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Silver sulphosalts from the Meerschaum Mine, Mt. Wills, Victoria, Australia

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ABSTRACT. A rich vein of silver and silver-lead sulphosalt minerals was discovered in 1906 in the Meerschaum Mine, on the Sunnyside goldfield at Mt. Wills, in north-eastern Victoria. Andorite, miargyrite, tetrahedrite (freibergite), owyheeite, and argentian gold are the main silver-bearing minerals present, and sphalerite, pyrite, arsenopyrite, and covelline also occur in the vein.

The vein was probably emplaced under epithermal conditions from ore fluids accompanying the intrusion of the Mt. Wills granite. The main silver-bearing minerals were probably deposited at temperatures ranging from about 350 ° to below 300 °C.

THE Meerschaum Mine was one of the richest mines on the Sunnyside goldfield, situated on the south-eastern flank of Mt. Wills, about 55 km north of Omeo, in north-eastern Victoria. The main mineralized belt measures about 5 by 1 km and is arbitrarily divided into the Glen Wills and Sunnyside fields to the south and north respectively.

Operations in the field commenced in 1891 and had mostly ceased by 1918, when water had become a major problem. In the Glen Wills field, to the south, several mines operated through until the 1950s under the name of the Maude and Yellow Girl Company. Documentation of the mines in the fields has concentrated on the gold production and general layout of the mine workings in relation to the reef system (e.g. Lidgey, 1895; Dunn, 1906; Kenny, 1946; Crohn, 1953, 1958), rather than on the mineralogy.

The total recorded production of gold from the fields is 200 000 ounces (119 000 oz from Glen Wills, 81 000 oz from Sunnyside). Records of silver production are represented by only a few silver assays on ore specimens.

The Sunnyside-Glen Wills area lies close to the eastern boundary of the Mt. Wills granite, which covers an area of about 13 × 13 km. The granite is medium grained, muscovite- and tourmaline-bearing and intrudes phyllites, schists, and hornfelses of probable Upper Ordovician age (Crohn, 1958). Near its southern and south-eastern margins, where the auriferous reefs are concentrated, the granite is extensively autometamorphosed. Feldspars are sericitized, muscovite is the only mica, and tourmaline and disseminated sulphides are abundant (Crohn, 1958).

On the Sunnyside field the reefs occupy three subparallel, roughly north-south trending, fracture systems; two in schist and the third (containing the Meerschaum Mine) within the granite. The reefs themselves are generally 7-15 cm thick and consist of massive quartz with a few crystal-lined cavities, or a series of quartz veinlets enveloping the host rock. These auriferous quartz veins carry variable amounts of finely disseminated sulphides, mainly pyrite and arsenopyrite (Rosales, 1897; Edwards, 1958).

There are few references to minerals other than gold, pyrite, and arsenopyrite, with the major work being that of Edwards (1958) on the mineralogy of the ore from the Maude and Yellow Girl Mine, on the Glen Wills field. The mineralogy of the Sunnyside ores is not well documented, although a number of authors (e.g. Dunn, 1906; Kenny, 1946) refer to 'sulphides of Cu, Pb, Zn, Sb, and Fe' being present in ore from some mines.

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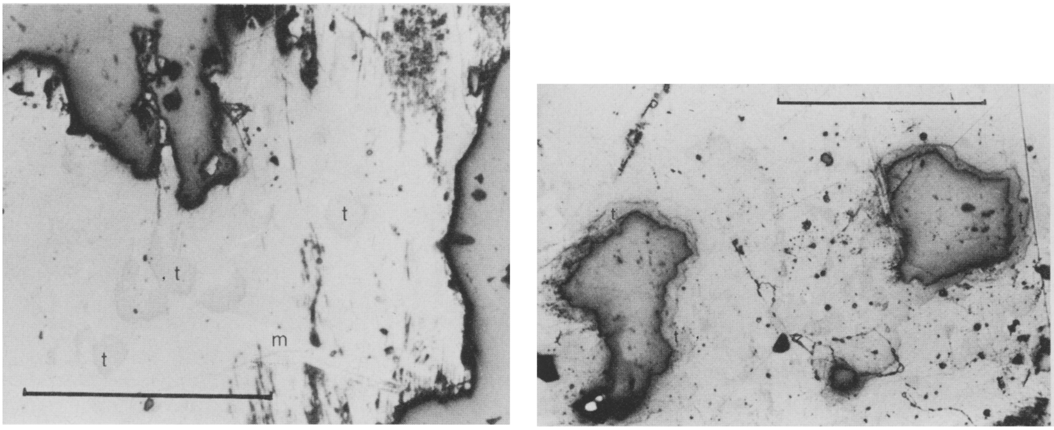
Discovery. Both the Sunnyside and Glen Wills fields contain silver-bearing minerals, mainly argentian gold and tetrahedrite. However, extreme silver enrichment occurred in the Sunnyside field with the emplacement of a vein of silver and silver-lead sulphosalt minerals in the Meerschaum Mine.

The vein was discovered in August 1906. The Inspector of Mines for the Mt. Wills field reported on the find as follows: 'During the year, a rich silver ore vein was cut in this mine (the Meerschaum), assaying as high as 2797 ounces of silver and 40 oz of gold per ton. Further prospecting is necessary before its extent and value can be judged.'

Dunn (1908) described the vein as being 4 inches wide, of rich antimonial silver ore, assaying up to 2613 oz of silver and 1 oz 6 dwt 3 gr of gold per ton. The vein was not showing at the surface, but was cut in a cross-cut in the Meerschaum Mine. To the present day, the exact location of the vein



FIGS. 1 and 2. FIG. 1 (*left*). Andorite grain with tetrahedrite inclusions (t) and blade of miargyrite (m). Reflected light. NMV specimen no. M33769b. Scale bar is 0.2 mm. FIG. 2 (*right*). Rims of tetrahedrite (t) around sphalerite grains enclosed within an andorite-miargyrite grain. Scale bar is 0.05 mm. Reflected light. (NMV specimen no. M33769b.)

is not known and only four specimens appear to have been preserved. These were apparently collected at the time of discovery and are in the collections of the National Museum of Victoria and the Geological Survey of Victoria. No similar specimens have been found on the mine dumps.

Mineralogy. Dunn (1908) described the main sulphosalt as being bright lead-grey with metallic lustre. Recalculation of his assay (Table I) somewhat resembled a mineral of the jamesonite group. However, the mineralogy of the vein remained undefined until 1977 when X-ray diffraction on one specimen revealed that the major phase was andorite. Subsequent investigations of the other specimens show the metallic grains may consist of a complex assemblage of andorite, miargyrite, tetrahedrite, sphalerite, and owyheeite.

Gold, pyrite, arsenopyrite, and covelline are also present in the vein, although they are always isolated from the andorite grains.

The andorite patches may be up to 8 × 4 mm, but do not show crystallographic outlines. Under reflected light the andorite is cream coloured, with fairly weak bireflectance and anisotropy. Each patch is made up of a coarse-grained mosaic of andorite grains, in slightly different orientations.

The andorite has an X-ray diffraction pattern near to identical to that of the JCPDS standard (Nuffield, 1945), and to another andorite specimen from the Itos Mine, Oruro, Bolivia (NMV No. M34260). The Meerschaum Mine andorite is therefore likely to be a mixture of the structural types andorite IV and andorite VI, as defined by Donnay and Donnay (1954).

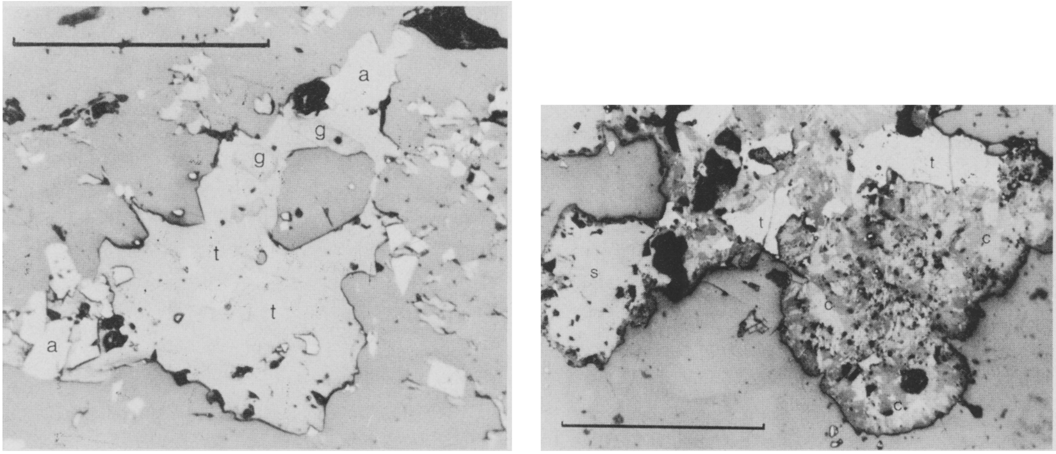
Miargyrite generally forms small randomly oriented inclusions within the andorite although in places it occurs as larger blades and patches (fig. 1). Under reflected light it may be distinguished from andorite by its more greyish-cream colour, and by stronger bireflectance and anisotropy.

Owyheeite grains proved difficult to distinguish under reflected light, as they are generally small and have very similar optical properties to the andorite which encloses them. However, larger blades of owyheeite occur in at least one of the andorite grains examined.

Tetrahedrite is abundant as inclusions within the andorite (fig. 1) and in reflected light has a characteristic pinkish-grey colour. It may form large ragged patches which are occasionally skeletal. In one thin section, tetrahedrite occurs as rims around sphalerite inclusions in andorite (fig. 2). Tetrahedrite may also enclose gold, pyrite, and arsenopyrite outside the andorite grains (fig. 3).

Sphalerite is common as inclusions within the andorite and covelline was encountered in several thin sections, forming mosaic-like aggregates associated with tetrahedrite and sphalerite (fig. 4). It is distinguished by bright blue to grey bireflectance.

The relationship between the silver-bearing minerals and the gold-sulphides mineralization is observable in several full-width specimens of the vein. In the specimen shown in fig. 5, pyrite, arsenopyrite, and gold are concentrated close to one edge of the vein (fig. 6). Small grains of tetrahedrite, which may enclose all three phases, are also present (fig. 3). An horizon of drusy quartz, with terminations directed into the vein, roughly delineates the boundary between the gold and the silver-lead sulphosalt mineralization. Andorite grains increase in size and abundance away from this boundary across the full width of the vein, and



FIGS. 3 and 4. FIG. 3 (*left*). Irregular grain of tetrahedrite enclosing gold (g) and arsenopyrite (a). Scale bar is 0.05 mm. Reflected light. (NMV specimen no. M30060b.) FIG. 4 (*right*). Covelline (c) associated with tetrahedrite (t) and sphalerite (s). Scale bar is 0.05 mm. Reflected light. (NMV specimen no. M33769b.)

form a sharp junction with quartz forming the vein wall. The four preserved specimens of the vein are all similar. Small cavities occur in two of the specimens, but no euhedral sulphosalt crystals are observed growing in them. Quartz is the only gangue mineral.

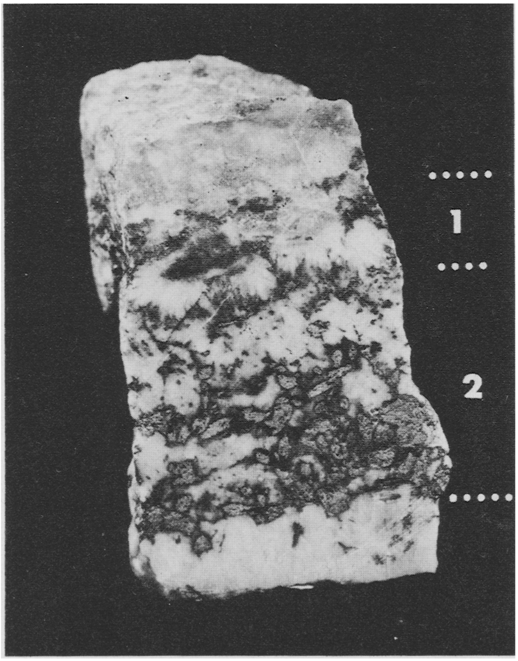
Mineral chemistry. All phases were analysed by electron microprobe, using appropriate metals and sulphides as standards. The specimen current ranged from 0.015 μa to 0.025 μa with a beam voltage of 20 kV. Possible interference between As and Pb was investigated but As was not detected in any

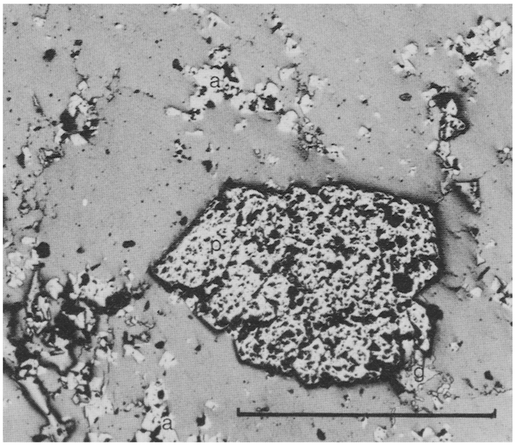
TABLE I. *Representative analyses of minerals from the silver-rich vein in the Meerschaum Mine*

	1	2	3	4	5	6	7	8
Fe	4.35%	—	—	—	—	3.41%	3.90%	—
Cu	2.50	0.17	0.37	0.23	0.77	23.92	—	66.19
Zn	1.50	—	—	—	0.16	3.04	62.60	—
Pb	19.15	25.40	22.74	0.95	41.78	0.11	0.07	—
Ag	9.95	11.86	11.77	37.15	6.32	19.65	—	0.24
Sb	36.47	41.86	43.28	42.29	31.69	28.56	—	0.21
S	25.40	21.17	21.52	21.00	19.83	22.56	33.54	34.54
Total	99.32	100.46	99.68	101.72	100.55	99.65*	100.11	101.18
Formulae								
Fe		—	—	—	—	1.13	0.07	—
Cu		0.02	0.05	0.01	0.29	6.94	—	0.97
Zn		—	—	—	0.05	0.85	0.92	—
Pb		1.11	0.98	0.01	4.89	0.01	—	—
Ag		1.00	0.98	1.05	1.42	3.36	—	0.002
Sb		3.13	3.17	1.06	6.31	4.33	—	0.002
S		6.00	6.00	2.00	15.00	13.00	1.00	1.00

1. Assay of andorite grains (Dunn, 1908)
2. Andorite (N.M.V. sample M33769a)
3. Andorite (N.M.V. sample M30060a)
4. Miargyrite (N.M.V. sample M30060a)
5. Owyheeite (N.M.V. sample M33769b)
6. Tetrahedrite (N.M.V. sample M30060a).
   * Sample contains 0.15% Au
7. Sphalerite (N.M.V. sample M30060a)
8. Covelline (N.M.V. sample M33769b)

Analyst: W. Birch (Nos. 2–8). (—) element not detected during analyses.





FIGS. 5 and 6. FIG. 5 (*left*). A specimen from the Meerschaum Mine silver vein showing the relationship between the gold-sulphides mineralization (zone 1) and the silver sulphosalts (zone 2). (See text for description.) The sample, NMV specimen no. M30060, is 6 cm high. FIG. 6 (*right*). Pyrite (p), arsenopyrite (a), and gold (g) mineralization from zone 1 in the vein shown in fig. 5. Scale bar is 0.2 mm. Reflected light.

Sb-bearing phases. Representative analyses are shown in Tables I and II. In general, the andorite and miargyrite compositions gave formulae close to those acknowledged for each phase. Several points are worthy of note:

Gold contains between 20 and 32 % silver. Small amounts (less than 0.4 %) of gold and silver are detectable in some of the pyrite and (less commonly) arsenopyrite crystals.

All the silver-bearing sulphosalts contain small amounts of copper (up to 0.5 wt % in andorite, 0.2 % in miargyrite and 0.9 % in owyheeite) probably substituting for the silver.

The tetrahedrite is rich in silver (up to 21 %) and hence is the variety freibergite (Riley, 1974). The formulae obtained is close to $(Fe,Zn)_2(Cu,Ag)_{10}Sb_4S_{13}$ (see Table I).

There is little evidence of an extensive solid solution field for the andorite (as encountered in the synthetic system by Hoda and Chang, 1975).

The owyheeite has a low Ag/Sb ratio (1:4.5) compared to both the acknowledged formula $(Pb_5Ag_2Sb_6S_{15})$, and to the owyheeite described by Hoffman and Trdlicka (1978).

Phase relationships. The compositional data for the Meerschaum Mine andorite, miargyrite and

TABLE II. *Representative electron microprobe analyses of gold, pyrite, and arsenopyrite from the Meerschaum Mine silver vein*

	1	2	3	4
Fe	—	—	46.32 %	36.33 %
Zn	—	—	—	0.04
Au	67.01	78.69	0.39	—
Ag	31.88	19.77	—	0.06
As	—	—	—	40.41
Sb	—	—	—	—
S	—	—	54.03	22.94
Total	98.89	98.46	100.74	99.78
		Formulae		
Fe			0.98	1.00
Au			0.002	—
As			—	0.83
S			2.00	1.10

1. Gold (N.M.V. sample M33769a)
2. Gold (N.M.V. sample M30060b)
3. Pyrite (N.M.V. sample M30060b)
4. Arsenopyrite (N.M.V. sample M30060b)

owyheeite are shown plotted in the Ag_2S-PbS-Sb_2S_3 system in fig. 7. Also plotted is the original assay of Dunn (1908), taking into account only Pb, Ag, Sb, and S. Although the Cu, Zn, and Fe values indicate contamination of Dunn's sample, the normalized assay composition plots very close to the microprobe analyses.

The synthetic Ag_2S-PbS-Sb_2S_3 system has been investigated and discussed by a number of workers (Hoda and Chang, 1975; Amcoff, 1976; Goodell, 1975; Craig and Barton, 1973; Keighin and Honea, 1969). There is, however, considerable complexity within the system, due mainly to the large number of possible phases along the PbS-Sb_2S_3 join and the presence of immiscibility gaps along the PbS-$AgSbS_2$ join below 500 °C (Hoda and Chang, 1975). Compositional limits of a number of other ternary phases have not been accurately defined. These complications are reflected in the profusion of so-called assemblages, many of them contradictory, described in the literature (Goodell, 1975).

Andorite displays extensive solid solution between 300 and 500 °C and may form equilibrium assemblages with all other phases in the PbS-$AgSbS_2$-Sb_2S_3 half of the system (with galena at 300 °C only). Monoclinic (β) miargyrite may coexist with andorite below 380 °C (Hoda and Chang, 1975). Owyheeite was not observed during the experimental work by Hoda and Chang on the PbS-Ag_2S-Sb_2S_3 system. However, it is possible that the assemblage andorite-miargyrite-owyheeite is stable below 300 °C, where reaction rates are too sluggish for equilibrium to be reached during experimental work. The three phases may be linked by the following reaction in which stibnite is a product.

$$5\ \underset{\text{andorite}}{PbAgSb_3S_6} \rightarrow 3\ \underset{\text{miargyrite}}{AgSbS_2} + \underset{\text{owyheeite}}{Pb_5Ag_2Sb_6S_{15}} + \underset{\text{(in solution)}}{3\ Sb_2S_3}$$

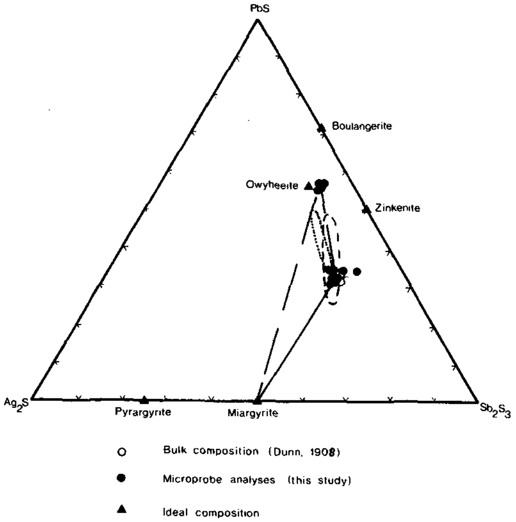


FIG. 7. Compositional data for the Meerschaum Mine sulphosalts plotted in the Ag_2S-PbS-Sb_2S_3 system. Dotted and broken lines define solid solution fields for andorite at 300 °C and 400 °C respectively (after Hoda and Chang, 1975).

Stibnite accompanied by zinkenite has been discovered in a specimen from the Meerschaum Mine dump, but its relationship to the Ag-mineralization is unknown.

Owyheeite was recorded by Williams (1968) as the youngest mineral in a complex silver ore in Nevada, supporting the suggestion that owyheeite is perhaps the lowest-temperature Ag-bearing phase in the Meerschaum Mine. There is no evidence in the Meerschaum silver vein for the assemblage andorite-galena, observed in the synthetic system at 300 °C by Hoda and Chang (1975).

The stability of tetrahedrite, $Cu_{12}Sb_4S_{13}$, was investigated by Tatsuka and Morimoto (1973) who found that the mineral decomposed below 250 °C. However, iron-bearing tetrahedrite is stable over a wide temperature range, from at least 500 to 25 °C (Tatsuka and Morimoto, 1977). Therefore, while tetrahedrite stability in the Cu_2S-Ag_2S-Sb_2S_3 system has not been investigated, it is likely that the considerable Ag for Cu substitution in the tetrahedrite-freibergite series (Riley, 1974) would not result in any significant decrease in the stability of the ternary phase over the same temperature interval, particularly as some Fe is also present in the structure (Table I, analysis 6).

Paragenesis of the silver ore. The generalized sequence of deposition in the silver sulphosalt vein in the Meerschaum Mine is: pyrite-arsenopyrite; gold; sphalerite; tetrahedrite; andorite-miargyrite-owyheeite; (covelline).

The initial pyrite-arsenopyrite-gold mineralization is common to the entire Sunnyside-Glen Wills field and the Ag-Pb-Sb-enriched fluids in the Meerschaum Mine probably exploited an open vein in which the gold had already been precipitated. The ore solutions giving rise to the Ag-Sb-Pb mineralization were probably late-stage fluids accompanying the intrusion of the Mt. Wills granite. Whether they are a derivative of the original solutions giving rise to the gold is conjectural, although the same conduits were obviously available. However, the high silver content of the Glen Wills-Sunnyside gold is an unusual feature considering the Victorian gold province as a whole and there appears to be an obvious genetic link between this early argentian gold and the richness of the late-stage silver sulphosalt assemblage. It may also be significant that, on the Sunnyside field, the silver-rich vein occurs in the only reef system within the granite.

The coexistence of pyrite and arsenopyrite over the entire field suggests (although does not prove) that the two minerals crystallized simultaneously. If equilibrium is assumed, then experimental work in the Fe–As–S system by Clark (1960) and Barton (1969) sets an upper limit of 491 °C for mineralization in the ore vein. However, the arsenopyrite is rich in sulphur relative to arsenic (see analysis 3, Table II) suggesting it crystallized at somewhat lower temperatures, possibly as low as 350 °C (Clark, 1960). On the basis of limited data presented by Barton (1969), the composition of the Meerschaum sphalerite ($\mathrm{Fe} = 3.5$ mole%) indicates a maximum temperature of about 280 °C for the assemblage sphalerite-arsenopyrite (assuming equilibration).

The tetrahedrite (freibergite) appears to have crystallized in the interval between the main pyrite-arsenopyrite-gold mineralization and the deposition of the silver sulphosalts. This, together with its widespread occurrence in the Sunnyside and Glen Wills fields, suggests it may have crystallized over a wider temperature range than the other phases. The upper stability limit for tetrahedrite is 543 °C (Tatsuka and Morimoto, 1977) for the Ag- Fe-free synthetic phase, while the maximum thermal stabilities of andorite and owyheeite are unknown. These uncertainties aside, a temperature change of around 350 °C to somewhat less than 300 °C appears likely for the main silver-bearing phases based on both the available experimental work and observations of natural epithermal vein occurrences (e.g. Hall and Czamanske, 1972; Iwano and Kuwarno, 1974). The occurrence of covelline as a possible supergene alteration product of tetrahedrite may represent re-equilibration at even lower temperatures (Rickard, 1973). There is, however, no evidence for the crystallization of any Ag-, Sb-, Fe- and Zn-bearing phases resulting from this tetrahedrite decomposition.

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