

Plumbian tennantite from Sark, Channel Islands

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SUMMARY. An unusual tennantite, containing 4.64% Pb, has been found on a mineral specimen from Sark's Hope Mine collected in 1843. An electron-probe analysis is given, together with visible spectrum reflectance data, quantitative colour values, VHN, and cell dimensions determined from X-ray powder diffraction photographs.

THE island of Sark comprises two unequal parts; the larger northern portion (Great Sark) is composed dominantly of Precambrian metamorphic rocks. It is joined by the narrow ridge of La Coupée to Little Sark in the south. Little Sark is composed of foliated granitic rocks of Late Precambrian age (Sutton and Watson, 1957), which, like all the rocks of the island, are cut by numerous dykes and faults, some of which afforded access to mineralizing fluids.

Ores of lead and silver were mined on Little Sark as early as 1609 but it was between 1830 and 1845 that mining operations were most intensive. An account of the mining activity of Sark is given by Mourant and Warren (1934), and there are several earlier accounts, of which that of Henwood (1871) is among the best.

There is in the Mineral Collection at the British Museum (Natural History) an unprepossessing specimen, B.M. 1964, R440, of mineralized breccia ($14 \times 8 \times 5$ cm in size) from Sark's Hope Mine in Little Sark. The specimen belonged to the late Sir Arthur Russell and was collected, according to the label, by 'Captain John Prince, manager of the mine, circa 1843'. It consists of an aggregate of fragments up to 2 cm across of quartz and fine-grained granitic material loosely cemented by anglesite and scorodite. A grey metallic mineral in the breccia, said to be argentite, had given an X-ray powder pattern indicative of tetrahedrite, a mineral hitherto unrecorded in the Channel Islands.

The specimen was examined during the course of an optical, chemical, and X-ray study of fahlerz and found to be an unusual variety of tennantite in that it contained a significant concentration of lead. It was for this reason that the occurrence was studied in more detail.

The presence of major lead in minerals of the tennantite-tetrahedrite series has not previously been established with any degree of certainty. Hoffmann (1895) reported 9.38% Pb in a tetrahedrite from West Kootenai district, British Columbia, claiming that the particular specimen analysed contained the pure mineral associated only with white opaline quartz. However, in other specimens from the same locality, the tetrahedrite was reported to be associated with galena. Guimarães (1934) found 14.76% Pb in a tetrahedrite from Ouro Preto, Brazil, but admits that the mineral could well be associated with jamesonite. In both cases, therefore, part or all of the lead may have been concentrated in minerals associated with the tetrahedrite, and only by modern microscopical and microanalytical techniques can the problem be settled.

Specimen preparation. Part of the hand specimen was sectioned with a diamond disc saw and then serially sectioned with a Lastec diamond-impregnated wire saw. The polishing procedure employed was that described in Clark *et al.* (1974). A thin section was also prepared from one of the slices.

Mineralogy. In thin section the rock fragments are composed of a fine-grained quartz aggregate and have probably suffered secondary silicification. Many of the fragments are surrounded by a zone of elongate quartz grains, which are arranged with their long axes perpendicular to the outline of the fragment. Of particular interest is a fragment that though silicified has a texture of a porphyritic basic igneous rock, and could be a fragment of a basic dyke, or (though less likely) of lava.

Tennantite and pyrite are the two major opaque constituents of the rock. In polished section pyrite is seen to occur in three different forms: as partially replaced euhedra (with a preponderance of hexagonal outlines—suggesting the common habit to be dodecahedral); as a slightly lower reflecting, yellower, collomorphic variety; and as framboids. The euhedral pyrite crystals, grain size from 40 μm to 200 μm , partially encrust the angular to rounded breccia fragments. They are commonly replaced by quartz or scorodite and anglesite and rarely by tennantite and chalcopyrite. The quartz contains complex arborescent tubular growths of minutely crystalline hematite.

The collomorphic pyrite contains approximately 5 to 6% arsenic, and is softer than the euhedral pyrite. In one section it completely infills areas between the breccia fragments and is itself severely fractured. The fracture pattern appears to result from syneresis rather than cataclasis. Quartz and the secondary minerals scorodite and anglesite infill the fractures. In other sections the collomorphic pyrite forms rotund rims on the rock fragments and consists of alternating layers of differing hardness and colour intermixed with spheroidal aggregates of harder pyrite. Polishing relief exaggerates these hardness differences. Radial and concentric shrinkage cracks are common.

Framboidal pyrite aggregates, with individual framboids varying from 2.5 μm to 12 μm , are distributed within the scorodite, anglesite, and covellite crusts surrounding and replacing the tennantite and other pyrite varieties.

Tennantite forms a crustification sequence (0.1 mm–2.0 mm thick) with, and upon, the euhedral and collomorphic pyrite; it completely fills cavities between the original rock fragments, fills fractures in, and replaces pyrite and quartz.

In one polished mount a continuous rim of tennantite encloses the silicified and pyritized core of breccia fragments without penetrating into its interior. In this specimen rare tennantite euhedra (40 μm –80 μm) occur on the outer or free surface.

A highly reflecting white phase is associated with the tennantite; it consists of oriented exsolved blebs of maximum diameter 0.5 μm , of rare, 0.1–0.5 μm thick up to 3.0 μm long, blades and of straight linear and curved veinlets of the same thickness but up to 12 μm in length. They are widely and randomly dispersed throughout the tennantite (individual blebs may be separated by as little as 5 μm or as much as 80 μm). The mineral resembles galena, but owing to the small size of the grains this identification cannot be confirmed; galena does not otherwise occur within the sections.

Chalcopyrite is intimately associated with the tennantite in complex veinlets in pyrite and quartz. It commonly occurs as discrete 'islands' replaced and overgrown by covellite. The covellite, scorodite, and anglesite separate or isolate the chalcopyrite from the more abundant tennantite and together act as a cementing medium. Veinlets of chalcopyrite penetrate tennantite and, rarely, form thin 10 to 20 μm bands within and concordant with the crustiform tennantite. In areas where the secondary minerals form the groundmass to replaced pyrite and quartz, chalcopyrite frequently occupies embayments in the sutured and replaced phases. It is also associated with very rare anhedral grains (up to 30 μm) of blende, where both are partially replaced by covellite.

The secondary constituents, finely crystalline covellite, scorodite, anglesite, and an unidenti-

fied phosphate phase (established by electron-probe analysis) form a complex network of veinlets entirely filling and cementing fractures in the other phases and replacing them. They form a crust to the exposed sulphides, within which framboidal pyrite, microcrystalline euhedral pyrite, and partially replaced chalcopyrite are found.

A simple paragenetic diagram summarizing the observations on four polished sections is included.

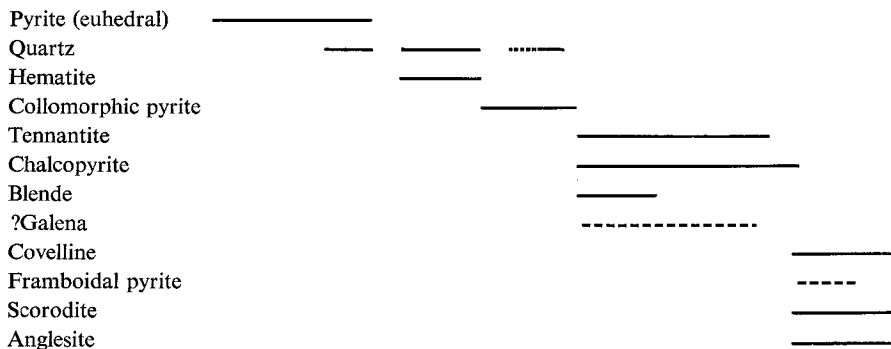


FIG. 1. Paragenetic relationship of minerals associated with tennantite

Chemical composition. The Sark tennantite was analysed using a Cambridge Geoscan electron probe microanalyser at an accelerating potential of 20 keV. The initial qualitative determination indicated that the mineral is an intermediate tennantite-tetrahedrite, but bearing lead in significant quantities. Owing to the overlap of the Pb- $L\alpha$ and As- $K\alpha$ lines, difficulty was experienced in measuring the two elements independently. Qualitatively, lead was confirmed unambiguously by the presence of the three major lead M lines and arsenic by As- $K\beta$.

Quantitative analysis of the mineral was carried out on a marked area using pure metal standards for all the elements determined apart from sulphur and lead, for which pyrite and anglesite respectively were used. The analysis is shown in Table I after correction for X-ray absorption, fluorescence, and atomic number differences. Also shown is the formula calculated on the basis of a unit cell containing 29 atoms.

The arsenic concentration was determined by two methods: in one, the As- $K\beta$ intensity was measured and converted to $K\alpha$, using a factor determined on a lead-free tennantite. This gave As 13.03% after correction. In the other, the As- $K\alpha$ intensity was estimated from its stoichiometric relation with Sb. This gave As 12.53% after correction, and is the figure used in Table I, since the As- $K\beta$ intensity was too low and the background too high to give an accurate intensity ratio in the first method.

The lead concentration was also estimated in two ways: first, the arsenic intensity determined as above (12.53%) was subtracted from the composite As- $K\alpha$ -Pb- $L\alpha$ peak, to give the Pb- $L\alpha$ intensity. This gave Pb 4.50% after correction. And secondly the Pb- $M\alpha$ intensity ratio was measured, giving Pb 4.78% after correction. The Pb figure in Table I is the mean of these two values.

Lead is present in the Sark tennantite at the expense of (Fe+Zn), which is about 5% lower than the expected value for a tennantite with this As/Sb ratio. The minute, highly reflecting, blebs in the tennantite, thought to be galena, could not be individually resolved in the electron probe. However, an area relatively rich in this phase was driven slowly under the electron beam for a distance of 200 μ m and the Pb- $L\alpha$ and Pb- $M\alpha$ signals plotted on chart recorders. They

showed a uniform lead concentration corresponding to the level reported in the analysis, but superimposed on this were a number of peaks, presumably caused by the beam passing over the inclusions. These peaks were only of the order of 7 to 8 % Pb showing that if the inclusions were galena they were only partially resolved in the instrument.

TABLE I (left). *Electron-probe analysis of the Sark tennantite*TABLE II (right). *Reflectance and quantitative colour values of Sark tennantite*

TABLE I			TABLE II								
Wt. %	Atomic ratios to $\Sigma(\text{atoms}) = 29$		λ	R		λ	R		λ	R	
	Air	Oil		Air	Oil		Air	Oil			
Cu	39.58	10.01	400 nm	29.1 %	15.2 %	520 nm	28.6 %	14.7 %	620 nm	27.1 %	12.8 %
Ag	2.60	0.39	420	29.0	15.2	540	28.7	14.6	640	26.6	12.2
Zn	2.27	0.56	440	28.9	15.1	546	28.7	14.6	650	26.3	12.0
Fe	1.29	0.37	460	28.8	14.8	560	28.6	14.3	660	26.1	11.8
Pb	4.64	0.36	470	28.6	14.7	580	28.3	13.8	680	25.8	11.5
As	12.53	2.69	480	28.5	14.6	589	28.0	13.7	700	25.5	11.4
Sb	11.03	1.46	500	28.5	14.6	600	27.7	13.3			
S	26.27	13.17									
	100.21										

Quantitative colour values:								
Air			Oil					
x	y	λ_D	x	y	λ_D			
0.3056	0.3152	483	0.2981	0.3120	486			
Pe % 1.0	Y 28.25		Pe % 4.8	Y 14.06				

Quantitative reflectance, VHN, and Colour Values. Reflectance measurements were made at approximately 25 nm intervals throughout the visible spectrum using a Vickers-EEL spectral microphotometer equipped with a continuous line interference filter. A Carl Zeiss calibrated SiC reflectance standard (no. 055) was used for all measurements as were a pair of Zeiss $\times 8$ air and oil objectives. Primary glare corrections were applied. The area measured was selected for freedom from inclusions and polishing imperfections by means of a $\times 40$ objective with Nomarski differential interference contrast equipment. The selected area was subsequently delimited with a diamond scribing objective so that VHN measurements and electron probe analyses were performed on exactly the same area, after which the material was removed for the purposes of X-ray powder photography.

The air and oil reflectance curves are characteristic of tennantite (Criddle *et al.*, in preparation), the R values being lower throughout the spectrum than those of tetrahedrite. The tabulated values (Table II) were extrapolated from the spectral curves at 20 nm intervals and at the four wavelengths recommended by the I.M.A. Commission on Ore Mineralogy. These curves were used to establish the Quantitative Colour Values for the mineral by the selected ordinate method. Qualitatively it is a pure white grey in air, but adjacent to pyrite it appears a darker grey. In oil it is grey with a perceptible blue tint. Observations were made with an unfiltered tungsten halogen source, of colour temperature 3000–3300 °K, and the Colour Values were calculated for an illuminant CIE.C, having a colour temperature of approximately 6750 °K. Nevertheless, the observed and calculated colour senses are in good agreement.

In air, although Sark tennantite's dominant wavelength (Table II) is in the blue (λ_D 483), its very low saturation level (Pe % 1) and moderate luminance (Y of 28.25) ensure that the mineral does not have a detectable spectral hue. In oil, the observed blueness of its grey is explained by the low luminance (Y 14.06) and higher saturation or excitation purity of 4.8 % and its dominant wavelength of 486.

Its Vickers Hardness Number (measured by G. S. Bearne) at 100 newtons is 250 with a range of 232–74, placing it at the lowest end of the VHN values for a member of the tennantite–tetrahedrite series.

X-ray study. An 11.46 cm diameter powder pattern (Co- $K\alpha$ radiation) was obtained with material removed from the marked area on the tennantite. High-angle graphical extrapolation gave the cell dimension as 10.2614(8) Å. This value falls well within the range of cell dimensions recently determined on a large number of minerals in the tennantite–tetrahedrite group, and we conclude that the presence of lead does not appreciably alter the cell size of the tennantite. This is not the case with mercury, which can substitute also for (Fe+Zn) and causes an appreciable increase in the cell dimension (Criddle *et al.*, in preparation). The Sark tennantite film did not show any of the strong lines of galena, indicating that the part of the specimen studied was reasonably free of inclusions, nor did it show any line splitting due to As–Sb zoning.

Conclusion. This study has shown that lead can substitute in members of the tennantite–tetrahedrite series, although it is the only specimen showing such substitution that has been found during the current wider investigation referred to earlier. More information on the possible extent of Pb solution in the fahlerz minerals requires an examination of other Pb-rich specimens.

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