Crystallographic and chemical constraints on the nature of the proustite–pyrargyrite solid-solution series

LUCA BINDI,1,2,* GIOVANNI PRATESI,1,3 AND PAUL G. SPRY4

1Museo di Storia Naturale, Sezione di Mineralogia, Università di Firenze, Via La Pira 4, I-50121 Firenze, Italy
2C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Firenze, Via La Pira 4, I-50121 Firenze, Italy
3Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, I-50121 Firenze, Italy
4Department of Geological and Atmospheric Sciences, Iowa State University, 253 Science I, Ames, Iowa 50011-3212, U.S.A.

ABSTRACT

The present paper reports a crystal-chemical study of minerals belonging to the proustite–pyrargyrite group by evaluating 32 natural samples of proustite and 27 samples of pyrargyrite from different localities that have variable chemical compositions. The unit-cell parameters were modeled as a function of the Sb contents. The $a$ parameter is strongly influenced by the As ↔ Sb substitution, whereas the influence on the $c$ parameter is very minor (nearly constant trend). The following equations were obtained from the linear fitting of the data:

$$a_{\text{pred}} = 10.8433(3) + 0.2019(4)\text{Sb (apfu)}$$
$$c_{\text{pred}} = 8.7189(6) + 0.0059(9)\text{Sb (apfu)}$$
$$V_{\text{pred}} = 887.77(7) + 34.0(1)\text{Sb (apfu)}.$$

The crystal structure of the members of the proustite–pyrargyrite solid solution consists of two sets of spiral chains parallel to the $c$-axis. Each chain contains alternating Ag and S atoms, with each chain being connected by As and Sb atoms, which are the apices of flat pyramidal $\text{AsS}_3/\text{SbS}_3$ groups. Each S atom is part of a different Ag-S chain.

The compositional data support the concept that proustite–pyrargyrite solid solutions re-equilibrate and exsolve to near end-member upon cooling. Examples of intermediate compositions are rare in nature and must have quenched above the solvus.

Keywords: Sulfosalts, electron microprobe, proustite, pyrargyrite

INTRODUCTION

Silver sulfosalts are an important source of silver and occur in a variety of hydrothermal ore deposits, particularly fissure vein polymetallic base-metal sulfide deposits (e.g., Loucks and Petersen 1988; Chutas and Sack 2004). These silver sulfosalts include, but are not restricted to, the pearceite–polybasite $[(\text{Ag}, \text{CuS}_4)\langle\text{As}, \text{Sb}\rangle_2\text{S}_7]-[(\text{Ag}, \text{CuS}_4)\langle\text{As}, \text{Sb}\rangle_2\text{S}_7]$, tennantite–tetrahedrite $[(\text{Cu}, \text{Ag})_6\langle\text{Fe}, \text{Zn}\rangle_2\langle\text{As}, \text{Sb}\rangle_2\text{S}_7]-[(\text{Cu}, \text{Ag})_6\langle\text{Fe}, \text{Zn}\rangle_2\langle\text{As}, \text{Sb}\rangle_2\text{S}_7]$, and proustite–pyrargyrite $[(\text{Ag}, \text{AsS}_3)-\langle\text{Ag}, \text{SbS}_3\rangle]$ solid-solution series.

Proustite and pyrargyrite were officially recognized as new mineral species by Beudant (1832) and Glocker (1831), respectively, although Proust reported proustite as early as 1804. Crystallographic studies of Harker (1936), Hocart (1937), and Engel and Nowacki (1966) show that proustite and pyrargyrite are trigonal and belong to space group $R3c$. It should be noted that xanthoconite and pyrostilpnite, the rare low-temperature polymorphs of proustite and pyrargyrite, respectively, are both monoclinic (e.g., Beland 1948; Weil and Hocart 1953; Hall 1966; Lange et al. 1993).

Although there is little doubt that there is a complete solid solution at high temperatures (e.g., Toulmin 1963), the amount of solid solution between proustite and pyrargyrite at low temperatures has been debated (Ghosal and Sack 1995 and references therein) and it is still a matter of contention. Indeed, it is based largely on interpretations derived from experimental studies and compositions of samples in natural geological settings. For example, Miers (1888) noted up to 2.6 wt% As in natural samples of pyrargyrite and up to 3.7 wt% Sb in proustite from the same deposit, whereas experimental studies of Jaeger and van Klooster (1912) for melting relations in the system $\text{Ag}_3\text{AsS}_3-\text{Ag}_3\text{SbS}_3$ suggested that there was a complete solid-solution series. Here we discuss the crystallographic and chemical constraints on the nature of the proustite–pyrargyrite solid-solution series by evaluating 32 natural samples of proustite and 27 samples of pyrargyrite.

PROUSTITE–PYRARGYRITE SERIES: THE STATE OF THE ART

Toulmin (1963) synthesized and annealed end-members and 11 intermediate compositions along the proustite–pyrargyrite solid-solution series at 450 °C. The results of his experiments lead Toulmin to concur with Jaeger and van Klooster (1912) that...