LETTER

Crystal structure of argentopyrite, AgFe$_2$S$_3$, and its relationship with cubanite

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ABSTRACT

The structure of argentopyrite, AgFe$_2$S$_3$, was determined for the first time with single-crystal X-ray diffraction. In contrast to the previously reported orthorhombic symmetry, our data show that argentopyrite is monoclinic with space group $P112_1/n$ (non-standard setting) and unit-cell parameters $a = 6.6902(2)$, $b = 11.4497(4)$, $c = 6.4525(2)$ Å, $\beta = 90.2420(8)^\circ$, and $V = 494.26(3)$ Å$^3$. Similar to cubanite (CuFe$_2$S$_3$), the structure of argentopyrite is also based on approximately hexagonal close-packed S atoms, with cations ordered over one half of the tetrahedral sites, forming corner-shared AgS$_4$ and FeS$_4$ tetrahedral sheets parallel to (001). The two structures differ chiefly in the linkage between the two adjacent tetrahedral sheets and the ordering patterns of cations within a tetrahedral sheet. Topologically, the structure of argentopyrite can be obtained by a displacement of a tetrahedral sheet in the cubanite structure along the ($a/2 + b/6$) direction relative to the sheet beneath, giving rise to a cluster of four edge-shared FeS$_4$ tetrahedra in argentopyrite, as compared to two in cubanite. There are two distinct Fe sites (Fe1 and Fe2) in argentopyrite, rather than only one, as in other MFe$_2$S$_3$ sulfide minerals (M = monovalent cations). Together with published Mössbauer data, we suggest that there exists some degree of Fe$^{3+}$-$Fe^{2+}$ order-disorder in argentopyrite, with Fe$^{3+}$ favoring the more distorted Fe2 tetrahedral site. Argentopyrite appears to possess all the features proposed by Putnis (1977) for a high-temperature ordered form of cubanite.

Keywords: Argentopyrite, AgFe$_2$S$_3$, Ag-Fe sulfides, cubanite-related mineral, sternbergite, crystal structure, single-crystal X-ray diffraction

INTRODUCTION

Ternary sulfides with a general chemical formula MFe$_2$S$_3$, where M represents a monovalent cation, such as Cu$^+$, Ag$^+$, K$^+$, Cs$^+$, Rb$^+$, or Tl$^+$, are characterized by Fe with a nominal valency of +2.5, due to rapid electron exchange between Fe$^{3+}$ and Fe$^{2+}$ ions (Greenwood and Whitfield 1968; Vaughan and Burns 1972; Amthauer and Bente 1983; Wintenberger et al. 1990; McCammon 1994; Reissner et al. 2004; Pareek et al. 2008). These materials exhibit numerous interesting electronic-magnetic properties (Sleight and Gillson 1973; Wintenberger et al. 1990; Reissner et al. 2006), as well as polymorphism at different temperatures or pressures (e.g., Putnis 1977; Miyamoto et al. 1980; McCammon 1994, 1995; Rozenberg et al. 1997; Pruseth et al. 1999). Moreover, different building blocks formed by FeS$_4$ tetrahedra in the MFe$_2$S$_3$ compounds are also found in several enzymes, ferredoxins, and other Fe-S bearing proteins, in which the valence-delocalized [Fe$^{3+}$-Fe$^{2+}$] clusters constitute active sites that are responsible for basic electron transfer reactions in many key biochemical pathways (e.g., Holm et al. 1996; Beinert et al. 1997). Geologically, although the MFe$_2$S$_3$ minerals, such as cubanite CuFe$_2$S$_3$, argentopyrite or sternbergite (a dimorph of AgFe$_2$S$_3$), rasvumite KFe$_2$S$_3$, pautovite CsFe$_2$S$_3$, and picotpaulite TlFe$_2$S$_3$, are relatively rare when compared to many binary sulfides, they reflect more extreme conditions of ore formation, and thus, may bear important information on geologic occurrence and significance of the various minerals and assemblages involved (Taylor 1970; Osadchii and Chareev 2006).

The crystal structures of all MFe$_2$S$_3$ minerals, except argentopyrite, have been previously determined, including cubanite (Buerger 1945, 1947; Azaroff and Buerger 1955; Fleet 1970; Wintenberger et al. 1974; Szymanski 1974; McCammon et al. 1992), sternbergite (Perlitz 1987), rasvumite (Clark and Brown 1980; Mitchell et al. 2004), pautovite (Mitchell et al. 2004), and picotpaulite (Balić-Zućić et al. 2008). A common structural feature of these minerals is that they all contain only one symmetrically nonequivalent tetrahedral Fe site. Their major differences are manifested in the coordination of M cations and the linkage of FeS$_4$ tetrahedra. In cubanite, each Cu is bonded to four S atoms and each FeS$_4$ tetrahedron shares one edge with another FeS$_4$ tetrahedron, forming a cluster of paired FeS$_4$ tetrahedra. In sternbergite, Ag is also coordinated by four S atoms, but each FeS$_4$ tetrahedron shares two edges with other FeS$_4$ tetrahedra, forming a single tetrahedral chain. In the isostructural minerals, rasvumite, pautovite, and picotpaulite, the large M cations are bonded to 10 S atoms and each FeS$_4$ tetrahedron shares three edges with other FeS$_4$ tetrahedra to form a double tetrahedral chain. Argentopyrite and sternbergite are the two best-documented ternary sulfides in the Ag-Fe-S system. Relative to sternbergite, argentopyrite is the stable form at lower temperatures (<150 °C) (Czamanske 1969; Taylor 1970) and is more common in nature. However, despite the long history since its first description (von
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Waltershausen (1866), the presence of severe twinning in all examined crystals has prevented the structural determination for this mineral. Argentopyrite from the type locality Joachimsthal, Bohemia, Czech Republic, was originally described as monoclinic (von Waltershausen 1866). However, Murdoch and Berry (1954) studied argentopyrite from both Freiberg (Saxony, Germany) and Joachimsthal, and concluded that the mineral is orthorhombic with \( a = 6.64, b = 11.47, c = 6.45 \text{ Å}, \) and space group \( Pnnm. \) They further reported that all minerals examined are markedly pseudohexagonal due to a combination of interpenetrating and lamellar twinning. The chemistry of argentopyrite from Andreasberg (Harz, Germany) was determined by Czamanske (1969) and its Mössbauer spectra by Vaughan and Burns (1972). Šrein et al. (1986) studied mineralogical features of argentopyrite and strombergite from a polyvalent vein in a skarn deposit (Czech Republic). Since then, no detailed crystallographic study on argentopyrite has been reported. In this paper, we present the first structure solution of argentopyrite based on single-crystal X-ray diffraction data and depict its structural relationships with cubanite and other MFe\(_3\)S\(_2\) minerals.

**EXPERIMENTAL METHODS**

Two argentopyrite samples were used in this study: one from Schaft 209, Aue, Niederschlema, Erzgebirge, Saxony, Germany, and the other from the original type sample (Joachimsthal, Bohemia, Czech Republic) (von Waltershausen 1866). Both samples are in the collection of the RRUFF project (deposition no. R090026 and R090027, respectively; http://rruff.info/). Argentopyrite crystals from the two samples appear as simple pseudohexagonal prisms and are bright dark-gray when a fresh surface is exposed, with metallic luster. Their chemical compositions were determined with a JEOL JXA-8900/R electron microprobe at the Geophysical Mineralogist Contents, find the table of contents for the specific MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

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However, with additional examinations of the argentopyrite crystals from R090026, we successfully found an untwined single crystal with a size of 0.06 × 0.06 × 0.07 mm. A set of X-ray diffraction data were then collected from this crystal. All reflections were indexed on the basis of a monoclinic unit cell (Table 1). The systematic absences of reflections confirm the unique space group \( P112_1/n, \) rather than orthorhombic with space group \( Pmmn. \) (Murdoch and Berry 1954). The adaptation of the non-standard setting provides consistency with the published unit-cell data and facilitates direct comparison with other MFe\(_3\)S\(_2\) minerals. The structure was solved and refined using SHELX97 (Sheldrick 2008), which yielded the \( R \) factors of 0.045 and 0.072 for the R090026 and R090027 samples, respectively.

**RESULTS AND DISCUSSION**

The structure of argentopyrite contains six symmetrically distinct atomic sites: one occupied by Ag, two by Fe (Fe1 and Fe2), and three by S (S1, S2, and S3) (Table 2), and it is analogous to that of cubanite in many aspects. For example, both structures are based on approximately hexagonal close-packed S atoms, with cations ordered over one half of the tetrahedral sites. Topologically, the two structures are composed of the same type of corner-shared tetrahedral sheets parallel to (001) (Fig. 1). One of the key differences between the two structures.
is the linkage (or relative position) between the two adjacent tetrahedral sheets. Without regard to the chemical contents in the tetrahedra, the structure of argentopyrite can be generated by a displacement of a tetrahedral sheet in the cubanite structure along the \((a/2 + b/6)\) direction relative to the tetrahedral sheet beneath. Another noticeable dissimilarity between the two structures is the ordering patterns of M and Fe cations within a tetrahedral sheet. As illustrated in Figure 1, the MS\(_1\) tetrahedron in cubanite is situated at the apical position of a three-member ring, whereas that in argentopyrite is at one of the basal positions. As a consequence, there is a cluster of four edge-shared Fe\(_2\)S\(_4\) tetrahedra in argentopyrite, but only two in cubanite (Fig. 2). For comparison, the edge-shared linkage of Fe\(_2\)S\(_4\) tetrahedra in sternbergite and rasvumite are also illustrated in Figure 2.

In argentopyrite there are two nonequivalent Fe sites, rather than only one, as in other MFe\(_2\)S\(_3\) minerals. Although the average Fe-S bond distances for the two Fe\(_2\)S\(_4\) tetrahedra are similar, the Fe\(_2\)S\(_4\) tetrahedron appears to be slightly more distorted than the Fe\(_1\)S\(_4\) tetrahedron in terms of the tetrahedral angle variance (TAV) and quadratic elongation (TQE) (Robinson et al. 1971) (Table 3). Intriguingly, Vaughan and Burns (1972) measured Mössbauer spectra of several sulfides containing four-coordinated Fe atoms, including cubanite, sternbergite, and argentopyrite. They noted that, while the Mössbauer spectra of both cubanite and sternbergite consist of only one single hyperfine set of six-lines, as have also been observed by others (Greenwood and Whitfield 1968; Wintenberger et al. 1974, 1990; McCammon 1994, 1995; Rozenberg et al. 1997; Pareek et al. 2008), the spectrum of argentopyrite is clearly characterized by two overlapping six-line sub-spectra, \(A\) and \(B\), of equal intensity, suggesting that Fe in argentopyrite may occur in two distinct tetrahedral positions. This observation is evidently supported by our structural data. The room-temperature isomer-shift parameters of this HTO phase are similar to those of cubanite, although the unit-cell parameters of this HTO phase are also illustrated in Figure 2. As a result, not only is the Fe\(_2\)S\(_4\) tetrahedron more distorted than the Fe\(_1\)S\(_4\) tetrahedron, but it is also more energetically favored by Fe\(^{2+}\) so as to minimize the cation-repulsion between the two edge-shared Fe\(_2\)S\(_4\) tetrahedra and within the cluster. Additionally, the Jahn-Teller effect may play a role in enhancing the order of Fe\(^{2+}\) in the Fe\(_2\) site as well because high-spin Fe\(^{2+}\) can gain extra stabilization energy in a more distorted tetrahedral environment (Vrajmasu et al. 2004 and references therein). The relatively longer distance between Fe\(_2\)-Fe\(_2\) \(2.8013(7)\) Å vs. Fe\(_2\)-Fe\(_1\) \(2.7502\) Å) is also a good indication of the enrichment of Fe\(^{2+}\) in the Fe\(_2\) site (see review by Makovicky 2006).

Cubanite is known to transform irreversibly to a disordered cubic polymorph, isocubanite, at \(-210^\circ\)C (Pruseth et al. 1999 and references therein). Annealing of the cubic phase below \(210^\circ\)C results in exsolution of chalcopyrite from the isocubanite matrix (Cabri et al. 1973; Dutrizac 1976). However, using in-situ high-temperature transmission electron microscopy, Putnis (1977) found that cubanite actually starts to undergo the cation-disordering process at \(-200^\circ\)C, giving rise to a hexagonal wurtzite-type structure. Annealing of the hexagonal phase below \(200^\circ\)C yields a high-temperature ordered (HTO) phase that Putnis (1977) claimed was probably orthorhombic. Although the unit-cell parameters of this HTO phase are similar to those of cubanite, we find that its symmetry is definitely different from that \((Pcmm)\) for cubanite because the electron diffraction patterns given by Putnis (1977) show the presence of \((h00)\) and \((00l)\) reflections with \(h + l \neq 2n\), which are prohibited in space group \(Pcmm\). By assuming that the transformation from the disordered hexagonal to the HTO phase results from cation ordering within the hexagonal close-packed sulfur structure, Putnis (1977) proposed a

**Figure 1.** Comparison of crystal structures of (a) cubanite and (b) argentopyrite. The green and yellow tetrahedra represents MS\(_1\) and FeS\(_3\) groups (M = Cu for cubanite and Ag for argentopyrite), respectively. A three-member ring of tetrahedra in each structure is outlined with a circle, showing the positional difference of the MS\(_1\) tetrahedra.

**Figure 2.** Comparison of the linkage among the FeS\(_4\) tetrahedra in (a) cubanite, (b) argentopyrite, (c) sternbergite, and (d) rasvumite.
possible cation ordering scheme for the HTO phase that is better viewed in terms of the distribution of sulfur atoms coordinated by metal cations. Green, gray, and small yellow spheres represent M (Cu in cubanite or Ag in argentopyrite), Fe, and S atoms, respectively.

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