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SILVER SULFOSALTS OF THE SANTO NIÑO VEIN, FRESNILLO DISTRICT, ZACATECAS, MEXICO

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ABSTRACT

The Santo Niño vein in the Fresnillo Ag-Pb-Zn district, Mexico, contains silver in acanthite and in the sulfosalts pyrargyrite, proustite, polybasite, selenian polybasite, tetrahedrite and stephanite, members of three silver-bearing sulfosalt solid-solution series. The sulfosalts, excepting proustite, are Sb-rich end members of their respective solid-solution series. The mineral assemblage evolved from (Cu-Ag)-bearing to Ag-bearing: a) tetrahedrite, polybasite and pyrargyrite; b) polybasite, pyrargyrite and stephanite; c) pyrargyrite and acanthite; and d) acanthite. The average sulfosalt formulas are: pyrargyrite $Ag_{3.02}(Sb_{1.00}As_{0.03})S_3$; proustite $Ag_{3.08}(Sb_{0.03}As_{0.95})S_3$; polybasite $(Ag_{15.40}Cu_{1.15})(Sb_{1.88}As_{0.19})S_{11}$; selenian polybasite $(Ag_{14.50}Cu_{1.15})(Sb_{1.92}As_{0.12})(Se_{1.85}S_{9.15})$; tetrahedrite $(Cu_{5.92}Ag_{4.21})(Fe_{1.43}Zn_{0.73})(Sb_{3.91}As_{0.11})S_{13}$; and stephanite $(Ag_{4.81}Cu_{0.13})(Sb_{1.05}As_{0.06})S_4$. Compositional tie-lines and relative semi-metal [Sb/(Sb + As)] values for coexisting pairs of pyrargyrite-polybasite, pyrargyrite–tetrahedrite, and polybasite–tetrahedrite, and for triplets of pyrargyrite–polybasite–tetrahedrite show systematic trends (pyrargyrite > tetrahedrite > polybasite) and appear to be temperature-dependent [higher temperature, lower Sb/(Sb + As) values]. Sulfosalt (Sb–As) and (Ag–Cu) patterns indicate that element substitution, not fractional crystallization, determines the semi-metal and metal variations in the silver-bearing sulfosalts of the Santo Niño vein. Pyrargyrite shows only (Sb–As) substitution, tetrahedrite shows coupled (Sb–As) and (Ag–Cu) substitution, whereas polybasite shows noncoupled (Sb–As) and (Ag–Cu) substitution. The distribution of Sb/(Sb + As) values in polybasite and of Ag/(Ag + Cu) values in tetrahedrite indicates that the ore-bearing solutions flowed from a deeper, southwestern part of the district to shallower levels in the northeast.

Keywords: sulfosalts, pyrargyrite, polybasite, tetrahedrite, stephanite, compositional tie-lines, geothermometry, paragenesis, epithermal vein, Fresnillo District, Mexico.

SOMMAIRE

Le filon de Santo Niño, dans le district minéralisé en Ag-Pb-Zn de Fresnillo, au Mexique, contient de l'argent dans l'acanthite et les sulfosels pyrargyrite, proustite, polybasite, polybasite sélénifère, tétraédrite et stéphanite, membres de trois solutions solides riches en Ag. A l'exception de la proustite, les sulfosels sont les pôles Sb de leurs séries respectives. Les assemblages ont évolués d'une composition Cu–Ag à simplement argentifère: a) tétraédrite, polybasite et pyrargyrite; b) polybasite, pyrargyrite et stéphanite; c) pyrargyrite et acanthite, et d) acanthite. Les formules moyennes sont: pyrargyrite $Ag_{3.02}(Sb_{1.00}As_{0.03})S_3$; proustite $Ag_{3.08}(Sb_{0.03}As_{0.95})S_3$; polybasite $(Ag_{15.40}Cu_{1.15})(Sb_{1.88}As_{0.19})S_{11}$; polybasite sélénifère $(Ag_{14.50}Cu_{1.15})(Sb_{1.92}As_{0.12})(Se_{1.85}S_{9.15})$; tétraédrite $(Cu_{5.92}Ag_{4.21})(Fe_{1.43}Zn_{0.73})(Sb_{3.91}As_{0.11})S_{13}$; et stéphanite $(Ag_{4.81}Cu_{0.13})(Sb_{1.05}As_{0.06})S_4$. La composition et la valeur Sb/(Sb + As) des couples pyrargyrite–polybasite, pyrargyrite-tétraédrite, polybasite–tétraédrite, et des triplets pyrargyrite–polybasite–tétraédrite, varient systématiquement (pyrargyrite > tétraédrite > polybasite) et semblent liées à la température [plus elle est élevée, plus le rapport Sb/(Sb + As) est faible]. Les relations Sb–As et Ag–Cu dans les sulfosels montrent que les exigeances des mécanismes de substitution et non la cristallisation fractionnée déterminent les variations en teneurs des métaux et semi-métaux dans les sulfosels argentifères du filon de Santo Niño. La pyrargyrite montre seulement une substitution (Sb–As), la tétraédrite, une substitution couplée (Sb–As et Ag–Cu), et la polybasite, une substitution non-couplée de Sb–As et de Ag–Cu. La distribution des valeurs de Sb/(Sb + As) dans la polybasite et de Ag/(Ag + Cu) dans la tétraédrite fait penser que les fluides responsables de la minéralisation se sont écoulés à partir d'une source profonde dans le sud-ouest vers des zones moins profondes du système dans le nord-est.

(Traduit par la Rédaction)

Mots-clés: sulfosels, pyrargyrite, polybasite, tétraédrite, stéphanite, compositions coexistantes, géothermométrie, paragenèse, filon épithermal, district de Fresnillo, Mexique.

INTRODUCTION

The Fresnillo District, located 750 km northwest of Mexico City, is a world-class silver–lead–zinc deposit that includes epithermal veins, replacement bodies in the form of mantos and chimneys, and an oxidized stockwork. The district is located in the northern part of a north-northwest-trending belt of silver–lead–zinc deposits that extends for more than 800 km and includes the mining districts of Taxco, Pachuca, Guanajuato, Zacatecas, and Sombrerete (Fig. 1). Since the mid-sixteenth century, the Fresnillo District has produced more than 10,000 t of silver, 19 t of gold, and 700,000 t each of lead and zinc (Ruvalcaba-Ruiz & Thompson 1988). Silver was discovered in the Fresnillo District in 1553, and mining

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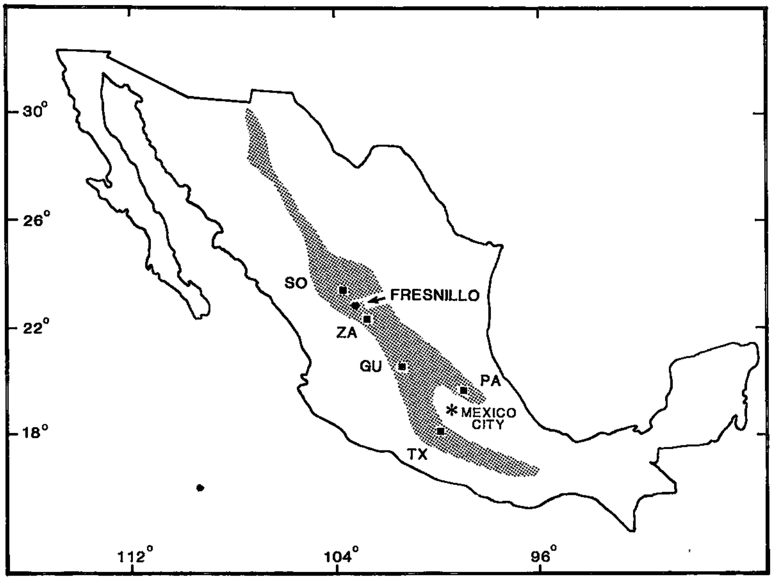

FIG. 1. Geographic location of the Fresnillo District in Mexico. Stippled area outlines belt of silver-lead-zinc deposits in central Mexico (after Damon *et al.* 1981). Abbreviations for mining districts: TX Taxco, PA Pachuca, GU Guanajuato, ZA Zacatecas, SO Sombrerete.

of the silver oxides in a near-surface stockwork began in 1554 (Church 1907, Baker 1923). Mining and milling of the sulfide ores were initiated in 1926 (Byler 1930). Reviews of the mineral deposits in the Fresnillo District are given by MacDonald *et al.* (1986), Zantop *et al.* (1986), Ruvalcaba-Ruiz & Thompson (1988), and García *et al.* (1989).

The Santo Niño vein, discovered by drilling in 1975, is located approximately 2 km southeast of the previously known veins in the district and at present is the major producer at Fresnillo. Among the several previous geological investigations and reports on the Santo Niño vein, Chico (1980) discussed the exploration strategies and discovery, Ruvalcaba-Ruiz (1980, 1983) described the geology, alteration and fluid-inclusion geochemistry of the upper levels, and Gemmell *et al.* (1985, 1988), Gemmell (1986), and Simmons (1986) described the vein geology. Simmons (1986), Simmons & Sawkins (1986), and Simmons *et al.* (1988) discussed the physicochemical conditions of the mineralizing solutions on the basis of fluid-inclusion and isotopic evidence.

One of the unusual aspects of the Santo Niño vein is the occurrence of three separate silver-bearing sulfosalt solid-solution series. In this study we sought to determine: (a) the identity and paragenesis of the sulfosalts, (b) the compositions and nature of the solid solutions in each sulfosalt series, and (c) their spatial variations throughout the vein. The scientific and practical significance of these investigations is illustrated by Birnie & Petersen (1977), Wu & Birnie (1977), Wu & Petersen (1977), and Hackbarth & Petersen (1984). Sixty-six locations throughout the vertical and lateral extent of the vein and core from drill holes between the main levels were selected for detailed mineralogical and geochemical studies. Preliminary data concerning the sulfosalt mineralogy and geochemistry were reported by Gemmell (1986) and Gemmell *et al.* (1986, 1988).

REGIONAL GEOLOGY

Tertiary felsic volcanic rocks overlie deformed Mesozoic marine sediments and submarine mafic volcanic rocks in the Fresnillo District. Arenas (1860), Stone (1941), Stone & McCarthy (1948), DeCserna (1976), Gemmell *et al.* (1988) and García *et al.* (1989) described the geology and stratigraphy of the district. The stratigraphic sequence and distribution of rock units in the Fresnillo District (Fig. 2) consist of Lower Cretaceous greywackes and shales (Proaño Group), overlain conformably by basaltic pillow lavas, breccias and intercalated sediments (Chilitos Formation), which in turn are unconformably overlain by a Tertiary continental conglomerate and arkosic sediments (Fresnillo Formation), rhyolite tuffs and pyroclastic flows, and isolated flows of olivine basalt. The total package of sedimentary and volcanic rocks has an aggregate thickness of greater than 2700 m. An Oligocene

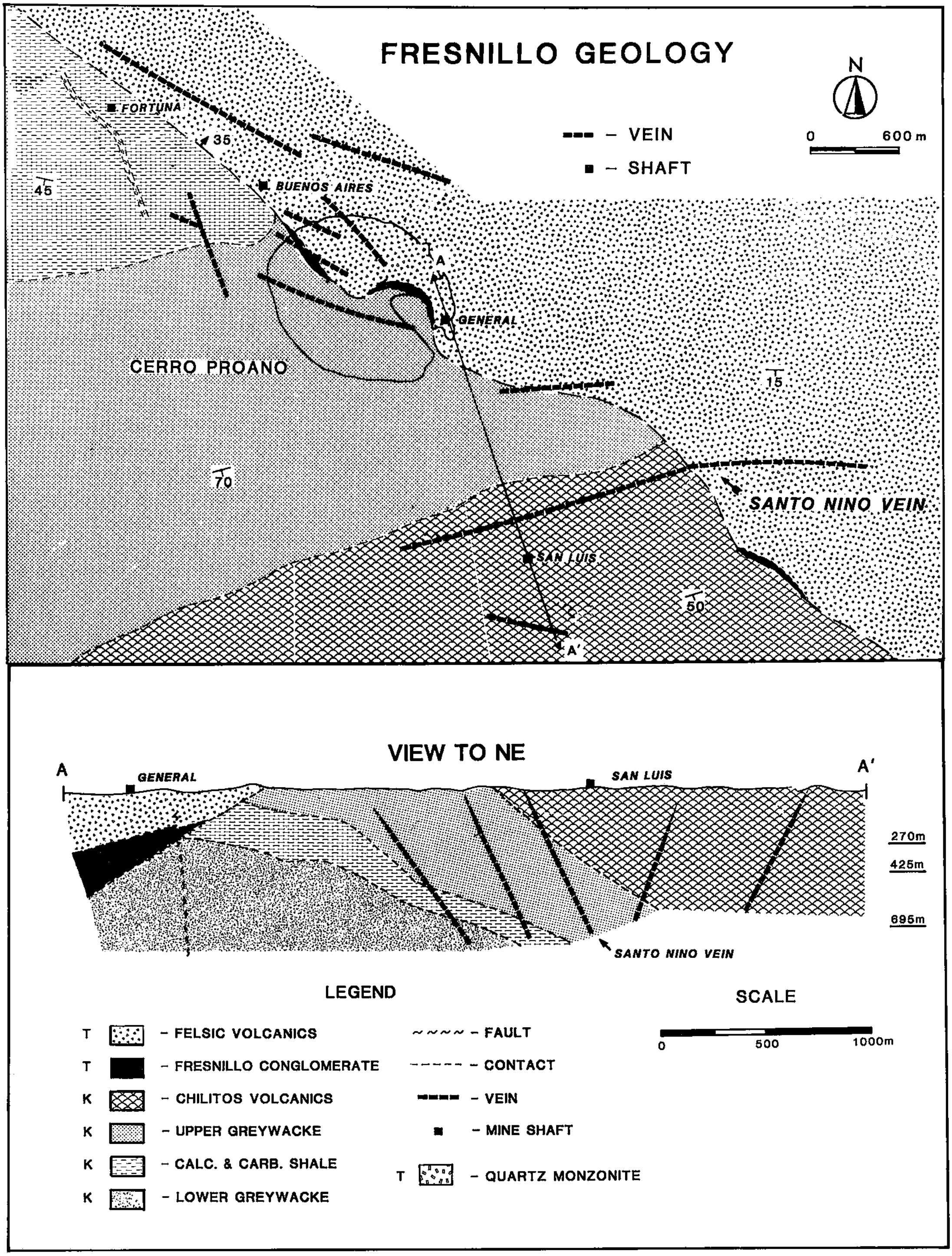

FIG. 2. Simplified geological map and cross section of the Fresnillo District showing location of the Santo Niño vein in relation to other major epithermal veins within the district. Symbols: T Tertiary, K Cretaceous.

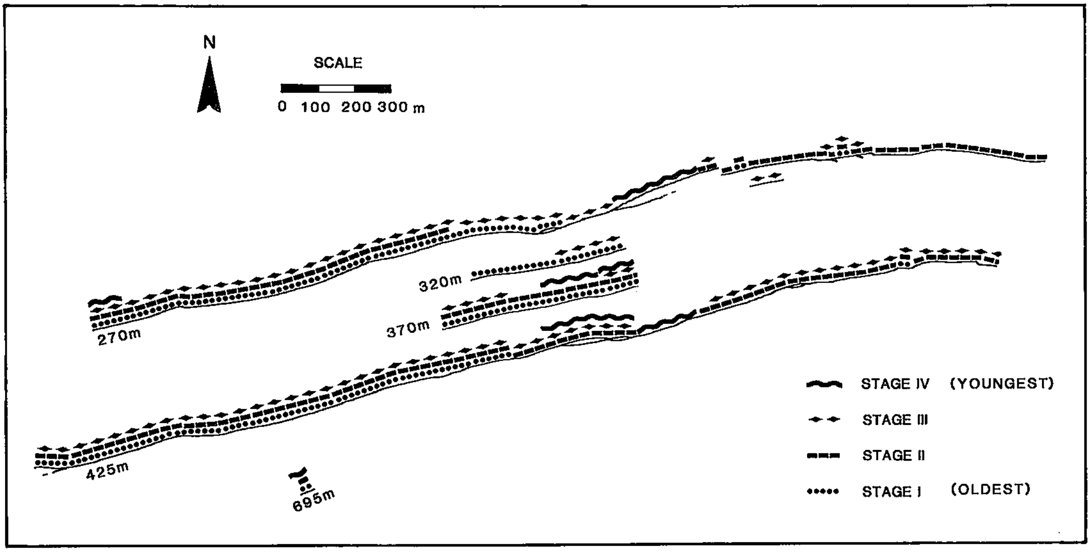

FIG. 3. Distribution of depositional stages in a plan view of the Santo Niño vein. Each symbol represents the distribution of that particular stage throughout the vein. Geological characteristics of each stage are discussed in the text.

quartz monzonite stock and younger rhyolite dykes cut the Cretaceous and Tertiary sedimentary and volcanic section.

The structure of the Fresnillo District is controlled by two separate deformational events that occurred during the Late Cretaceous and Middle to Late Tertiary. Within the Proaño Group sediments, a broad anticlinorium plunging gently to the southeast below Cerro Proaño (Fig. 2) reveals crumpling and contortion, which resulted from Late Cretaceous folding and associated thrust faulting. Block faulting, which caused a regional, southward tilt of the Cretaceous sequence and the overlying Tertiary continental sedimentary and volcanic rocks, occurred in the Middle to Late Tertiary. The most prominent example of this deformation in the mine area is the Fresnillo fault, which brings the Fresnillo Formation and Tertiary felsic volcanic rocks into contact with the underlying Upper Greywacke unit and Chilitos Formation (Fig. 2). Extensive development of minor tensional faults and fractures followed and coincided with the hydrothermal activity that resulted in the vein mineralization described in this paper.

GEOLOGY OF THE SANTO NIÑO VEIN

The Santo Niño vein trends N 70°E, dips 60° to 80°SE, has a strike length of greater than 2.5 km, and a vertical extent of greater than 500 m. Vein width ranges from less than 10 cm to greater than 4 m, and average 2.5 m. The Santo Niño vein has proven reserves of 1.2 million tonnes grading at 769 g/ton Ag, 0.56 g/ton Au, 0.99% Zn, 0.50% Pb, and 0.03% Cu (García *et al.* 1989). Host rocks for the vein are greywackes and shales of the Cretaceous Upper Greywacke unit, mafic volcanic rocks of the Cretaceous Chilitos Formation, and a conglomerate of the Tertiary Fresnillo Formation. The age of mineral deposition is Eocene–Oligocene (Lang *et al.* 1988).

The Santo Niño vein can be divided into three structural zones, all of which are related to oblique deformation with dominant right-lateral strike-slip. Total lateral displacement seems to have been only a few meters. The western structural zone is characterized by a linear strike with pinching and swelling, the central structural zone by cymoid loops, and the eastern structural zone by right-stepping *en échelon* segments. Four separate stages of vein formation record the multiple openings of fissures that provided a conduit for hydrothermal solutions responsible for the mineral deposition in the vein (Fig. 3). Stage I is divided into a crackle breccia found adjacent to the footwall contact and a fragment-to-matrix supported breccia containing unaltered fragments, well-developed cockade layering of sulfides and quartz, and a matrix of white and grey quartz. Stage II is predominantly a fragment-supported breccia with highly altered fragments, poorly developed cockade layering with minor sulfides, and a distinct chlorite-rich, green-tinted quartz matrix. Stage III consists of crustiform layers of quartz and sulfides. Stage IV is a massive flooding of coarsely crystalline calcite. Stage I contains the greatest amount of ore within the vein, followed by Stages III, II, and IV.

Hydrothermal alteration is generally weakly devel-

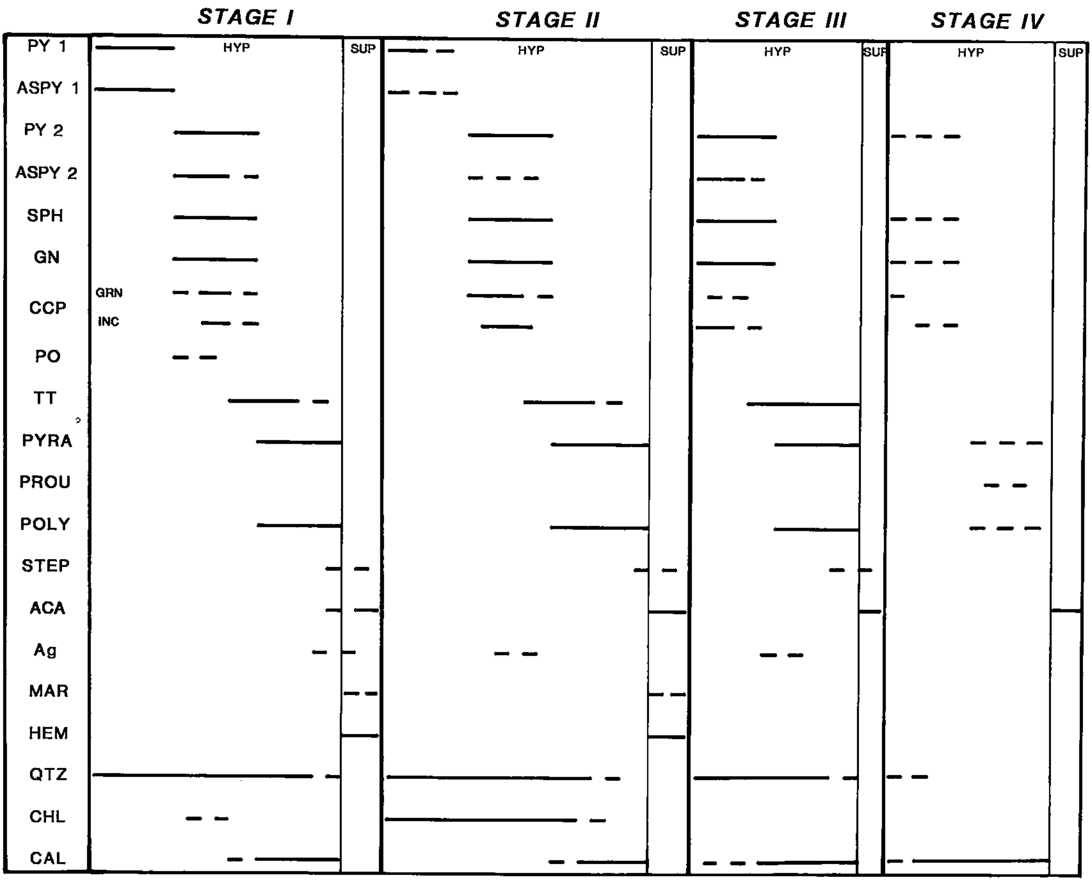

FIG. 4. Paragenetic sequence of ore and gangue mineral deposition in Stages I through IV. Dashed line indicates trace amounts. Abbreviations: PY pyrite, ASPY arsenopyrite, SPH sphalerite, GN galena, CCP chalcopyrite, PO pyrrhotite, TT tetrahedrite, PYRA pyrargyrite, PROU proustite, POLY polybasite, STEP stephanite, ACA acanthite, Ag native silver, MAR marcasite, HEM hematite, QTZ quartz, CHL chlorite, CAL calcite, GRN grains, INC inclusions, HYP hypogene minerals, and SUP supergene minerals.

oped around the veins in the Fresnillo District and rarely extends more than a few meters away from the veins. The types of alteration observed in the wallrocks are propylitization of the volcanic rocks of the Chilitos Formation and silicification of the sediments of the Upper Greywacke unit. Conglomerates of the Fresnillo Formation contain both silicification and weak propylitic alteration. Silicification, argillization, and propylitization of fragments in the breccia stages are observed in the Santo Niño vein.

Sulfide and Sulfosalt Mineralogy and Paragenesis

The ore minerals of the Santo Niño vein are a complex intergrowth of fine-grained base metal sulfides and silver-bearing sulfosalts. In order of abundance, these are pyrite, sphalerite, galena, pyrargyrite, polybasite, chalcopyrite, arsenopyrite, tetrahedrite, acanthite, stephanite, marcasite, proustite, pyrrhotite, and selenian polybasite. The ratio of sulfide to sulfosalt is approximately 5:1, with sulfides and sulfosalts making up less than 5% by volume of the vein. Gangue minerals include quartz, chalcedony, calcite, chlorite, and several clay-mineral species (montmorillonite, kaolinite, mixed-layer chlorite–smectite, and trace amounts of illite or sericite). The ore and gangue minerals occur as crustified layers, cockade textures, disseminations and stringers within breccia matrix, and replacement of breccia fragments. Oxidized fractures contain limonite, hematite, Mn oxide, malachite, azurite, and native silver.

Mineral deposition is divided into four paragenetic phases: 1) pyrite and arsenopyrite, 2) sphalerite,

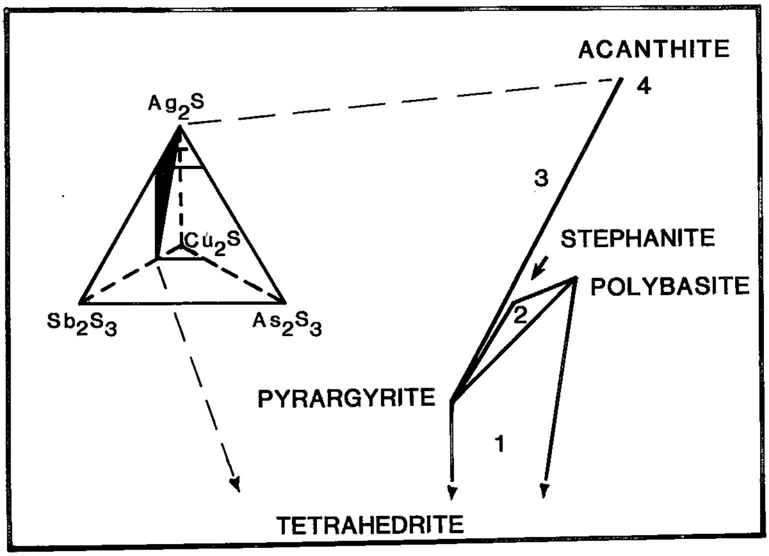

FIG. 5. Paragenesis of the silver-bearing sulfides and sulfosalts of the Santo Niño vein within the quaternary system Ag_2S–Sb_2S_3–As_2S_3–Cu_2S. The numbers indicate the sequence of minerals corresponding to precipitation from the systems [(Cu,Ag) (Fe,Zn)–Sb–S; Cu–Ag–Sb–S, Ag–Sb–S], [Cu–Ag–Sb–S; Ag–Sb–S], [Ag–Sb–S; Ag–S], and [Ag–S]. The diagram is generalized because members of the tetrahedrite–tennantite series have a slight excess in sulfur (1 of 13 atoms) and do not plot precisely on the Sb_2S_3–As_2S_3–Cu_2S plane.

galena, and chalcopyrite, with a second generation of pyrite and arsenopyrite, 3) silver-bearing sulfosalts and sulfides, and 4) supergene sulfides and oxides. The paragenetic sequence of the ore and gangue minerals for each stage of the Santo Niño vein is similar (Fig. 4).

The paragenetic evolution of the silver-bearing sulfosalt and sulfide minerals is from (copper–silver)-bearing to pure silver-bearing: a) tetrahedrite, polybasite, and pyrargyrite, b) polybasite, pyrargyrite, and stephanite, c) pyrargyrite and acanthite, and d) acanthite. This paragenesis of the silver-bearing minerals within the Ag_2S–Sb_2S_3–As_2S_3–Cu_2S quaternary system is shown in Figure 5. Tetrahedrite was the first sulfosalt to precipitate, initially with chalcopyrite and subsequently with pyrargyrite and polybasite. Complex symplectitic intergrowths of pyrargyrite, polybasite, tetrahedrite, chalcopyrite, and galena are beautifully developed (Figs. 6a,b). Pyrargyrite and polybasite replaced earlier generations of sulfides and tetrahedrite. Pyrargyrite and polybasite commonly fill tiny fractures and cracks in other ore minerals, and rarely fill voids between crystals of late-stage euhedral quartz and calcite gangue. Trace quantities of stephanite are associated with polybasite, as a pseudomorphic replacement. Minor amounts of acanthite are intergrown with the silver-bearing sulfosalts, mainly late-stage pyrargyrite.

COMPOSITION OF THE SULFOSALTS

The Santo Niño vein contains three separate silver-bearing sulfosalt solid-solution series: pyrargyrite–proustite [$Ag_3(Sb,As)S_3$], polybasite–arsenpolybasite [$(Ag,Cu)_{16}(Sb,As)_2S_{11}$], and tetrahedrite–tennantite [$(Cu,Ag)_{12}(Sb,As)_4S_{13}$]. Stephanite ($Ag_5SbS_4$) is observed, but does not form a solid-solution series with an arsenic analog.

Compositions were determined by electron-microprobe analysis from samples selected to

FIG. 6. Microphotographs of sulfosalt mineral textures in the Santo Niño vein. (a) Symplectitic intergrowth of galena (GN) and pyrargyrite (PYRA) enveloped by polybasite (POLY). Black grains are gangue. Stage I, oil; (b) Symplectitic intergrowth of tetrahedrite (TT) and galena (GN) surrounded by pyrargyrite (PYRA) and sphalerite riddled with inclusions of chalcopyrite. Black grains are quartz. Stage III, air; c) Intergrowth of coexisting polybasite (POLY), tetrahedrite (TT), and pyrargyrite (PR). Sulfosalts precipitated after cockscomb quartz crystals (black, hexagonal crystal outline) and minor amounts of pyrite (PY), galena (GN), and sphalerite (SPH). Sphalerite is riddled with tiny inclusions of chalcopyrite. Stage I, oil.