 (Table 1) to be accurate chemical analyses representing the true composition of end-member schallerite. Analyses #7-10 are of the spherical aggregate schallerite shown in Figure 2. Care was taken to analyze only schallerite crystals, and we are certain that the analyses represent the average compositions of the individual crystals. The compositions of individual crystals within any aggregate spherule ("augen") are all the same. However, the amount of arsenic in these analyses is much lower than that in the more reliable analyses (# 1-6) which were conducted on homogeneous material. We inter-

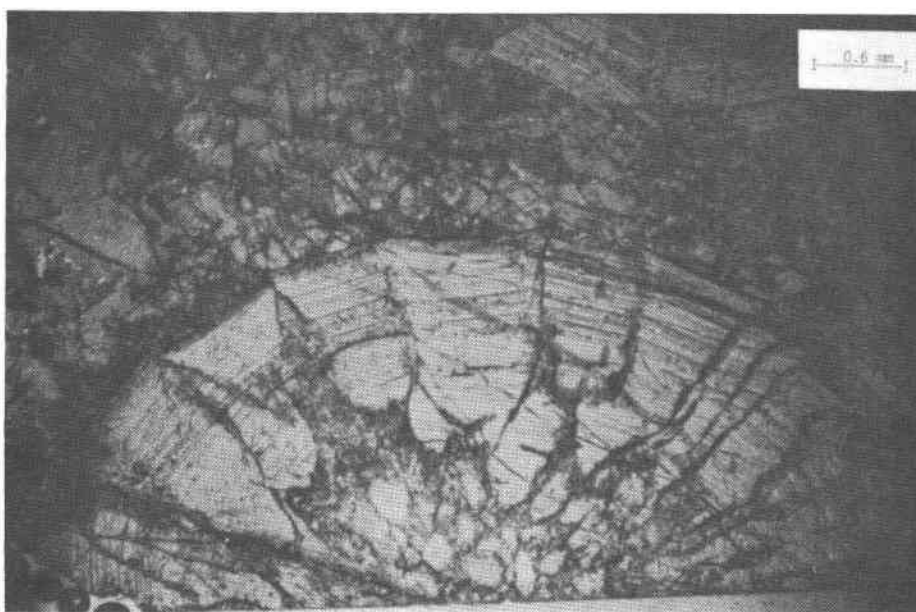


Fig. 3. Thin-section in plane-polarized light showing the orientation of the individual schallerite crystals within one of the "augens."

pret these lower arsenic values as possibly due to mixed layering of other members of the pyrosmalite group, but cannot rule out solid solution mechanisms in the absence of a crystal structure determination on schallerite. We note that Bauer (Bauer and Berman, 1928) (Table 1, analysis #10) obtained a low As_2O_3 value of 7.50 wt.% for similar material, but we interpret this as being due to admixed rhodonite which likely was not noted at the time, because of the extremely small particle size and the limitations of available instrumentation. Bauer was a superb analyst but we doubt that he could have separated the microcrystalline rhodonite from the interior of the composite schallerite-rhodonite "augens" even if he had known of its presence. Hence, we consider as fortuitous the fact that he obtained a value for As_2O_3 similar to our microprobe analyses which were obtained without interference from the rhodonite inclusions.

We note that the analyzed schallerite samples all contain small amounts of Fe^{3+} , which has been included among the octahedral cations in our calculations (Table 1). Dunn and Nelen (1980) have shown that Fe^{3+} is a constant constituent of arsenosilicates from Sterling Hill even though present in very small amounts.

Inasmuch as the data given for these analyses (#7, 8, and 9) is admittedly, in our opinion, of possible mixtures with other members of the manganopyrosmalite group, the calculation of water by difference would be in error. Hence, those columns and sums are vacant in Table 1.

Schallerite crystal chemistry

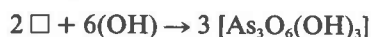
Table 1 lists chemical analyses of schallerite. As the ideal formula of friedelite (and of its supposed polytypes schallerite and manganopyrosmalite) is $\text{Mn}_8\text{Si}_6\text{O}_{15}(\text{OH})_{10}$ we have normalized the data to the eight cations which we assume to be octahedrally coordinated. The number of Si atoms is close to six in every case. This clearly implies that the As^{3+} does not substitute for Si or octahedrally coordinated cations. Both of the latter possibilities are extremely unlikely in any event. As^{3+} commonly is bonded to only three anions forming a trigonal pyramid with As^{3+} as the principal vertex, a coordination which grades into tetrahedral in some compounds. Substitution into octahedral or tetrahedral sites is therefore extremely unlikely.

Until we obtained new, accurate analyses for As^{3+} , the weight percent of As for several analyses ap-

peared to be quite variable, suggesting a solid solution series. The analyses of Table 1 (# 1-6) show, however, that the number of As^{3+} atoms per eight octahedrally coordinated cations is close to 1.5. As there are four formula weights per unit cell, the analytical data is close to six As^{3+} per cell. Because 6 is a possible equipoint rank for hexagonal and trigonal structures, this implies that As may be ordered in a single equipoint. Because As does not substitute for Si, the solid solution mechanism must be one of addition as originally inferred by Hey (1956).

The analytical data of Table 1 indicate a clear relation between high As values and low (OH and Cl) relative to friedelite. Although the (OH) values are quite variable, the number of (OH) cluster near 8.5 per formula unit. As there are 10 (OH) per ideal friedelite formula unit, there is a deficiency of 1.5 (OH) per schallerite formula unit. Because the As values cluster near a maximum of 1.5 per formula unit, there is an implication that for each As^{3+} added to the ideal structure, one (OH) is subtracted. This conclusion, based on the analytical data for (OH), is tentative and should be treated with caution.

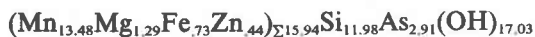
It is difficult to rationalize the simultaneous addition of As^{3+} and subtraction of (OH) in the structure proposed by Takéuchi *et al.* (1969). We have, however, been able to suggest one reasonable mechanism which maintains the basic structural relations and preserves charge balance. This is represented by the relation:



This involves the direct substitution of 2 O for 2(OH) of the octahedral layer (per addition of one As^{3+}), with the concomitant addition of one (OH) associated with the As. The 2 oxygen atoms must be adjacent anions, such that these anions plus the added (OH) form a triangle, with the As^{3+} completing a trigonal pyramidal polyhedron. This mechanism preserves local charge balance at all sites. All other mechanisms appear to result in unreasonable coordination of As^{3+} or severe local charge imbalance. This implies an end member formula for schallerite of $\text{Mn}_{16}\text{Si}_{12}\text{O}_{30}(\text{OH})_{14}[\text{As}_2^{3+}\text{O}_6(\text{OH})_3]_2$ with $Z = 2$.

Our analytical data for samples #1-6 is consistent with this end member formula. Its validity can be directly tested with a calculation of unit-cell contents. Density was therefore measured for several samples using heavy liquid techniques. In particular the density of C6218, for which single-crystal X-ray data had confirmed the structural relations, was determined to be 3.365 g/cm³. The cell contents (divided by two to

normalize to a single 7Å layer) as determined from the analysis given in Table 1 are:



This is in excellent agreement with the formula proposed above and confirms that As is present as an additional component and not in substitution for Mn and/or Si. Whether or not there is a solid-solution series cannot be determined. The similarity of data from all specimens may be fortuitous due to the fact that all samples come from only one occurrence at the same locality. Where intermediate As^{3+} and (OH) values are obtained, the results may be due to mixed layering of end-member stoichiometric schallerite (with As^{3+}) and another member of the friedelite family.

We still must show that there are vacant sites in the As-free structure which would accommodate the added As^{3+} and (OH). Such sites are available in connection with either the very large 12-member rings or, less likely, the smaller 6-member rings. There are major voids in the tetrahedral layer in the center of the 12-member rings, directly between two octahedral layers. Thus, reasonable sites exist, although this in no way proves that this additional mechanism actually occurs.

Because analyses (# 1-6) of schallerite seem to show approximately the same As and (OH) contents, and thus indicate that they are essential constituents, it is of interest to speculate on the relation of schallerite to other As-free members of the family, manganpyrosomalite and most friedelite. These are the one and three-layer polytypes, respectively, while schallerite is a two-layer species. The addition of As and (OH) to sites between octahedral layers must introduce distortions in both the tetrahedral and octahedral layers. These certainly affect the stacking sequence of octahedral layers. We therefore tentatively propose that the stacking sequence and As^{3+} content are dependent variables. If so, the term *polytype* is not precisely applicable to schallerite in relation to manganpyrosomalite and friedelite. Again we caution that this hypothesis is based on analyses from a limited occurrence of schallerite.

A crystal structure analysis should define the nature of the As^{3+} site and the relation to stacking sequence. We therefore systematically examined a number of analyzed schallerite samples using single-crystal X-ray techniques in order to identify a crystal suitable for structure determination. Although the substructure gave rise to sharp reflections ($A = 3.35$, $C = 14.28\text{\AA}$, space group $P\bar{3}C$) the superlattice reflec-

tions (which quadruple the a -axis) were always relatively diffuse parallel to C^* . The octahedral-layer stacking sequence defines the substructure while relative tetrahedral layer positions determine the superstructure. The tetrahedral layer positions are therefore disordered in our schallerites, and the crystals are all unsuitable for a structure analysis. Donnay *et al.* (1980) have commented that the same relations have prevented a structure analysis for mcGillite.

Caryopolite

In 1978, Mr. Steven Sanford, Mr. John Kolic and Mr. Ewald Gerstmann submitted to us interesting samples of reddish-brown rosettes from Sterling Hill, New Jersey. The X-ray powder patterns of these rosettes matched that of caryopolite. However, we included samples of these and other rosettes in our microprobe analyses and found that they contained As. This led us to examine many specimens labelled schallerite or friedelite and, as a result, additional samples of caryopolite, from both Franklin and Sterling Hill, were found and analyzed.

The "Sanford" caryopolite occurs as reddish-brown rosettes composed of hexagonal plates slightly offset from one another. Scanning electron microscope photomicrographs of these crystals, together with some provided by Mr. John Kolic, are shown in Figures 4 and 5. The individual crystals are composed of only prism and pinacoid or pedion forms.

Caryopolite was recently shown by Peacor and Essene (1980) to probably have a friedelite-family-like structure rather than that of the serpentine family. They showed that the X-ray powder pattern (no single crystals large enough for single-crystal studies have ever been found) is closely related to those of other members of the friedelite family. We have obtained both chemical analytical (Table 2) and X-ray powder diffraction data for a number of additional samples. The X-ray patterns are quite distinctive and duplicate those of Peacor and Essene. Indeed we note that schallerite, friedelite, pyrosomalite and caryopolite all yield distinctive and unique powder patterns. The powder pattern of mcGillite is extremely similar to the pattern of friedelite, and will be discussed in a later section.

The analytical data in Table 2 support the conclusions of Peacor and Essene (1980) that caryopolite is friedelite-like rather than being related to serpentine, as the octahedral cation to Si ratio is close to 8:6. There is significant As in the analyses, which is quite variable in amount but significantly less than that in schallerite (Tables 1 & 3). It is tempting to

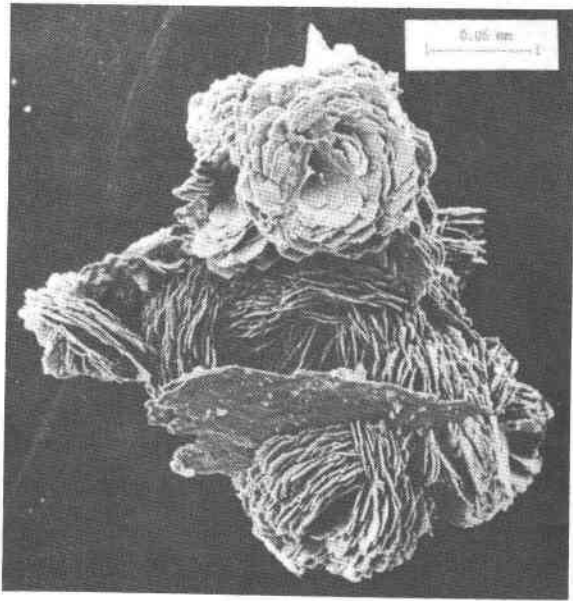


Fig. 4. Composite cluster of caryopilite crystals showing the typical rosette aggregate habit (NMNH 143781) SEM photomicrograph.

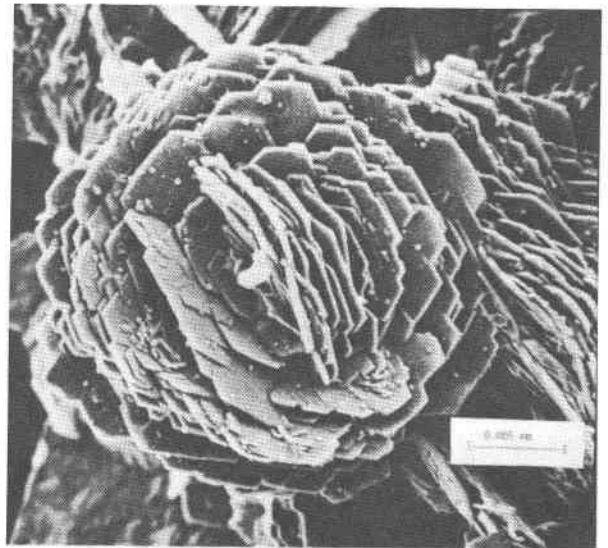


Fig. 5. One isolated caryopilite rosette which clearly shows the hexagonal tabular habit of the individual crystals (NMNH 143781). SEM photomicrograph.

postulate that these analyses are representative of a partial solid solution by addition as postulated for As^{3+} in schallerite. If so, As^{3+} substitution in caryopilite is severely restricted. The layer sequence in ca-

ryopilite is apparently not ordered. Such disorder is compatible with a mixed layer structure in which a small proportion of layers consists of end-member schallerite, giving rise to an intermediate composition for the whole structure. Such a mechanism cannot be

Table 2. Chemical analyses of caryopilite. The number of cations computed from each weight percent is calculated on the basis of eight octahedrally coordinated cations.

Sample #	SiO ₂	FeO***	MgO	ZnO	MnO	As ₂ O ₃	Cl	H ₂ O	Other	O ≡ Cl	Total	Locality
JK-303	31.2	1.5	1.8	1.0	48.2	6.9	0.9	8.4**	0.3 ϕ	0.2	100.0	Sterling Hill
NMNH 143781	32.1	1.7	1.9	0.9	48.8	6.5	n.d.	8.1**			100.0	Sterling Hill
SG-1215	32.1	1.9	2.1	1.1	47.2	5.1	0.4	9.9**	0.3 ϕ	0.1	100.0	Sterling Hill
NMNH 147364	36.8	0.7	6.7	3.4	41.6	1.4	0.0	8.98*			99.6	Franklin
NMNH 147363	36.0	0.7	6.6	3.4	41.7	1.2	0.0	9.09*			98.7	Franklin
NMNH 144447	36.5	0.7	6.2	1.7	43.7	1.2	0.0	9.8**	0.2 ϕ		100.0	Sterling Hill
<u>Ions per unit cell</u> ψ												
JK-303	5.49	0.22	0.47	0.13	7.18	0.74	0.27	9.85				
NMNH 143781	5.55	0.25	0.49	0.12	7.15	0.68		9.34				
SG-1215	5.64	0.28	0.55	0.14	7.03	0.54	0.12	11.61				
NMNH 147364	6.09	0.10	1.65	0.42	5.83	0.14		9.92				
NMNH 147363	5.97	0.10	1.63	0.42	5.86	0.12		10.05				
NMNH 144447	6.07	0.10	1.54	0.21	6.16	0.12		10.87				

Accuracy of microprobe data: ± 3 percent of the amount present.

* Determined by Penfield method; accuracy: ± 2 percent of the amount present.

ψ on the basis of eight octahedrally coordinated cations.

n.d. - not determined

** by difference

*** calculated as FeO

ϕ Al₂O₃

tr = trace

Table 3. Chemical analyses of friedelite. The number of cations computed from each weight percent is calculated on the basis of eight octahedrally coordinated cations.

Sample #	SiO ₂	FeO	MgO	MnO	ZnO	CaO	Cl	H ₂ O***	O = Cl	Total	Locality
Friedelite*	34.80			54.75			3.42	7.80	0.77	100.0	Theory
C5736	34.6	0.8	2.4	50.3	1.4	0.1	3.4	7.8	0.8	100.0	Franklin
R8287	34.7	2.5	1.5	50.2	0.8	0.1	3.3	7.6	0.7	100.0	Sterling Hill
105490	34.6	1.5	2.1	49.6	1.1	0.1	3.0	8.7	0.7	100.0	Franklin
142888	34.6	3.4	1.4	48.4	1.0	0.1	2.9	8.9	0.7	100.0	Sterling Hill
R11359	33.9	2.9	1.4	50.2	1.1	0.1	2.9	8.2	0.7	100.0	Franklin
R11234	34.5	3.4	1.0	48.9	1.1	0.1	2.5	8.8	0.6	100.0	Franklin
C6823	34.7	1.0	2.6	49.5	1.0	0.1	2.8	8.4	0.6	100.0	Sterling Hill
R8977	33.7	0.6	0.9	51.3	1.1	0.1	2.3	10.5	0.5	100.0	Franklin
C6212	34.3	0.4	1.3	51.3	0.9	0.1	2.3	9.9	0.5	100.0	Franklin
C2867	34.1	0.5	1.2	50.6	1.1	0.1	2.2	10.7	0.5	100.0	Franklin
95216	34.1	0.5	1.3	50.9	1.2	0.2	2.2	10.1	0.5	100.0	Franklin
C5175	34.0	0.4	0.9	52.3	0.7	0.3	0.8	10.8	0.2	100.0	Franklin
Friedelite**	35.44			55.74				8.82		100.0	Theory
Ions per unit cell ψ											
Friedelite*	6.00			8.00			1.00	9.00			
C5736	5.77	0.11	0.60	7.10	0.17	0.02	0.96	8.67			
R8287	5.84	0.35	0.38	7.15	0.10	0.02	0.94	8.53			
105490	5.85	0.21	0.53	7.10	0.14	0.02	0.86	9.81			
142888	5.92	0.49	0.36	7.01	0.13	0.02	0.84	10.15			
R11359	5.66	0.41	0.35	7.09	0.14	0.02	0.82	9.13			
R11234	5.91	0.49	0.26	7.10	0.14	0.02	0.81	10.06			
C6823	5.85	0.14	0.65	7.06	0.12	0.02	0.80	10.00			
R8977	5.83	0.09	0.23	7.52	0.14	0.02	0.67	12.12			
C6212	5.71	0.06	0.33	7.48	0.10	0.02	0.67	11.36			
C2867	5.93	0.07	0.31	7.46	0.14	0.02	0.65	12.42			
95216	5.86	0.07	0.33	7.41	0.15	0.04	0.64	11.57			
C5175	5.81	0.06	0.23	7.57	0.09	0.06	0.23	12.31			
Friedelite**	6.00			8.00				9.97			

* Theoretical composition for Mn₈Si₆O₁₅(OH)₉Cl;** Theoretical composition for Mn₈Si₆O₁₅(OH)₉(OH) ψ on the basis of 8 octahedrally coordinated cations. *** Water by difference except for theoretical compositions.Accuracy of data: ± 3 percent of the amount present; all elements except H determined by electron microprobe.

definitively tested until material of high enough quality for direct TEM imaging of layer sequences by high-resolution-lattice-fringe-imaging becomes available.

Relationship between mcGillite and friedelite

McGillite was described by Donnay *et al.* (1980) as a chlorine-rich member of the friedelite family (ideally Mn₈Si₆O₁₅(OH)₈Cl₂) having a value of *c* (85.66 Å) which is four times that reported for friedelite. We present here both chemical analytical and single-crystal X-ray diffraction data which clarify the relation between friedelite and mcGillite.

In conjunction with our study of schallerite we obtained analyses of a number of samples of friedelite from Franklin and Sterling Hill. The analyses are presented in Table 3. All of the analyzed samples yielded X-ray powder diffraction patterns in basic agreement with those of friedelite and mcGillite.

Donnay *et al.* (1980) have shown that the patterns of the latter phases are "extremely similar."

Palache (1935) observed that there is a chlorine-deficient friedelite in addition to the more abundant chlorine-containing friedelite. Of our analyses (Table 3), none exceeds 3.4% Cl, as consistent with older analyses in the literature. This corresponds to the composition Mn₈Si₆O₁₅(OH)₉Cl. Considering all available friedelite analyses, the chlorine content thus varies from a maximum of one per formula unit to none, with apparent solid solution with (OH) to Mn₈Si₆O₁₅(OH)₉(OH).

Donnay *et al.* (1980) note that mcGillite appears to be characterized by ordered Cl relative to (OH), giving rise to the formula Mn₈Si₆O₁₅(OH)₈Cl₂, and they state that because of the composition difference due to ordered chlorine, mcGillite is not, *sensu strictu*, a polytype of friedelite. These relations carry the additional implication that it may be the compositional

difference that leads to the difference in superstructure, much as we propose above that the As^{3+} content of schallerite may be essential to the stacking sequence in that mineral.

In order to investigate these relations we obtained single-crystal diffraction results for friedelite. Results were obtained for samples N.M.N.H. C5736, R8287, C6216 and 95216; analyses of three of these are given in Table 3. All of these samples gave rise to superstructure diffractions indicative of a superstructure like that of mcGillite; *i.e.*, the value of c is approximately 86 Å. Samples R8287 and C5736 yielded patterns with relatively sharp superstructure diffractions, but those for the other samples were very diffuse parallel to c^* . As the diffraction relations for such a large superstructure are difficult to interpret, we compared our photographs with those for mcGillite which were provided by Dr. G. Donnay. This direct comparison verified the analogy in diffraction patterns.

Our single-crystal diffraction results are, therefore, compatible with a mcGillite-like superstructure for samples having a friedelite-like composition. We were unable to find single-crystal diffraction data in the literature apart from those of Frondel and Bauer (1953). As that work was done well before it was known that there are very subtle and difficult-to-define superstructure reflections in friedelite-group minerals, we surmised that such reflections might exist, but simply have been overlooked. Dr. C. Frondel kindly provided material from the specimens of the original study of Frondel and Bauer (1935). In particular, we examined their friedelite sample number H.U. 89854 using single-crystal techniques. The superstructure reflections are so diffuse parallel to c^* that an interpretation would be difficult without direct comparison with photographs having relatively sharp diffractions. However, such a comparison shows that the intensity distribution correlates with that for crystals having $c \sim 86$ Å. Thus this friedelite also has a mcGillite-type superstructure, albeit one which is highly disordered.

In summary, certain so-called friedelites with low Cl-contents relative to mcGillite yield a mcGillite-like, relatively well-ordered superstructure. They therefore may represent a separate species with composition approaching $Mn_8Si_6O_{15}(OH)_{10}$. In addition, there is no really firm evidence for the existence of friedelite of these compositions having a value of $c \sim 21.4$ Å. Thus friedelite may be the OH-rich equiva-

lent of mcGillite, but simply with a superstructure of widely variable order. The latter interpretation is more probably the correct one.

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