Tetrahedrite-tennantite series compositional variations in the Cofer Deposit, Mineral District, Virginia

J. William Miller
Department of Geology
University of Georgia
Athens, Georgia 30602

And James R. Craig
Department of Geological Sciences
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

Abstract

The tetrahedrite-tennantite series minerals occur as minor but important constituents in the stratiform massive sulfide deposits of the Mineral District of Virginia. These minerals exhibit wide compositional variation in which there is complete substitution of Sb for As and substitution of Ag for half of the Cu. Ag substitution for Cu is a permissive function of the Sb-content remaining below 1 atomic percent when Sb is less than 10 atomic percent but rising to 18.6 atomic percent (=29.5 weight percent) when Sb rises to 14.7 atomic percent. Tetrahedrite series minerals locally decompose to form a "graphic intergrowth" of arsenopyrite ± gudmundite, sphalerite and chalcopyrite.

Introduction

The tetrahedrite-tennantite series minerals (hereafter referred to as the tetrahedrite series), also commonly known as the fahlerz or fahlore minerals, are nearly ubiquitous in stratiform and stratabound massive sulfide ores. In these ores and in many hydrothermal vein deposits of the Cu-Pb-Zn-Ag affinity, the tetrahedrite-tennantite minerals constitute a major, if not the major, source of silver. Although crystals are occasionally reported, the tetrahedrite-tennantite minerals generally occur as small (<1 mm) anhedral grains intermixed with or in grains of galena, sphalerite, chalcopyrite, pyrite and other sulfosalts.

Members of the fahlerz mineral series, ranging from tetrahedrite, Cu$_{12}$Sb$_4$S$_{13}$, to tennantite, Cu$_{12}$As$_4$S$_{13}$, are complex derivatives based upon the sphalerite structure (Wuensch 1964, 1966, 1974). One-fourth of the metal atom sites are occupied by Group V metals (As, Sb and rarely Bi). The copper atoms in the pure end members are split equally in two types of sites, one of which is a four-coordinated nearly tetrahedral site, and the other a three-coordinated triangular site. The resulting structural formula is $\text{Cu}_6^{[4]}\text{Cu}_6^{[3]}\text{Sb}_4\text{S}_{13}$. Considerable substitution of Fe, Zn, Ag, and Hg has been reported in the fahlerz minerals and a general chemical formula (Cu,$\text{Ag})_{10}(\text{Fe},\text{Zn})_2(\text{As},\text{Sb})_4\text{S}_{13}$ has been widely used (Pauling and Neuman 1934, Springer 1969, Takeuchi 1971). Although the structural position of all metals is not well established, it is apparent that the base metals substitute for copper, that mercury is accommodated in the tetrahedral site and that the silver preferentially occupies the three-coordinated copper site (Kalbskopf 1972). The chemical formula demonstrates that in addition to copper-silver diadochy, a reciprocal relationship also exists between iron and zinc.

Minerals of the tetrahedrite series are minor but widespread and important ore minerals in the stratiform and stratabound massive sulfide deposits of the Mineral District, Louisa County, Virginia. They are especially significant in the Cofer Deposit where they display wide chemical variations and well-defined positive and negative correlations in terms of metal contents. These minerals are estimated to contain more than 90% of the silver present in the mineralized zone (Miller 1978) and are thus important economically as well as mineralogically.
General geology of the Cofer Deposit and the Mineral District

The Cofer Deposit lies within the Mineral District of Louisa County in the Central Virginia Piedmont (Fig. 1). The geology of the District is described in more detail by Miller, 1978, Cox 1979, and Craig, 1980, and is thus only briefly recounted here. The Mineral District contains two principal subparallel trends of mineralization that extend northeast from the town of Mineral. The eastern trend consists primarily of small deposits that were worked for native gold occurring in quartz veins. The western trend consists primarily of larger stratiform, strata-bound base metal deposits which contain disseminated to massive, pyritic ores with significant amounts of sphalerite, galena, and chalcopyrite and minor amounts of tetrahedrite, pyrrhotite, and sulfosalts. The total original ore mass in the District

Fig. 1. Generalized map of the Mineral District of Louisa County, Virginia showing the location of the Cofer Deposit. Stratiform massive sulfide deposits are designated by (py) and gold-bearing quartz vein occurrences are designated by (Au).
has been estimated at 10 million tons (Gair and Slack, 1980).

The exposed and near-surface portions of the sulfide bodies were mined for gossan iron ores in the 1700's and first half of the 19th century (Luttrell 1966). Supergene copper was extracted from 1847 until 1865 when attention turned to the massive pyrite for use in sulfuric acid manufacture. The Mineral District accounted for more than half of the nation's output of pyrite before 1900 (Watson 1907), but development of the Frasch process for sulfur extraction made pyrite mining uneconomic and resulted in closing of the mines in the 1920's. The Arminius was the largest mine in the District yielding more than two million tons; the Sulfur Mine yielded more than one million tons. The Cofer Deposit was discovered in the 1950's and was opened for exploration by a decline and two drifts in 1975; it is presently flooded and on stand-by status.

The deposits of the Mineral District lie within the early Cambrian Chopawamsic Formation which consists of quartz-sericite-biotite schist, sericite-pyrite quartzite, quartz-sericite phyllite, amphibolites, and meta-agglomerates.

The Cofer deposit, which lies between the two major mineralized trends, includes three major massive sulfide lenses which lie conformably within the enclosing schists and strike N60°E and dip 45° to the SE. The bodies range in thickness from a few centimeters to more than 15 meters. Little stratigraphic zoning of ore minerals is seen, but along strike a distinct change from massive pyrite-rich ore in the north to disseminated sphalerite-rich ore in the south is observed.

Regional metamorphism at amphibolite grade has resulted in extensive recrystallization of the ore and gangue minerals. Cox (1979) estimated a metamorphic maximum at 465±35°C and 4.6 kbar at the Arminius Mine which lies approximately 2.5 km to the southwest. The similarity of metamorphic features and minerals of the Cofer and Arminius deposit suggests a similar degree of metamorphism.

Ore mineralogy and the occurrence of tetrahedrite

The mineralized zones of the Cofer Deposit generally correspond with the ore types which have been described from numerous “kuroko” or volcanogenic deposits. Locally four different recognizable ore types are observed: (1) pyritic ore—massive pyrite with minor amounts of interstitial chalcopyrite, galena and gangue minerals; (2) yellow ore—subhedral to euhedral pyrite with signifi-cant amounts of interstitial chalcopyrite and minor amounts of sphalerite, sulfosalts, and the tetrahedrite-series minerals; (3) black ore—subequal amounts of dark sphalerite and pyrite with 5 to 10 volume percent galena, minor chalcopyrite, sulfosalts, and tetrahedrite-series minerals; (4) disseminated ore—dispersed pyrite with minor sphalerite, chalcopyrite, and galena in host silicates.

The ores of the Mineral District have been coarsely recrystallized during regional metamorphism to lower amphibolite facies (Hodder et al., 1977) but appear to have suffered little deformation. The pyrite is subhedral to euhedral where dispersed either in ore or gangue minerals. Where massive, the pyrite has recrystallized and exhibits 120° triple junctions characteristic of annealing. The ores retain primary banding and breccia textures locally (Miller 1978, Craig 1980).

The tetrahedrite series minerals occur in trace to minor amounts in all ore types at the Cofer deposit but is much more abundant in the black ore, a mode of occurrence similar to that in kuroko deposits (Matsukuma and Horikoshi 1970). Antimony-rich grains (Fig. 2) tend to be strongly correlated with

Fig. 2. Photomicrograph of a typical occurrence of tetrahedrite-series (ttg) minerals in the Cofer Deposit. The tetrahedrite is associated with sphalerite (dark), galena (light gray at left), and bournonite (light gray at right). Field of view is 0.45 mm.
galena but may occasionally be found with the graphic intergrowth discussed below. In contrast, arsenic-rich grains tend to occur with arsenopyrite and chalcopyrite and have been observed associated with the graphic intergrowth. The tetrahedrite series minerals occur as anhedral, commonly interstitial, grains with the other sulfides and are homogeneous within each individual grain. Any initial heterogeneity, analogous to that reported in tetrahedrites from kuroko deposits (Yui, 1971), which may have existed has apparently been homogenized by the metamorphism. There does not appear to be any well-defined lateral or stratigraphic zoning of the tetrahedrites in terms of composition.

**Table 1. Electron microprobe analyses of tetrahedrite-series minerals from the Cofer Deposit**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu</th>
<th>Fe</th>
<th>Zn</th>
<th>As</th>
<th>Sb</th>
<th>Bi</th>
<th>S</th>
<th>Total</th>
<th>Cu</th>
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<th>Fe</th>
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<th>Zn</th>
<th>As</th>
<th>Sb</th>
<th>Bi</th>
<th>S</th>
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<td>26.3</td>
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<td>40/449 C</td>
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<td>23.0</td>
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<td>73/1-1059 F</td>
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<td>16.6</td>
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**Table 2.** Tetrahedrite chemical variations and correlations

| Sample | Cu | Ag | Fe | Zn | As | Sb | Bl | S | Total | Cu | Ag | Fe | Zn | As | Sb | Bl | S | Total |
|--------|----|----|----|----|----|----|----|---|-------|----|----|----|----|----|----|----|---|-------|----|----|----|----|----|----|----|---|-------|
| 112/386.6 C | 19.3 | 29.5 | 4.9 | 0.9 | 0.2 | 26.3 | 0.1 | 20.3 | 97.7 |
| 747/536 C | 23.3 | 19.4 | 5.3 | 0.5 | 0.1 | 27.5 | 0.1 | 23.0 | 99.1 |
| 747/1008.6 C | 21.9 | 20.9 | 5.4 | 0.1 | 0.1 | 26.3 | 0.1 | 22.3 | 97.9 |
| 546/307 C | 29.5 | 12.2 | 5.1 | 2.4 | 0.2 | 27.5 | 0.1 | 21.6 | 98.6 |
| 40/449 C | 37.2 | 1.6 | 4.9 | 2.7 | 9.3 | 26.2 | 0.1 | 22.7 | 99.5 |
| 322/405 C | 36.8 | 1.3 | 3.1 | 3.0 | 2.2 | 28.5 | 0.1 | 24.2 | 99.0 |
| 112/386.5 C | 36.7 | 3.8 | 5.7 | 1.6 | 2.2 | 24.0 | 1.0 | 23.5 | 99.4 |
| 70/384 B | 21.1 | 14.4 | 4.9 | 2.0 | 0.2 | 26.8 | 0.1 | 23.0 | 99.9 |
| 73/1-1059 F | 25.7 | 16.6 | 5.3 | 2.0 | 0.2 | 25.5 | 0.1 | 22.5 | 97.7 |

The fahlerz minerals of the Cofer deposit exhibit wide compositional ranges in terms of copper, silver, arsenic, and antimony and minor variations in iron and zinc. The 32 samples (Table 1) span virtually the entire tetrahedrite-tennantite series in terms of Sb- and As-contents as shown in Figure 3 (bottom). Samples have been plotted in order of decreasing atomic percent antimony. It is apparent that, whereas the sum of antimony and arsenic is nearly constant, the arsenic content rises virtually monotonically as the antimony decreases, thus demonstrating the diadochy of the two elements. This is consistent with the observations of some other workers (e.g., Shikazona and Kouda, 1979). The sum of antimony, arsenic, and bismuth (Table 1) ranges from 13.1 to 15.2 atomic percent and averages 14.2 percent which is close to the 13.8 percent predicted for stoichiometric Cu12(As,Sb,Bi)S3. With few exceptions, bismuth, which might substitute for arsenic and antimony, rarely rises about 0.1 atomic percent.

Copper is nearly always the principal cation...
Hence, along any vertical line, the compositional data for antimony, arsenic, copper and silver in any one sample are plotted. The sum of copper plus silver (Table 1) ranges from 33.4 to 35.6 atomic percent with an average of 35.0 atomic percent which corresponds very closely with that expected (34.5%) for the \( (Cu,Ag)_{10}(Fe,Zn)_{2}(As,Sb)_{5}S_{13} \) formula proposed by Pauling and Newman (1934) and Springer (1969).

Although no monotonic correlation exists between silver and antimony, there is a clear relationship between these two elements in the samples from the Cofer Deposit. Figure 5 illustrates this relationship with a plot of silver versus antimony contents. In the Cofer Deposit tetrahedrites, the silver contents never exceed 1 atomic percent unless the antimony contents exceed 10 atomic percent. However, when antimony contents exceed 10 atomic percent, and especially when they exceed 13 atomic percent, silver contents rise to as much as 18.6 atomic percent (=29.5 weight percent). This chemical substitution is similar to, but more pronounced than, that found in the analyses of other workers. The data from several other published studies are also plotted in Figure 5 to illustrate the similarity of behavior. Only the data from Chen and Petruk (1980) from the Heath Steele Mines shows a more pronounced rise of silver contents with antimony contents than do the Cofer Deposit samples. The observed trend of increasing silver with increasing antimony content demonstrates that the correlation is not a "necessary" one but rather a within the tetrahedrite series but does show a well-defined reciprocal variation with silver in the samples analyzed in this study. The relationship of these two elements is clearly illustrated in Figure 4 in which samples have been arranged in order of decreasing copper content. As copper decreases (from 35.8 to 16.3 atomic percent), the silver content rises (from 0.01 to 18.6 atomic percent) such that it ultimately substitutes for slightly more than one-half of the possible copper. Shikazono and Kouda (1979) indicate in a figure that a similar trend exists in tetrahedrites from Japanese deposits. Neither copper nor silver contents of tetrahedrites in the Cofer Deposit correlate in the same simple manner with antimony and arsenic. This is demonstrated in Figure 3 (top) in which the silver and copper contents are plotted in the same order as the antimony and arsenic data in Figure 3 (bottom).

Fig. 3. (Bottom) Plot of antimony and arsenic variations within Cofer Deposit tetrahedrite-series minerals arranged in order of decreasing antimony content. The sum of antimony and arsenic are nearly constant as shown by the heavy line (very small amounts of bismuth may also be present—see Table 1). (Top) Plot of copper and silver also arranged in order of decreasing antimony content; thus the values of As, Sb, Cu and Ag along any vertical line are for the same sample. The sum of copper and silver is given by the heavy line.

Fig. 4. Plot of copper and silver variations within Cofer Deposit tetrahedrite-series minerals arranged in order of decreasing copper content. The nearly constant sum of the copper and silver is shown at the top of the diagram by the heavy curve.
ideal Cu$_{12}$Sb$_3$S$_{13}$ stoichiometry. However, the average composition (Table 1) does lie within the experimentally determined tetrahedrite fields at 300$^\circ$C (Tatsuka and Morimoto 1973) and 400$^\circ$C (Skinner et al. 1972) and within the room temperature tetrahedrite solid solution as defined by the former workers. The observed average composition is approximately 0.4 atomic percent more (Sb$+$As$+$Bi)-rich than the determined limits of the tennantite solid solution as experimentally defined in the range of 300–500$^\circ$C by Maske and Skinner (1971).

The tetrahedrite-series minerals also occur within the yellow ores of the Cofer Deposit in or associated with a “graphic intergrowth” of arsenopyrite $\pm$ gudmundite, sphalerite and chalcopyrite (Fig. 6). Small amounts of native bismuth, kobellite, galena and pyrrhotite may also be present. This “graphic intergrowth” appears to be a product of the decomposition of a tetrahedrite-series mineral because it appears in all stages of development from merely occupying small central cores of tetrahedrite-series grains to areas in which it occupies nearly all of the original grain with only small remnants of tetrahedrite remaining around the edges. The bulk composition obtained by point counting four intergrowths is (Cu,Ag)$_{3.4}$Fe$_{6.7}$Zn$_{0.5}$Pb$_{0.05}$ (As,Sb,Bi)$_{4.9}$S$_{10.1}$ which approximates a copper and sulfur-deficient and iron- and zinc-rich tetrahedrite. The predominance of arsenopyrite over gudmundite indicates that the progenitor was arsenic-rich. Any remaining tetrahedrite-series phase with the graphic intergrowth is always antimony-rich and may also be silver-rich.

The intergrowth appears to represent the product of desulfidation of a copper-poor tetrahedrite-series phase. This type of desulfidation reaction is compatible with the known fields of stability of the minerals in terms of log $a_{SS} - 1/T$ space above 300$^\circ$C (Barton and Skinner, 1980). It is not clear, however, when the intergrowth formed relative to the metamorphism of the ores. Such intergrowths have not, to the authors’ knowledge, been described from the unmetamorphosed volcanogenic ores of Japan. The only description of a similar occurrence is that of Juvê (1974) who observed the same mineral association in the metamorphosed volcanogenic ores of the Stekenjokk Deposit. He also interpreted the origin of the texture to be the result of breakdown of a tetrahedrite-series mineral.

Acknowledgments

The authors are grateful to the Callahan Mining Corporation for permission to publish the data derived from their deposit.
Fig. 6. Photomicrographs illustrating the progressive development of the "graphic intergrowth" from incipient development in the interior of a grain (a) to total breakdown of the tetrahedrite series phase (d). All photomicrographs have a field-of-view of 0.45 mm.

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