Arsenites related to layer silicates: Manganarsite, the arsenite analogue of manganpyrosmalite, and unnamed analogues of friedelite and schallerite from Långban, Sweden

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Abstract

Manganarsite, ideally $Mn_3As_2O_4(OH)_4$, is a new mineral from Långban, Sweden. X-ray diffraction data imply it has space group $P\bar{3}1m$, $P31m$ or $P312$, with $a = 11.451(6)$, $c = 7.252(6)$ Å, $Z = 4$, although optical data imply a lower symmetry. The powder-diffraction pattern has principal reflections (d, I/I_0, hkl) 3.62,50,002; 2.662,100,221; 1.845,70,223,331; 1.652,60,600; 1.531,40,224, 503. There is a perfect {001} cleavage; hardness = 3; $D_{calc} = 3.60$, $D_{obs} = 3.64$ g/cm^3.

Two other polymorphs are described, which together with manganarsite are analogous to the three principal members of the friedelite group, manganpyrosmalite, schallerite, and friedelite. Manganarsite and its polymorphs are 7-Å layered structures that apparently differ in the stacking sequence of pyrochroite layers, as is true for members of the friedelite family. However, indirect evidence implies that manganarsite and its polymorphs have a layer based on arsenite chains or rings in place of the tetrahedral sheet of friedelite.

Introduction

Manganarsite and the two other phases described herein were originally discovered during a systematic investigation of the minerals from reduced vein assemblages from Långban, Varmland, Sweden. Because they have a unique but similar appearance, X-ray powder-diffraction patterns were obtained for a variety of specimens. The X-ray patterns revealed both single phases and mixtures of more than one phase. From these data, we concluded that the specimens comprise three minerals. Each gives a X-ray powder-diffraction pattern that is similar to those of the members of the friedelite group, the principal representatives of which are manganpyrosmalite, schallerite, and friedelite.

Members of the friedelite group all have the approximate composition $(Mn,Fe)_8Si_6O_{15}(OH)_{10}$, although schallerite and nelenite (Dunn and Peacor, 1984), as defined, have essential As. All give closely related single-crystal diffraction data in that all appear to be hexagonal or rhombohedral (Frondel and Bauer, 1953) and have equivalent values of $a = 13.4$ Å; manganpyrosmalite, schallerite, and friedelite have apparent values for c of approximately 7, 14, and 21 Å, respectively. Until recently they were believed to be polytypes related by variations in the stacking sequence of 7-Å layers. However, Ozawa et al. (1983) and

Iijima (1982a, 1982b) have shown that friedelite has a 1-layer monoclinic structure. Ozawa et al. showed that mcGillite has a 12-layer structure based on twinning of the 1-layer monoclinic structure and that the friedelite structure is based on the same sequence. Takéuchi et al. (1983) have theoretically derived the polytypes and illustrated their characteristics in transmission-electron microscope images.

Although the data of this paper verify a close relation between the three arsenites described herein and manganpyrosmalite, schallerite, and friedelite, respectively, we have chosen to name only one of these because of ambiguities in the superstructure relations of the other two, so as to keep the nomenclature simple until the crystal structures of these phases are well understood. We have named the arsenite analogue of manganpyrosmalite *manganarsite* in allusion to the chemical composition. This species and name were approved by the Commission on New Minerals and Mineral Names, I.M.A. Type material is preserved at the Smithsonian Institution under catalogue number NMNH no. R5795. We refer to the two unnamed phases as the "arsenite equivalent of schallerite," or friedelite, respectively, or as being "schallerite-like" or "friedelite-like," because the respective silicate-arsenite pairs have similar X-ray powder-diffraction

Table 1. Powder X-ray diffraction data for manganarsite

I/I₀	d_obs	d_calc	hkl	I/I₀	d_obs	d_calc	hkl
10	7.22	7.25	001	2	1.329	1.327	253
30	5.74	5.73	110			1.328	305
30	4.49	4.49	111	1	1.293	1.293	711
50	3.62	3.63	002			1.294	225
5	3.31	3.33	211	5	1.232	1.231	631
		3.31	030			1.232	443
						1.235	712
2	3.070	3.063	112				
5	3.007	3.008	301	2	1.222	1.221	604
2	2.932	2.927	202			1.222	801
100	2.662	2.663	221			1.222	533
30	2.244	2.247	222			1.222	703
1	2.034	2.032	123	1	1.153	1.150	216
70	1.845	1.847	223			1.154	713
		1.846	331			1.155	335
60	1.652	1.653	600				
40	1.531	1.532	224	10	1.123	1.123	444
		1.533	503			1.124	641
						1.124	543
10	1.505	1.504	602			1.125	515
5	1.450	1.450	005	2	1.114	1.114	226
		1.455	522			1.116	730
20	1.404	1.404	441			1.116	534
		1.406	115			1.116	704
				20	1.0897	1.0894	901
						1.0902	605
				10	1.0697	1.0702	821

Note: Indexed on unit cell with $a = 11.451$, $c = 7.252$ Å.

Table 2. Powder X-ray diffraction data for the As³⁺ equivalent of schallerite

I/I₀	d_obs	d_calc	hkl
10	7.22	7.24	002
20	5.70*		
5	4.49*		
60	3.62	3.62	004
40	2.809	2.811	101
100	2.665	2.664	102
50	2.466	2.463	103
20	2.248	2.246	104
10	2.036	2.036	105
40	1.845	1.845	106
60	1.654	1.654	110
20	1.531	1.530	108
20	1.504	1.504	114
10	1.448	1.447	0,0,10
20	1.405	1.402	202
		1.405	109
2	1.374	1.373	203
2	1.233	1.232	206
2	1.177	1.178	207
5	1.123	1.123	208
20	1.0889	1.0892	1,1,10
10	1.0711	1.0710	209
		1.0696	212

Note: Indexed on subcell with $a = 3.3084$, $c = 14.471$ Å.
* Supercell reflection, but with a contribution from manganarsite.

patterns and *related* structures. However, we show below that the silicate-arsenite pairs have different formulae and major differences in structure, and the term "equivalent" implies only a very general similarity. The studied samples of the other two phases are NMNH no. C4252 (arsenite-equivalent of schallerite) and NMNH no. 94913 (arsenite-equivalent of friedelite).

CRYSTALLOGRAPHY

X-ray powder-diffraction data are listed in Tables 1–3 for manganarsite and the two closely related phases. Powder-diffraction patterns were all obtained using a 114.6-mm-diameter Gandolfi camera, Mn-filtered Fe$K\alpha$ radiation, polycrystalline samples, and N.B.S. Si as an internal standard.

Precession and Weissenberg photographs of manganarsite imply that it is trigonal with space group $P\bar{3}1m$, $P31m$, or $P312$, with $a = 11.451(6)$ and $c = 7.252(6)$ Å. The lattice parameters were obtained by least-squares refinement of the powder-diffraction data. Because the manganpyrosmalite (p) and manganarsite (m) powder patterns are very similar, their lattice parameters and single-crystal diffraction patterns were directly compared. The values of c are equivalent ($\simeq 7.3$ Å) as consistent with a layer structure consisting of a tetrahedral and octahedral layer; the a values are different, but have the simple relation $a_p(\sqrt{3}/2) = a_m$. This gives rise to common elements in their reciprocal lattices (Fig. 1). Manganpyrosmalite has a substructure based on a pyrochroite-like octahedral layer which is expressed by intense reflections having h_p and $k_p = 4N$. These reflections are common to the mangan-

arsite diffraction pattern, and they define the same substructure. We refer to them as type A. They have indices $h_m - k_m = 3N$; h and $k = 2N$ relative to the manganarsite unit cell. Some other superlattice reflections of manganpyrosmalite are also common to the two patterns. They have indices $h_m - k_m = 3N$; h or $k = 2N + 1$; we refer to them as type B. Those superlattice reflections of manganarsite that are not in common with those of manganpyrosmalite are referred to as type C. Single-crystal diffraction patterns of manganarsite invariably yield sharp and intense type A reflections, and sharp type B reflections of moderate intensity. Type C reflections are very weak and usually very diffuse, although in the case of one exceptionally small crystal they were weak, but sharp.

In the manganpyrosmalite structure (Takéuchi et al., 1969; Kato and Takéuchi, 1983), the substructure reflections represent the transform of the trioctahedral pyrochroite-like layer. The common substructures of manganarsite and manganpyrosmalite, combined with their related compositions (see below), imply that the manganarsite structure is also based, in part, on such layers.

Single-crystal X-ray diffraction data were also obtained for the arsenite equivalent of schallerite, but suitable crystals of the friedelite equivalent could not be found. The single-crystal patterns for the As³⁺ equivalent of schallerite also showed strong reflections corresponding to the substructure reflections of friedelite. The identifications were made, in part, by directly superimposing single-crystal patterns of friedelite and schallerite on those of the As³⁺ equivalent of schallerite. Thus the crystals of the As³⁺ equivalent of schallerite have packets of layers that

Table 3. Powder X-ray diffraction data for the As^{3+} equivalent of friedelite

I/I_0	d_{obs}	d_{calc}	hkl
20	7.26	7.24	003
5	5.72*		
80	3.62	3.62	006
90	2.849	2.849	101
30	2.776	2.778	012
100	2.539	2.540	104
80	2.393	2.397	015
20	2.108	2.108	107
60	1.732	1.733	1,0,10
60	1.657	1.659	110
20	1.628	1.627	0,1,11
10	1.508	1.508	116
10	1.449	1.444	1,0,13
		1.448	0,0,15
2	1.435	1.434	021
5	1.389	1.389	024
30	1.354	1.364	205
10	1.199	1.198	0,2,10
1	1.163	1.162	2,0,11
		1.167	0,1,17
20	1.0908	1.0909	1,1,15
5	1.0627	1.0621	1,0,19
10	1.0530	1.0542	2,0,14
		1.0538	1,2,5

Note: Indexed on unit cell with $a = 3.3186$, $c = 21.718$ Å.
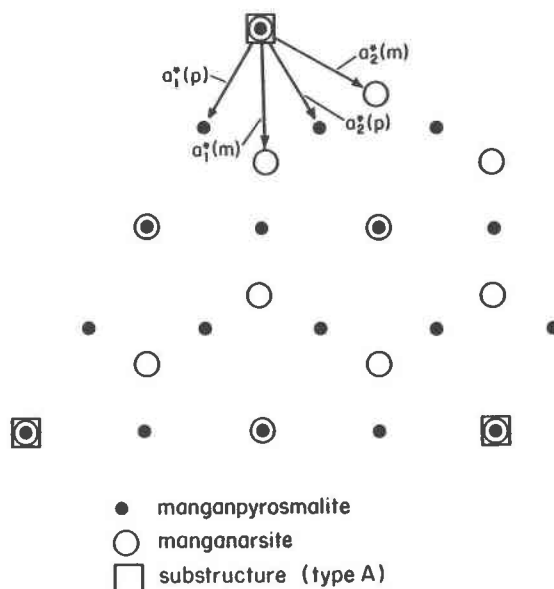* Supercell reflection.

Fig. 1. Relation between diffraction patterns for $hk0$ reflections of manganpyrosmalite (p) and manganarsite (m). Type A reflections are substructure reflections and are common to both patterns. Type B reflections are also common to both patterns, but type C reflections do not overlap.

are dominantly schallerite-like, but there is a small proportion of friedelite-like layers.

The type B reflections in these crystals are weak and so diffuse as to give continuous streaks parallel to $\mathbf{c}^*$. The type C reflections are so weak and diffuse that they could be discerned only by careful examination with photographs of manganarsite for direct comparison.

These relations show that there are three As^{3+} phases that are apparently related to one another in a manner equivalent to that of manganpyrosmalite, schallerite, and friedelite. However, the superstructure of only manganarsite, the As^{3+} equivalent of manganpyrosmalite, could be unambiguously defined. The powder patterns of the As^{3+} equivalents of schallerite and manganpyrosmalite have therefore been indexed only on type A reflections; that for the schallerite-equivalent phase originally contained reflections from other minerals, including the As^{3+} equivalent of friedelite. These have been deleted. The superstructure reflection(s) occurring in the powder patterns correspond to the strongest superstructure reflections of manganarsite and, although they are very diffuse, are seen to be the strongest type B reflections in the single-crystal patterns. The lattice parameters for the As^{3+} equivalents of schallerite ($A = 3.3084$, $C = 14.471$ Å) and friedelite ($A = 3.3186$, $C = 21.718$ Å) were obtained by least-squares refinement of the powder-diffraction data, as indexed on the subcells. The subcell parameter, A, is related to a of manganarsite by the relation $a = (2\sqrt{3})A$.

CHEMICAL COMPOSITION

The minerals described herein were chemically analyzed using an ARL-SEMQ electron microprobe, with op-

erating voltage of 15 kV, and a beam current, measured on brass, of 0.025 μA. All three samples were subjected to wavelength-dispersive scans that indicated the absence of any other elements with atomic number greater than 9. The standards used were manganite (Mn), synthetic olivenite (As), hornblende (Fe, Mg), and synthetic Sb$_2$O$_3$ (Sb). The data were corrected using a modified version of the MAGIC-4 program. The oxidation state of Fe was determined by microchemical tests. As was assumed to be trivalent based in part on the intimate association with arsenite minerals and in part based on crystallochemical considerations discussed below.

The water content of manganarsite was determined using a Mettler TA-1 thermoanalyzer equipped with an IQ200 quadrapole mass spectrometer for the detection of gases evolved during heating. A sample was stored for several days under standard conditions of 24°C and 40% RH and then found to weigh 16.689 mg. There was no significant weight loss from the sample in the thermoanalyzer during several hours of pumping to establish a vacuum of 1×10^{-8} torr. The sample was heated in an open Pt crucible at 10°C/min from 20 to 725°C with a quartz-glass furnace. A loss of 7.9 wt% occurred in a well-defined, single step between 190 and 550°C with a peak at 435°C. At least 7.7 wt% was due to H$_2$O and less than 0.2 wt% to arsenic oxides. A further loss of 2.5 wt% occurred between 550 and 725°C. This was made up of minor CO$_2$ peaking at 660°C and arsenic oxides peaking at 685°C.

The most significant value from the thermoanalysis is the 7.7 wt% H$_2$O loss that can be attributed to OH from the structure of manganarsite. The small CO$_2$ peak can

Table 4. Comparative data for manganarsite and its two polymorphs

	Manganarsite	As equivalent of schallerite	As equivalent of friedelite
a	11.451 Å	3.308 Å	3.319 Å
c	7.252 Å	14.471 Å	21.72 Å
V	823.5 Å^3	137.1 Å^3	207.1 Å^3
Z	4	⅔	1
D_{obs}	3.64	3.64	3.6
D_{calc}	3.60	3.57	3.57
Optic sign	(−)	(−)	(−)
α	1.78	1.79	1.74
β	1.81	1.81	1.80
γ	1.81	1.81	1.81
		Composition	
FeO	1.8	1.1	0.0
MgO	1.7	1.0	1.7
MnO	43.1	45.3	45.1
As$_2$O$_3$	44.3	44.0	44.2
Sb$_2$O$_3$	1.3	0.4	1.2
H$_2$O	7.7	8.2*	7.8*
Total	99.9	100.0	100.0

* Water by difference.

be attributed to a minor calcite impurity, and the two losses of arsenic oxides to the further breakdowns of the residual compounds produced by the manganarsite decomposition.

The analytical data are presented in Table 4. The data for manganarsite lead to the cell contents $(Mn_{10.97}Mg_{0.76}Fe_{0.45})_{12.18}(As_{8.08}Sb_{0.16})_{8.24}O_{16.84}(OH)_{15.4}$. The ideal formula is considered to be $Mn_3As_2O_4(OH)_4$, for which $Z = 4$. The value of Z for the As^{3+} equivalent of schallerite as given in Table 4 (⅔) is not an integer because Z was calculated for the subcell rather than the unit cell.

PHYSICAL AND OPTICAL PROPERTIES

Manganarsite is light pinkish brown and has a light pink streak. It forms imperfect 1.0-mm-diameter hexagonal crystals with vitreous luster; most material is massive and fine grained. The hardness is approximately 3, and cleavage is perfect {001}. The density, determined using heavy-liquid techniques, is 3.64 g/cm³, compared with the calculated value of 3.60 g/cm³.

Under crossed polars, most larger grains show irregular patchy and undulose extinction and a distinct gridlike twinning pattern. The pattern appears to be the result of two sets of lamellar twins at approximately 60°. However, at higher magnification the individual twins are irregular and indistinct with a "ropey" or braided appearance reminiscent of some exsolution lamellae in K-feldspars. Other grains show evidence of twinning on a larger scale. Several wedge-shaped fragments composed of two twin individuals were also observed.

The combination of complex optical orientation and twinning makes it difficult to determine the optical constants. Only very small fragments a few micrometers in their maximum dimensions appear optically uniform, and it is difficult to make accurate measurements on such small grains. However, the figures are clearly biaxial negative

in character. The $2V$ values range from 28 to 43°. The best figures give a mean value of 33°. The maximum and intermediate refractive indices are indistinguishable: $\gamma = 1.81$ and $\beta = 1.81$; $\alpha = 1.78$. The only aspect of the optical orientation that can be established is that X is perpendicular to the prominent basal cleavage. No dispersion is apparent in the thin grains that give the sharpest figures. However, thicker grains with less distinct figures show $r > v$ and dispersion at extinction.

Physical and optical properties for the two unnamed phases were obtained in the same manner and are presented in Table 4 for comparison.

OCCURRENCE AND PARAGENESIS

Manganarsite and the two related phases occur at Långban, Varmland, Sweden; they were found on museum specimens, and nothing is known of their precise geologic relations.

Manganarsite is known from only one sample; it is the same sample that provided an armangite crystal for crystal-structure analysis (Moore and Araki, 1979). The matrix is coarse grained (>1.0 cm) calcite and barite with minor hematite. A large vug in this matrix is partially filled with granular (2–4 mm) fluorite, and dark-red, 2-cm armangite crystals. Manganarsite occurs as a late phase in this assemblage, coating armangite, and also as a fracture filling. It forms thick aggregates of 1.0-mm platy brown crystals. Small spherules of calcite are the last phase formed.

The two unnamed phases, the arsenite analogues of schallerite and friedelite, occur in a vein assemblage well represented in systematic collections. These phases are associated with finnemanite, trigonite, and calcite, on magnetite-calcite ore. Less common associated minerals are magnussonite, nadorite, and rouseite (Dunn et al., 1986). The schallerite-like phase and the friedelite-like phase are among the last phases to form; they may be contemporaneous with late-stage secondary calcite. Both of these unnamed phases are commonly intergrown. Most samples of both phases are light brownish pink, but can grade into colorless material.

DISCUSSION

According to Takéuchi et al. (1969) the substructure reflections of manganpyrosmalite are primarily a function of the trioctahedral pyrochroite layer, but the superstructure reflections are principally a measure of the structure of the tetrahedral sheet. Insofar as manganpyrosmalite, schallerite, and friedelite have substructures in common with those of manganarsite and the two other Mn-arsenites, respectively, this implies that both families have equivalent layer structures with octahedral layers stacked in the same ways. On the other hand, the differing superlattices, in part expressed by the different a values for the silicates and arsenites, respectively, imply that the tetrahedral layer in the friedelite family differs from that in manganarsite and related structures.

The formula $Mn_{12}As_8O_{16}(OH)_{16}$ is compatible with a hypothetical structure in which the pyrochroite-like unit

has formula $Mn_{12}O_8(OH)_{16}$. An arsenite unit is compatible with the usual 3-fold coordination of As, wherein each of the eight AsO_3 polyhedra has one vertex as one of the eight oxygen atoms of the pyrochroite layer and two vertices that are shared with adjacent AsO_3 groups to form either rings or chains. The number of shared oxygen atoms with such rings or chains is equal to the number of As atoms, and this unit has composition As_8O_8. Such a hypothetical structure is significantly different from the sheet structures of the friedelite family but is compatible with the reasonable expectation of major differences in the structures of arsenites and silicates. It is also consistent with local charge balance and the usual 3-fold coordination geometry for As^{3+}. However, it would apparently be incompatible with trigonal symmetry and implies that manganarsite is of symmetry lower than $\bar{3}2/m$, but is complexly twinned below a level resolvable with single-crystal X-ray diffraction techniques.

The optical properties of manganarsite correspond to those of a biaxial phase, in apparent disagreement with the diffraction data showing that manganarsite is trigonal. Great care was taken in obtaining a variety of single-crystal patterns in order to detect possible deviations from trigonal symmetry. None were detected. This implies either that (1) manganarsite is not trigonal, but exists in domains much smaller than single-crystal size for X-ray diffraction, and which are averaged by twinning over a crystal, or (2) strain causes a deviation from high-symmetry optics as it does in phases such as certain garnets, synthetic corundum, etc., and as might be expected from the misfit of a pyrochroite layer and arsenite chains or rings. The optical data imply that the former is true. However, there is at present no way of directly verifying that and/or determining the relations for the hypothetical untwinned structure. We have therefore chosen to report the symmetry and unit-cell data as they are directly determined from the available diffraction evidence, recognizing that these results may be subject to revision.

Schallerite is defined as having essential As^{3+}, and Dunn et al. (1981) proposed that it has the formula $Mn_{16}Si_{12}O_{30}(OH)_{14}[As_3^{3+}O_6(OH)_3]$ based on the substitution $2\square + 6(OH) \leftrightarrow 3[As_3^{3+}O_8(OH)_3]$. Likewise, Dunn and Peacor (1984) showed that nelenite apparently has that same formula, but with the friedelite structure. The existence of separate arsenites and silicates having topologically similar structures suggests that the As content of schallerite and nelenite may be due to the intercalation of manganarsite-like arsenite layers within a sequence consisting primarily of silicate layers, rather than being due to a complex substitution. The constancy of composition of both schallerite and nelenite argues against such a relation, but it must now be considered as a definite possibility to be investigated, perhaps by high-resolution transmission-electron microscopy using type material.

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