

POLYMETALLIC Ag-Te-BEARING PARAGENESIS OF THE CERRO NEGRO DISTRICT, FAMATINA RANGE, LA RIOJA, ARGENTINA

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ABSTRACT

Mineralization in the Famatina Range, La Rioja, Argentina, is related to silicic to intermediate magmatism of Lower to Middle Pliocene age. This metallogenic subprovince includes 1) silver-bearing deposits with a very rich and complex Ag-Pb-Zn (Cu-Ni-Co-Te-Sb) paragenesis, 2) Cu-Au districts, and 3) Cu-Mo districts. Detailed microscopic and geochemical studies of the Peregrina deposit, of the first group, revealed the occurrence of tellurides such as altaite and native tellurium. The paragenesis consists of gold, silver-bearing minerals (acanthite, argyrodite, miargyrite, pyrargyrite, proustite, stephanite, freibergite), Co-Ni minerals (nickel-skutterudite, nickeline, rammelsbergite, safflorite), base-metal sulfides (sphalerite, chalcopyrite, pyrite, galena) and gangue minerals (siderite, quartz, barite and calcite). Textural and structural evidence indicates that mineralization took place during three stages from solutions under epithermal conditions. During the first stage, base-metal sulfides were deposited in a gangue of siderite. During the second stage, gold was deposited at the beginning, followed by the main deposition of silver antimonides and arsenides, and Ni-Co-bearing minerals in a gangue of quartz and ferroan rhodochrosite. Studies of fluid inclusions in sphalerite indicate a temperature of formation ranging from 265° to 190°C and fluids with a salinity of 4.2 to 6.2 eq.% NaCl. The third stage is characterized by the deposition of scarce base-metal sulfides and Ni-Co-bearing minerals, and the main deposition of acanthite, silver, altaite, tellurium and marcasite in a gangue of calcite and quartz.

Keywords: silver, proustite, acanthite, freibergite, altaite, tellurium, Cerro Negro district, Peregrina, Famatina Range, Argentina.

SOMMAIRE

La minéralisation dans la chaîne de Famatina, à La Rioja, en Argentine, est liée à un magmatisme felsique à intermédiaire d'âge pliocène inférieur à moyen. Cette province métallogénique comprend 1) des gisements d'argent avec une paragenèse complexe et très riche en Ag-Pb-Zn-(Cu-Ni-Co-Te-Sb), 2) des districts enrichis en Cu-Au, et 3) d'autres enrichis en Cu-Mo. Nos études pétrographiques et géochimiques détaillées du gisement de Peregrina, qui fait partie du premier groupe, révèlent la présence de tellurures, dont altaïte, et tellure natif. La paragenèse contient de l'or, des minéraux argentifères (acanthite, argyrodite, miargyrite, pyrargyrite, proustite, stéphanite, freibergite), des minéraux à Co-Ni (nickel-skutterudite, nickeline, rammelsbergite, safflorite), des sulfures de métaux de base (sphalérite, chalcopyrite, pyrite, galène) et des minéraux de gangue (sidérite, quartz, baryte et calcite). D'après l'évidence texturale et structurale, la minéralisation aurait eu lieu en trois stades, à partir de solutions sous conditions épithermales. Les sulfures des métaux de base sont apparus au cours du premier stade, dans une gangue de sidérite. Au cours du second, l'or a d'abord été déposé, suivi par les antimoniures et les arséniures d'argent, et par les minéraux à Ni-Co dans une gangue de quartz et de rhodochrosite ferrifère. Les inclusions fluides dans la sphalérite indiquent une température de formation entre 265 et 195°C, et une salinité entre 4.2 et 6.2% de NaCl (équivalent). Le troisième stade est marqué par la déposition de rares sulfures de métaux de base et de minéraux à Ni-Co, et de la plupart de l'acanthite, l'argent, l'altaïte, le tellure et la marcasite dans une gangue de calcite et de quartz.

(Traduit par la Rédaction)

Mots-clés: argent, proustite, acanthite, freibergite, altaïte, tellure, district de Cerro Negro, Peregrina, chaîne de Famatina, Argentine.

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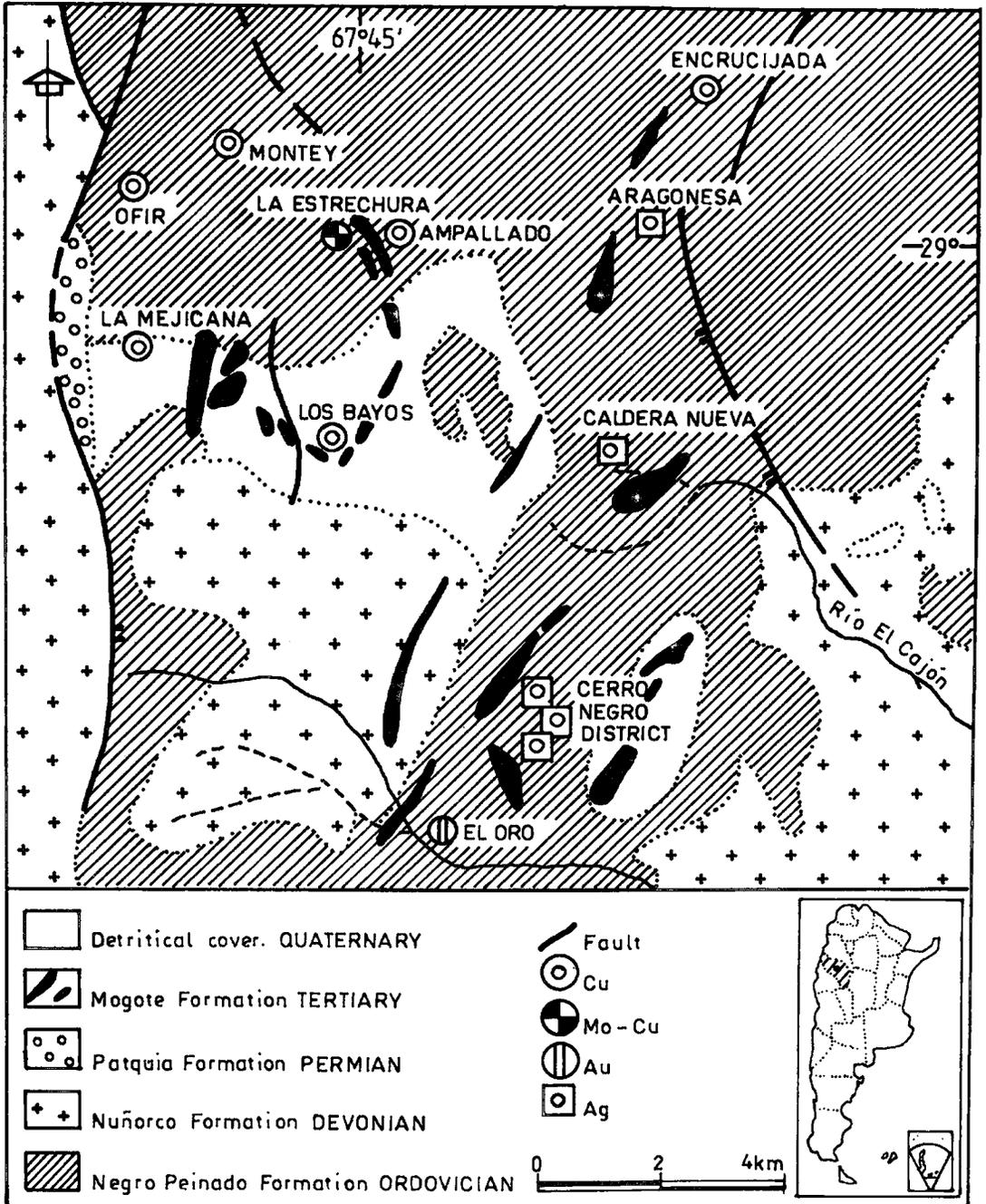


FIG. 1. Geological sketch of the eastern side of the Famatina Range showing the metallogenic subprovince with Cu-Au, Cu-Mo and Pb-Ag-Zn districts. Geology modified from various regional geological studies: Bassi (1953), De Alba (1960, 1972) and Turner (1962, 1964, 1971).

INTRODUCTION

Polymetallic and precious metal deposits occur in the Famatina Range, province of La Rioja, Argentina and define a polymetallic and monocyclic subprovince. Although the size of this metallogenic subprovince is about 200 km², the majority of the mineral concentrations occur in an area of 20 km² (Fig. 1). Three distinct zones are recognized: 1) the Pb-Ag-Zn (Cu-Ni-Co-Te-Sb) deposits of the Caldera, Tigre and Cerro Negro districts (La Viuda and Peregrina mines), which form a north-south-trending band on the eastern side of the Famatina Range, 2) the Cu-Au districts known as La Mejicana, Los Bayos, Offir and Ampallado, located in the northwestern region, and the El Oro mine, in the southeastern corner of the study area, and 3) the La Estrechura Cu-Mo district, located in the northwestern region. The regional zoning of Cu-Mo, Cu-Au and Pb-Ag-Zn (Cu-Ni-Co-Te-Sb) assemblages shows similarities to that shown by mineralization in Colorado.

The complex and interesting mineral paragenesis of the Peregrina mine motivated this detailed mineralogical and geochemical study, in which we sought to identify the Te-bearing minerals. The veins in the Peregrina mine that we studied are located in the western part of the Cerro Negro (Fig. 1).

Some of the argentiferous deposits were mined by natives, then (1780-1810) by Spaniards (laic Jesuits), and also sporadically in the late 1800s and early 1900s. The major mining activity was concentrated in the Cerro Negro district, where the bonanzas could contain 10-12 kg of silver per tonne. In the Peregrina mine, the ore was recovered from open-cast workings and galleries down to 300 meters.

Although exploitation has been sporadic, and none of the mines has been active in the last several decades, these areas are believed to still have economic potential. In the last few years, regional research as well as detailed mapping, geophysical studies and drilling of the Cu-Au and Cu-Mo mineralizations have been completed (Marcos & Zanettini 1981, Méndez 1981). Angelelli (1984), Schalamuk *et al.* (1977), Bodenbender (1913, 1922) and Allchurch (1895) reported information about the Pb-Ag-Zn concentrations in Famatina.

ANALYTICAL METHODS

Compositions of altaite, tellurium, Pb(As,Sb)Te_{2.22-2.54}, freibergite, sphalerite and carbonates were determined by the authors with a CAMECA SX 50 electron microprobe at the Comisión Nacional de Energía Atómica (CNEA) in Buenos Aires. The analytical parameters are reported in footnotes to the Tables. All analyses were performed under an acceleration voltage of 20 kV and a beam intensity of 20 nA, except for the analysis of the Te-bearing minerals, in which case the beam intensity was 30 nA. In the analyses of altaite, native tellurium and freibergite, pure elements were used as standards for Cu, Pb, Zn, Bi, Te, Sb, Au and Ag, pyrite for S and Fe, and a synthetic As-Se compound for As and Se. The following standards were used in the analyses of sphalerite and carbonates: MnTiO₂ for Mn, MgCO₃ for Mg, FeS₂ for S and Fe, CaCO₃ for Ca, synthetic ZnS for Zn, and synthetic CdS for Cd. CO₂ was calculated by difference. The following incorporated programs were used: CALIB (Calibration of standards), DECLAR (Declaration of analytical conditions) and QUANTI

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF ALTAITE

No.	1	2	3	4	5	6	7	8
wt. %								
Te	40.73	39.35	39.49	39.13	39.84	39.47	39.57	40.19
Pb	58.32	58.03	58.97	59.82	57.07	58.43	58.32	60.10
Sb	0.30	0.25	0.36	0.30	0.33	0.21	0.40	0.27
Au	0.12	-	-	-	-	-	-	-
Ag	0.03	-	-	0.08	-	-	-	0.06
Se	0.19	-	0.04	-	-	0.08	-	0.19
Sum	99.69	97.63	98.86	99.33	97.24	98.19	98.29	100.81
at. %								
Te	52.13	52.22	51.79	51.22	52.87	52.07	52.13	51.62
Pb	46.94	47.43	47.63	48.23	46.64	47.47	47.30	47.54
Sb	0.40	0.35	0.49	0.41	0.47	0.29	0.56	0.36
Au	0.10	-	-	-	-	-	-	-
Ag	-	-	-	0.13	-	-	-	0.09
Se	0.39	-	0.09	-	-	0.18	-	0.40

Lines used (analyzing crystals): TeLa (LiF), PbLa (LiF), SKα (PET), SbLa (PET), AuLa (LiF), AgLa (PET), SeKα (LiF), and AsLa (LiF).

(Quantitative analysis).

Data on trace elements in sphalerite and galena were obtained by neutron-activation analyses by Dr. I.M. Cohen at the Comisión Nacional de Energía Atómica, Ezeiza, Argentina. In order to avoid interferences produced by some nuclides present in the matrix (^{69m}Zn and ^{65}Zn), samples were irradiated for a very short period of time to identify most of the elements. Irradiations were performed in the RA-3 atomic reactor at the Comisión Nacional de Energía Atómica, Ezeiza, Argentina, with a flow of 10^{13} n/cm²·s, using thermal or epithermal neutrons according to the nuclide to be analyzed. Pure elements were used as materials of reference. In some cases, the samples to be irradiated were coated with cadmium, in order to absorb or minimize the flow of thermal neutrons where a flow of epithermal neutrons was used. The measurements of the samples were obtained with a Ge(Li) detector of 27 cm³, with a resolution of 3.2 keV for 1332 keV, corresponding to the second peak of ^{60}Co , connected to a Packard model 46 multi-channel analyzer, with 4096 channels. The time of decay required for the measurements ranged between a few minutes (In and Cd) and 24 hours (Tl).

Microthermometric studies on sphalerite were performed with a freezing-heating CHAIXMECA stage (-192° to 600°C) at the University of Canarias by Dr. J. Mangas Viñuelas. The calibration curve was obtained by measuring phase-changes in solid standards (melting point) at atmospheric pressure. In the heating process between +25° and 600°C, various Merck synthetic standards were used. Standard inclusions of CO₂ (-56.6°C) and water (0°C) were used to calibrate the freezing intervals. Salinities were calculated from tables of freezing-point depression. Temperatures of homogenization were obtained by progressive heating of the sample.

GEOLOGICAL SETTING

The study area consists of low-grade metamorphic and sedimentary rocks intruded by Devonian and Pliocene igneous rocks. The Negro Peinado Formation, the best represented lithological unit, is a thick N-S-striking marine metasedimentary sequence composed of siltstone and subordinate shale and sandstone, which locally show contact metamorphism. Regional metamorphism and deformation, related to the Caledonian Orogeny, occurred during the Lower Ordovician (480 ± 15 Ma, Toselli 1978). The beds show a slight schistosity and a high degree of silicification. Biotite granite and hornblende granodiorite of the Ñuñorco batholith (310 ± 15 Ma, De Alba 1972) intruded the Ordovician metasedimentary rocks. Permian continental sediments (Patquía Formation) overlie unconformably the Negro Peinado Formation. The Lower to Middle Pliocene magmatism (5.9 ± 0.2 Ma, McBride 1972; 5.7 ± 0.2 Ma, Stipanich &

Linares 1975) is represented in the area by the Mogote rhyodacite-dacite complex (Fig. 1). These rocks generally have a granophyric texture made up of large phenocrysts of plagioclase, quartz and biotite in a microgranular groundmass with the same mineralogical composition as the phenocrysts, plus abundant K-feldspar. At depth, the rhyodacite grades into a granodiorite in the area of La Estrechura and Ampallado (Marcos & Zanettini 1981). In many areas, intense hydrothermal alteration has been superimposed on the primary assemblages.

Structurally, the Famatina Range is characterized by the presence of step faults and by large north-south boundary faults. The altitude of the fault blocks increases toward the west. Their uplift persisted at least into the Lower Pliocene (McBride 1972). The structure is the result of different tectonic movements; however, the Famatina Range acquired its present appearance during the Andean Orogeny. The intrusion of the Mogote rhyodacite-dacite complex took place between Andean Movements II and III (Marcos & Zanettini 1981). The mineralization in the Famatina Range may have occurred during the earliest phase of Andean Movement III. These deposits were formed late in the orogenic cycle, during the subduction phase, in a compressional environment in the back-arc basin of the Tertiary magmatic arc. The veins were formed in secondary fractures after the formation of reverse faults, during tensional relief (V. Ramos, pers. comm.). In the study area, east-west-striking fractures coincide with the main mineralized structures of La Mejicana, Offir and Montey (Cu-Au), and Caldera, Tigre and Cerro Negro (Pb-Ag-Zn). The veins dip between 40° and 70° north and south. Northwest-striking faults with variable dips (30-80°) control the Los Bayos zone of mineralization and, to some extent, the Caldera (Pb-Ag-Zn) and El Oro (Au-Cu) districts.

MINERAL PARAGENESIS

Hydrothermal alteration

Hydrothermal alteration has affected the different lithological units with varying degrees of intensity. In the region, many major types of alteration were identified by Marcos (1975) and Méndez (1981), including propylitic, argillic, alunite, sericitic, potassic and silicic. The last one is the most extensive and affects all the units. Based on the type of hydrothermal alteration and the mineral assemblages (ore and gangue), we consider in this study that the Cu-Au and Pb-Ag-Zn districts can be grouped into two types of environment. These correspond to the acid sulfate and adularia-sericite types of Heald *et al.* (1987). The La Mejicana, Los Bayos and Offir Cu-Au deposits, whose most commonly occurring minerals are enargite, bornite, chalcopyrite and pyrite in a gangue of quartz and alunite, belong to the first type. The

advanced argillic alteration in these districts is characterized by the presence of hypogene alunite, which in some areas is the dominant mineral. Chlorite is absent. Another characteristic feature is the common presence of free gold and gold-bearing minerals like sylvanite and goldfieldite (Losada-Calderón & Bloom 1990).

The adularia-sericite type of deposit is represented by the La Viuda, Caldera, Cerro Negro and Tigre argentiferous districts. These contain a large number of species including: pyrite, chalcocopyrite, sphalerite, wurtzite, galena, covellite, digenite, nickeline, nickel-skutterudite, rammelsbergite, safflorite, freibergite, pyrargyrite, proustite, miargyrite, stephanite, pearceite-polybasite, argyrodite, barite, acanthite, native silver (identified microscopically and chemically by Schalamuk *et al.* 1977), altaite, native tellurium and an unknown arsenotelluride (identified microscopically and by electron-microprobe analysis in this study) in a gangue of siderite, ferroan rhodochrosite, calcite and quartz. The sericitic alteration surrounds the silicified zones near the veins. The potassic alteration, essentially defined by the biotite - K-feldspar - quartz assemblage, is not lithologically controlled and is superimposed on porphyry as well as granite and shale. The silicification occurred in at least two stages. Propylitization is confined to a localized band along the eastern boundary of the zone.

Mineralization

The argentiferous districts of Famatina (Cerro Negro, Caldera and Tigre) are typical epithermal deposits. In the case of Cerro Negro, the mineralization occurs in veins. Ore shoots are associated with the development of breccias. The host rocks consist of Ordovician shale. The main vein in the Peregrina mine strikes N30°W and dips 70°NE, has a length of 350 m and an average thickness of 0.75 m. A breccia structure is common, consisting of angular and elongate clasts of light to dark grey shale, occasionally with fine banding, from 1 to 5 cm in length. Fine-grained siderite forms the cement and encloses the sulfides. Cavities 1 to 3 cm in diameter are common; the silver-bearing minerals occur in the largest ones. The ore occurs in two different forms: 1) fine-grained veinlets with siderite, pyrite, sphalerite and galena, and 2) coarse-grained veinlets with ferroan rhodochrosite and silver-bearing minerals. Open-space-filling textures are common, indicating a shallow environment of emplacement. They occur in two forms: 1) as vugs and cavities, which are interpreted as incomplete open-space filling, and 2) as crustifications, which were formed owing to changes in the composition of the mineralizing solutions. The earlier-formed crystals are enclosed by the later. Symmetrical banding also is present.

The hypogene mineralization is represented by pyrite, chalcocopyrite, marcasite, sphalerite, galena,

freibergite, and silver-bearing minerals like acanthite, argyrodite and silver. Silver antimonides and sulfarsenides include miargyrite, pyrargyrite, pearceite-polybasite, proustite-pyrargyrite, stephanite and freibergite. The Ni- and Co-bearing minerals include nickel-skutterudite, nickeline, rammelsbergite and safflorite. The Te-bearing minerals are altaite, native tellurium and an unknown arsenotelluride. The gangue minerals are siderite, ferroan rhodochrosite, quartz, barite and calcite. For purposes of discussion, the minerals have been divided into the following compositional groups without regard to abundance or order of deposition: (1) Ag-bearing minerals and gold, (2) Ni-Co-bearing minerals, (3) Te-bearing minerals, (4) other sulfide minerals and (5) gangue minerals. These are described in the sections that follow.

Silver-bearing minerals and gold

Gold occurs as small grains of 10–15 µm in size included in quartz of the second stage of mineralization, and associated with the Te-bearing minerals in the third stage.

Proustite appears together with pyrargyrite, native silver and acanthite, and forms one of the main components of the Cerro Negro mineralization. It is dominant over pyrargyrite. It occurs as small granular red aggregates up to 1.5 cm in diameter. Microscopically, it appears as xenomorphic grains that replace galena, and also in veinlets that cross-cut and replace freibergite, galena, siderite and, rarely, sphalerite (Fig. 2A). It may be intergrown with polybasite and stephanite. Lamellar twinning is common. A chemical analysis reveals the following composition: 64.0 wt.% Ag, 13.3% As, 18.8% S and trace of Sb (Schalamuk *et al.* 1977).

Pyrargyrite occurs as irregular grains in association with proustite in prismatic and scalenohedral crystals 2–3 cm long. Veinlets 5 mm in width cross-cut preferentially sphalerite and siderite. Pyrargyrite also fills cavities in association with pearceite-polybasite, native silver and argentite. The internal reflections are not very intense.

Acanthite is relatively abundant; two generations are distinguished. The first one follows the deposition of silver-bearing sulfosalts and replaces galena, sphalerite, proustite and pyrargyrite, forming cusp-and-carries textures and occasionally intergrowths (Fig. 2A). It is characterized by its greenish grey color in immersion oil, low hardness, poor polish and low anisotropy. A later generation appears in open spaces and vugs in siderite as elongate crystals of up to 2 mm in length. The absence of transformation twinning and the isotropy in many sectors indicate that it was formed at a temperature below 179°C (Ramdohr 1980). Inclusions of nickeline were identified by reflected light microscopy.

Silver occurs as grains or plates up to 1.5 mm

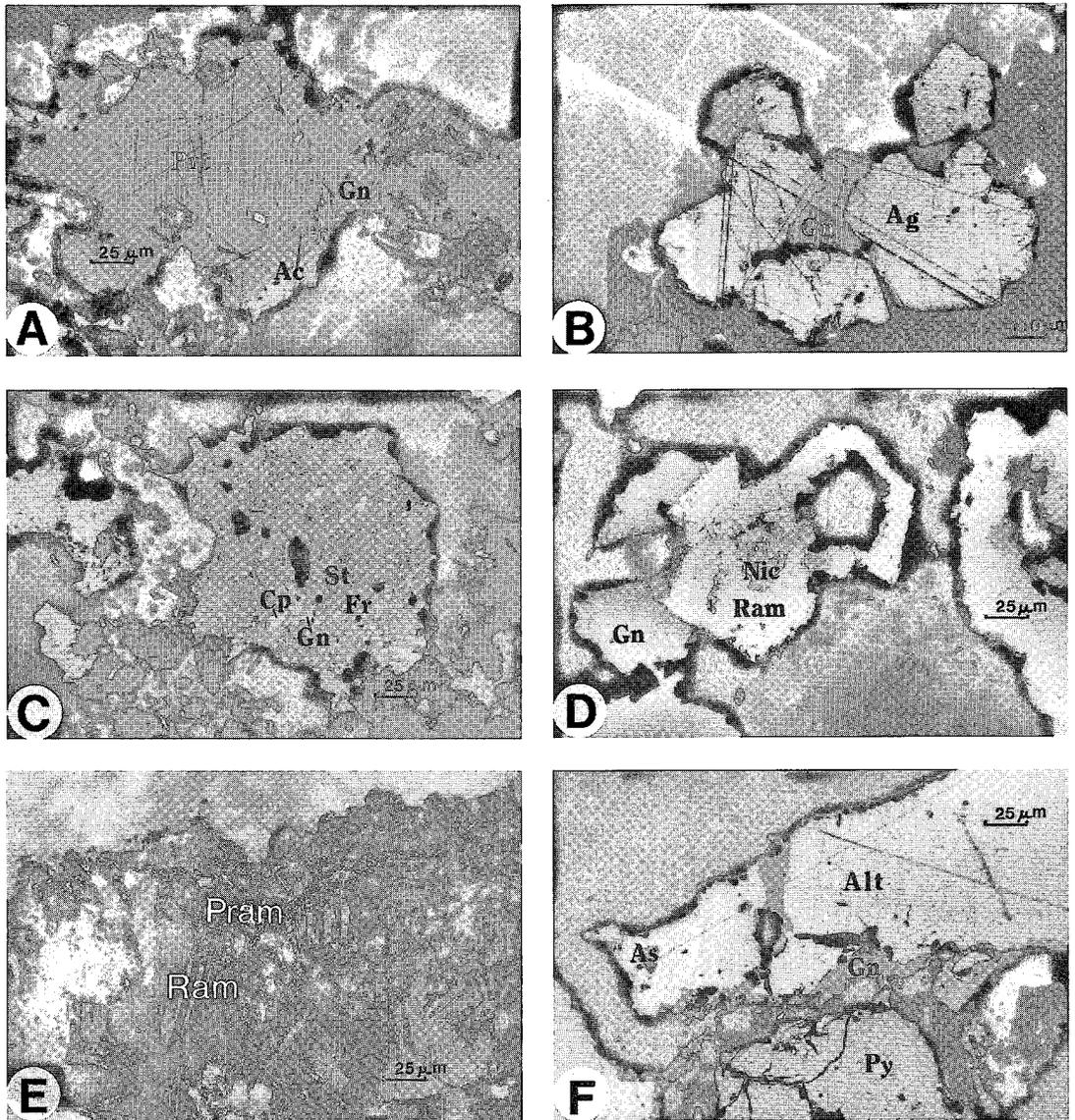


FIG. 2. Photomicrographs of some of the ore minerals of the Peregrina mine showing: A) proustite (Prt), acanthite (Ac) and galena (Gn), B) native silver (Ag) and galena (Gn), C) freibergite (Fr), stephanite (St), chalcopyrite (Cp) and galena (Gn), D) nickeline (Nic), rammelsbergite (Ram) and galena (Gn), E) rammelsbergite (Ram) and pararammelsbergite (Pram), and F) altaite (Alt), galena (Gn), pyrite (Py) and PbAsTe_2 (As). Photomicrographs A, C, D, E and F taken in oil immersion, B taken in air. Crossed nicols were used in E.

across. In the first stage of mineralization, it occurs in association with ferroan rhodochrosite, galena, sphalerite and acanthite (Fig. 2B). In the second stage, it appears more commonly as teeth up to 2 mm in width in drusy siderite, and as dendritic masses. In most cases, it displays a cusp-and-carries texture and replaces acanthite. Bodembender (1913) considered it

to be hypogene, although where it appears as a thin film in association with quartz and limonite, it is probably secondary.

In general, a member of the *pearceite-polybasite* series appears as anhedral grains that replace galena, as symplectitic intergrowths with galena, and as veinlets. In open space, it occurs in vugs as tabular crystals

up to 2 cm with the characteristic striations and perfect (001) cleavage. Red internal reflections are abundant. It has a poor polish, is etched by a light source, and a number of characteristic dots are formed. An X-ray-diffraction (XRD) analysis performed by the powder method with Cu cathode and Ni filter by Schalamuk *et al.* (1977) showed that the main lines are comparable to a sample of Aspen, Colorado (PDF 8-130), indicating, therefore, that the mineral found in the Peregrina mine corresponds to the arsenoan end-member of the series (pearceite). A semiquantitative spectrographic analysis (Schalamuk *et al.* 1977) showed traces of Ni, Ge, Sn and Pb.

Freibergite occurs as individual grains or as anhedral aggregates as well as in veinlets. It is characterized by a grey color with an olive hue, exceptionally with red internal reflections. It displays cusp-and-carries textures with galena. It is replaced by polybasite and locally by other silver-bearing minerals. An electron-microprobe analysis performed in the context of this study [CuK α (analyzing crystal: LiF), AsL α (TAP), SbL α , SK α , AgL α (PET), PbK α , ZnK α , FeK α , BiL α (LiF)] indicates the following composition (average of 15 analyses): 16.28 wt.% Cu, 6.18% As, 20.94% Sb, 13.62% S, 28.91% Ag, 1.46% Zn, 6.37% Fe and 6.20% Pb.

Miargyrite appears either a) in association with proustite and pyrargyrite, forming symplectitic intergrowths or as fine grains up to 150 μ m across, or b) in veinlets cross-cutting ferroan rhodochrosite. In oil immersion, it shows strong anisotropy and rare internal reflections.

Stephanite is scarce and appears as irregular aggregates. It usually forms intergrowths with polybasite, proustite, pyrargyrite, argyrodite, freibergite and galena (Fig. 2C).

Argyrodite seems intergrown with pearceite-polybasite, in close association with stephanite, proustite, galena and, rarely, sphalerite, in grains up to 60 μ m in size. Argyrodite was determined microscopically and by XRD (Schalamuk *et al.* 1977). A spectrographic analysis indicated more than 1000 ppm Ge and 100 ppm Sn. The presence of Ge and the very low concentration of Sn indicate that the mineral in the Peregrina mine corresponds to the Ge-rich member of the argyrodite (Ag₈GeS₆) - canfieldite (Ag₈SnS₆) series (Schalamuk *et al.* 1977).

Co-Ni-bearing minerals

Rammelsbergite is abundant among the Ni-Co-bearing minerals. Microscopically, it shows different forms, such as sheaf-like groups that enclose and replace nickeline (Fig. 2D) as a consequence of an increase of As in the solutions, colloform aggregates, and skeletal crystals in siderite. This arsenide also appears as fringes or crowns that surround galena, sphalerite, proustite-pyrargyrite, polybasite and

freibergite. It is also found in association with pararammelsbergite (Fig. 2E). The textural evidence indicates that there are at least two types of rammelsbergite. The younger one is colloform, whereas the older one replaces galena and acanthite. In some sections, polysynthetic twinning can be recognized with crossed nicols and previous etching with nitric acid.

Nickeline is scarce and appears as small compact masses in association with silver-bearing minerals. Usually it is enclosed in rammelsbergite or safflorite and displays an atoll texture (Fig. 2D).

Nickel-skutterudite is very rare and occurs as isolated grains up to 70 μ m across enclosed in sideritic gangue. The zoning, which consists of an increase in the Ni content toward the center of the crystals, as determined spectrographically by Schalamuk *et al.* (1977), is also recognizable by fine differences in hardness.

Safflorite occurs as very fine grains (smaller than 60 μ m). The characteristic star-shaped twinning caused by an intergrowth of triplets is very common. It is generally associated with sphalerite, although it appears also as a rim lining small grains of nickeline.

Te-bearing minerals

Altaite (PbTe), though rare, was identified microscopically by XRD and electron-microprobe analyses in some samples of the Peregrina mine. It forms anhedral grains in aggregates in association and intergrown with galena and pyrite (Fig. 2F). In oil immersion, it shows a white color and strong reflectivity, galena-like cleavage and isotropy. The associated galena displays cusp-and-carries texture and shows a violet-grey color where in contact with altaite. Electron-microprobe studies of altaite performed by the authors during this study (Table 1) indicate that it has a composition varying from 39.35 to 39.84 wt.% Te and from 58.03 to 57.07% Pb (PbTe_{1.08} - PbTe_{1.14}). The most common impurity is Sb, with concentrations from 0.21 to 0.40%. These concentrations increase together with enrichment in Te. Gold was found in quantities up to 0.12% and silver, up to 0.19%. Ge, Fe, Ni and Bi were also sought but not found.

Tellurium, rare in nature and identified in only a few deposits such as Cripple Creek, Colorado (Guilbert & Park 1986) and Musariu in the Metaliferi Mountains, Romania (Berbelec & David 1982), was identified in the Peregrina mine during this study as blebs a few micrometers in size. They are located along the rims of the altaite crystals; their identification is only possible through secondary electron images in scanning electron microscopy (Fig. 3). Electron-microprobe analyses performed by the authors (Table 2) revealed the following composition: 88.47 to 97.24 wt.% Te, 9.19 to 4.12% Pb, 0.47 to 1.95% S and 0.65 to 0.70% Sb.

In this association of Te-bearing minerals, an

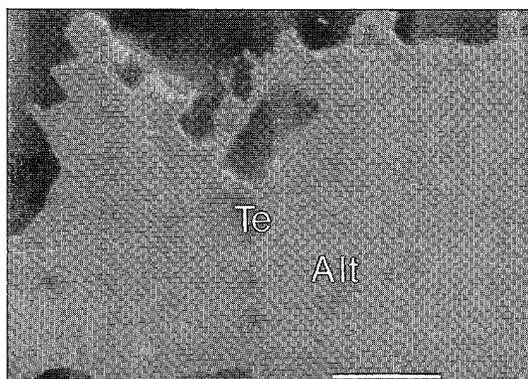


FIG. 3. Scanning electron micrograph showing blebs of tellurium (Te) in altaite (Alt) Secondary electron image, scale bar 10 μm .

unknown mineral occurs as irregular aggregates of 20 μm in size that replace altaite, displaying cusp-and-carries textures (Fig. 2F). It is characterized by low reflectivity, strong pleochroism (grey to greyish blue) and strong anisotropy (greyish brown to greyish blue). Electron-microprobe analyses indicate that its formula ranges from $\text{Pb}(\text{As},\text{Sb})_{1.1}\text{Te}_{2.22}$ to $\text{Pb}(\text{As},\text{Sb})_{1.09}\text{Te}_{2.54}$. The Sb content varies from 0.25 up to 0.37 wt.%, whereas the Se concentration reaches 0.16%. The gold content is as high as 0.53%, whereas the silver content is less than 0.085%.

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF NATIVE TELLURIUM

No.	1	2	3	4
wt. %				
Te	96.68	97.24	88.47	95.91
Pb	2.59	4.12	9.19	3.37
S	—	0.47	1.95	0.31
Sb	0.73	0.70	0.65	0.66
Au	—	—	—	—
Ag	0.02	0.04	0.02	0.15
Se	0.02	—	—	0.32
Sum	105.17	102.57	100.28	100.75
at. %				
Te	97.56	94.91	86.22	95.32
Pb	1.61	2.48	5.51	2.06
S	—	1.84	7.58	1.23
Sb	0.77	0.72	0.66	0.69
Au	—	—	—	0.02
Ag	0.02	0.05	0.03	0.18
Se	0.03	—	—	0.51

Lines used (analyzing crystals): TeLa (LiF), PbLa (LiF), $\text{SK}\alpha$ (PET), SbLa (PET), AuLa (LiF), AgLa (PET), $\text{SeK}\alpha$ (LiF), and AsLa (LiF).

Other sulfide minerals

Two types of *sphalerite*, corresponding to the first and second stages of mineralization, appear in grains up to 6 mm, in places as rhombododecahedra; one is light, and the other is dark. *Wurtzite* appears in coarser-grained aggregates, usually zoned and with concentric structures of the "schalenblende" type (Ramdohr 1980), formed by alternating sphalerite and wurtzite. Occasionally, the latter appears as radiating acicular aggregates in concentric bands. The two habits may form a colloform fabric together with marcasite, pyrite and galena. As a consequence of crystallization from a gel, fine rhythmic structures were formed. Sphalerite shows yellowish brown internal reflections and displays cusp-and-carries texture in galena, being cross-cut by silver sulfosalts and veinlets of freibergite.

Electron-microprobe analyses performed by the authors allow the identification of two different kinds of sphalerite (Table 3). Type-I sphalerite has a higher content of Fe and Mn (2.58 to 6.49 mole % FeS, 0.06 to 0.61 mole % MnS), whereas the cadmium concentration is lower (0.24 to 0.59 mole % CdS). Type-II sphalerite is characterized by a low concentration of Fe and Mn (0.68–1.18 mole % FeS, 0.09–0.12 mole % MnS) and an enrichment in Cd (0.74–1.03 mole % CdS) with respect to type I. The trend (Fig. 4) suggests that whereas the ore-forming solutions were progressively depleted in Fe and Mn, they were becoming enriched in Cd. Falling values of FeS in sphalerite are interpreted by Scott & Kissin (1973) as a consequence of an increase of sulfur in the system. Neutron-activation analyses indicate that the Ga and In contents are similar in both types of sphalerite. Type-I sphalerite tends to have generally higher contents of As and Tl, whereas the concentrations of Ge are higher in type-II sphalerite (Table 4). Fluid inclusions in sphalerite of the second stage are composed of two phases, vapor and liquid. Neither daughter crystals nor $\text{CO}_2(\text{g})$ are present. The temperature of homogenization deter-

TABLE 3. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF SPHALERITE

	I1	I2	I3	II4	II5	II6	II7
wt. %							
Zn	64.80	62.65	61.80	65.40	64.80	65.70	66.30
Fe	1.75	1.90	4.30	0.68	0.78	0.64	0.46
Mn	0.35	0.40	0.04	0.08	0.07	0.06	0.06
Cd	0.40	0.35	0.16	0.69	0.49	0.51	0.61
S	33.00	33.10	33.20	32.70	32.80	32.90	32.40
Sum	100.30	98.40	99.50	99.50	98.94	99.81	99.83
mole %							
ZnS	95.72	95.94	93.21	97.83	97.97	98.19	98.32
FeS	2.58	2.91	6.49	1.02	1.18	0.96	0.68
MnS	0.52	0.61	0.06	0.12	0.11	0.09	0.09
CdS	0.59	0.54	0.24	1.03	0.74	0.76	0.90

I1–I3: Type-I sphalerite, II4–II7: Type-II sphalerite.
Lines used (analyzing crystals): $\text{ZnK}\alpha$ (LiF), $\text{FeK}\alpha$ (LiF), $\text{MnK}\alpha$ (LiF), $\text{CdK}\alpha$ (PET) and $\text{SK}\alpha$ (PET).

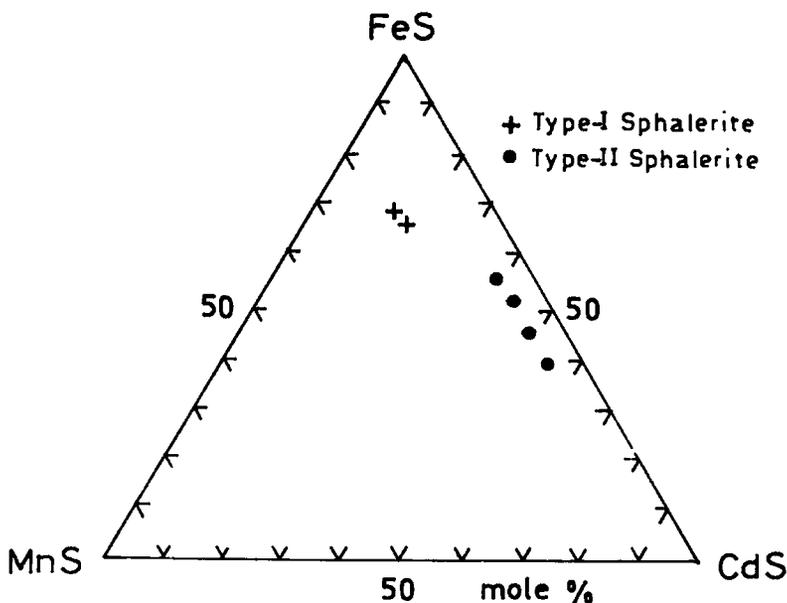


Fig. 4. Composition of the different types of ZnS.

mined during this study ranges between 190 and 265°C, and the salinity, between 4.2 and 6.2 eq. % NaCl.

Pyrite, the first-formed metallic compound, is abundant in only a few samples, occurring as fine aggregates or as isolated grains. In some cases, it is almost completely replaced, and isolated; seemingly suspended remnants of pyrite crystals form atoll structures or remain as skeletal crystals in sphalerite, galena and chalcopyrite.

Galena appears as irregular aggregates in association with sphalerite and other sulfides in a gangue of siderite and ferroan rhodochrosite. Three different forms of galena were identified and correspond to three distinct stages of deposition. The first stage occurs in association with more or less contemporaneous sphalerite, and the second one is replaced by sphalerite-wurtzite. In the latter case, the galena tends

to be idiomorphic and is closely related to silver-bearing minerals such as proustite, pyrargyrite, polybasite and freibergite, with which it may form a symplectitic intergrowth. The third stage of galena occurs associated with pyrite and silver, and is replaced by altaite. Neutron-activation data on galena of the Cerro Negro district indicate that type-I galena contains 2 850 ppm of silver, whereas that of type II contains up to 3 680 ppm (Table 5). Type-II galena is characterized by an enrichment in Bi, As, Hg and Cd (180, 640, 300 and 70 ppm, respectively) with respect to type-I galena. An electron-microprobe analysis

TABLE 4. RESULTS OF NEUTRON-ACTIVATION ANALYSES OF SPHALERITE

No.	I1	I2	I3	I14	I15	I16	I17
ppm							
Ga	18.5	28.4	22.6	14.3	21.5	17.8	16.5
In	5.6	4.3	7.2	4.2	2.8	3.6	6.8
Cd	74	33	28	260	210	180	85
Bi	-	-	-	<3	<3	<3	<3
As	630	110	198	280	155	190	250
Tl	32	12	18	4	3	8.6	6.5

I1-I3: Type-I sphalerite, I4-I7: Type-II sphalerite.

TABLE 5. RESULTS OF NEUTRON-ACTIVATION ANALYSES OF GALENA

	I1	I12	I13
ppm			
Ag	2850	1680	3680
Sb	1650	1340	1460
Bi	23	180	140
Se	44	<5	<5
As	68	550	640
Ga	-	2	3
Ge	-	<1	<1
In	-	<1	<1
Hg	45	280	300
Cd	28	55	70
Sn	25	3	5

I1: Type-I galena, I12-I13: Type-II galena.

TABLE 6. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF CARBONATES

	S1	S2	S3	S4	S5	R1	R2	R3	R4	A
wt. %										
FeO	41.60	44.50	46.80	41.70	44.60	23.60	26.50	27.10	23.70	25.80
MnO	15.80	14.90	12.30	15.80	15.00	31.20	28.80	26.60	31.00	2.40
MgO	2.70	2.60	1.20	—	—	6.10	5.20	5.90	0.50	16.80
CaO	0.20	0.40	0.30	3.00	2.80	0.80	0.60	0.50	6.00	4.20
CO ₂	38.15	37.20	39.10	38.40	37.30	38.10	38.40	38.40	38.20	50.40
Sum	98.45	99.60	99.70	98.90	99.70	99.80	99.50	98.50	99.40	99.60
mole %										
FeCO ₃	68.99	71.31	77.23	68.93	71.47	38.25	43.37	45.06	35.27	52.44
MnCO ₃	26.20	23.88	20.30	26.12	24.04	50.57	47.14	44.23	46.13	4.88
MgCO ₃	4.48	4.17	1.98	—	—	9.89	8.51	9.81	0.74	34.17
CaCO ₃	0.33	0.64	0.49	4.96	4.49	1.30	0.98	0.83	8.93	8.54

S1-S5: Siderite, R1-R3: ferroan rhodochrosite, A: ankerite.

Lines used (analyzing crystals): FeK α (LiF), MnK α (LiF), MgK α (PET), and CaK α (TAP).

(performed with the same equipment and analytical conditions as the analyses of Te-bearing minerals) indicated that Te is present in galena of the third stage only (1 400 ppm).

Chalcopyrite formed later than pyrite. It presents no special characteristics, except for a weak anisotropy. It occurs as anhedral grains surrounded or cross-cut by galena and sphalerite, and it replaces pyrite. It also occurs in veinlets or intergrown with freibergite and polybasite.

Marcasite is less common than pyrite, with which it is associated in well-developed tooth-like aggregates. A later generation of marcasite comprises the cement

of a microbreccia, which is mainly composed of fragments of sphalerite, siderite, proustite and galena.

Gangue minerals

Two forms of *Fe-Mn carbonates* were recognized on the bases of habit and composition, an iron-rich one (siderite) and a manganese-rich one (ferroan rhodochrosite). Siderite occurs as masses of larger crystals than ferroan rhodochrosite, forming bands of 2 cm in thickness. The crystals have a light brown, honey-like color where fresh, and are dark where lightly altered. In the "La Viuda" deposit, siderite forms bands with a

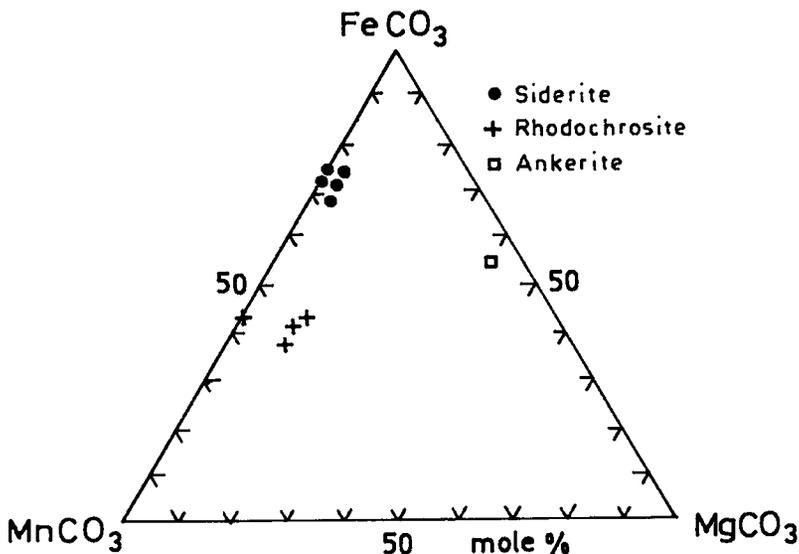


FIG. 5. Composition of the carbonate gangue minerals.

fibrous texture. Ferroan rhodochrosite occurs as rosette-like masses with grains up to 2 mm, with a very light pinkish brown color. It may appear alone or with minor sulfides. The veins of the eastern part of the Cerro Negro are richer in carbonates than those in the Peregrina mine. Electron-microprobe studies of these carbonates indicate that siderite contains 41.6–46.8 wt.% FeO, 12.3 to 15.8% MnO, and less than 2.7% MgO. In contrast, the rhodochrosite contains only 25.8 to 26.5 wt.% FeO, higher MnO concentrations (26.6 to 31.2%), and MgO contents up to 6.1%, whereas the Ca content is in general less than 1% CaO (Table 6). In terms of FeCO_3 – MnCO_3 – MgCO_3 (Fig. 5), two populations of carbonates can be clearly distinguished. Ankerite occurs as crystals of a few μm in size; the textural relationships indicate that it crystallized after siderite and ferroan rhodochrosite.

Barite was identified in two forms. In the second stage, it occurs as platy crystals from 0.5 to 1 mm in length, and in the third stage, as smaller grains.

Quartz tends to occur in fine veinlets in association with fibrous siderite or as fine crystals lining cavities.

Calcite is rare and occurs as fine aggregates with the silver minerals.

PARAGENETIC SEQUENCE

The diverse mineralogy, the geochemical relationships and the textural and structural characteristics of the Pb–Ag–Zn (Cu–Ni–Co–Te–Sb) ores suggest that the mineralization took place in at least three stages (Fig. 6). The first stage is characterized by the deposition of sphalerite, pyrite, chalcopyrite and siderite. The main deposition of the Ag- and Ni–Co-bearing minerals occurred during the second stage, with some continuation into the third. The paragenetic sequence of the third stage concludes with the deposition of Te. It should be noted that no zone of supergene enrichment could be distinguished, and the zone of oxidation is insignificant.

CONCLUDING REMARKS

The deposits of the eastern side of the Famatina Range are epithermal in origin. On the basis of the products of hydrothermal alteration and the ore–gangue mineral assemblages, three types of deposits in this metallogenic subprovince associated with the intrusion of the rhyodacite–dacite porphyry complex were identified: porphyry Mo–Cu–Au deposits, acid-sulfate-type deposits (the Cu–Au districts) and adularia–sericite type deposits (the Pb–Ag–Zn mineralizations).

The La Mejicana, Los Bayos and Offir Cu–Au districts seem to be spatially and temporally related to shallow hydrothermal systems. This close relationship with a magmatic source is made evident by a high fugacity of sulfur, indicated by the extensive acid sulfate alteration and the assemblage enargite – covellite – pyrite. The interaction of the sulfuric acid solutions (formed from SO_2 in contact with water) and the host rock produced the advanced argillic alteration associated with the ore. The deposits in the La Mejicana, Los Bayos and Offir districts are, therefore, interpreted as the near-surface, low-temperature equivalents of porphyry copper systems.

In contrast, the Pb–Ag–Zn (Cu–Ni–Co–Te–Sb) mineralizations of the Caldera, Tigre and Cerro Negro districts, characterized by the presence of sericitic and potassic alteration, show a diverse mineralogy that is very different from that of the acid-sulfate-type deposits, consisting of rare base-metal sulfides and abundant silver-bearing sulfosalts and tellurium-bearing minerals in a gangue of siderite and ferroan rhodochrosite. The structural characteristics of the area, such as the fault density, are an important control on the extent of the mineralization. The structurally enhanced permeability allowed extensive circulation

PARAGENETIC SEQUENCE

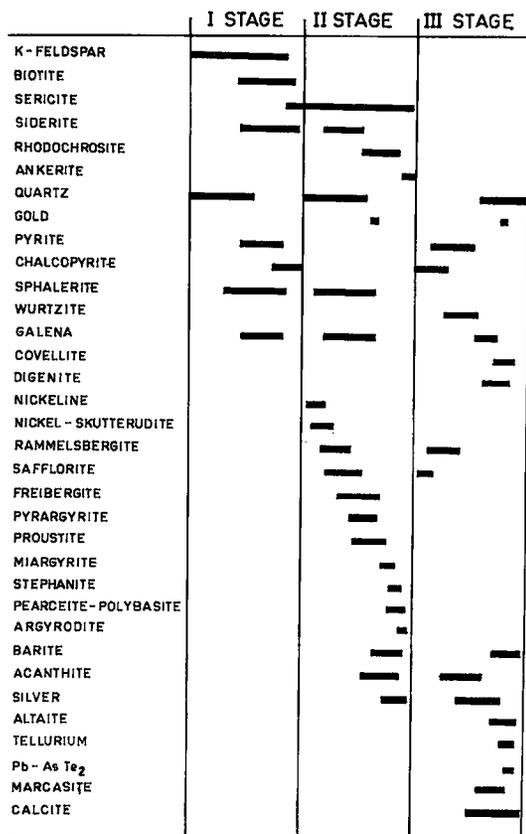


FIG. 6. Paragenetic sequence of minerals.

of fluid in the host rocks. The K-feldspar – sericite occurrence indicates almost neutral pH conditions. In accordance with Henley's ideas (in Heald *et al.* 1987) about hydrothermally active systems, we believe that these silver-rich deposits with minor base metals were probably formed from relatively saline fluids (4.2 to 6.2 eq. % NaCl) with a low H₂S content at a considerable distance from the heat source, which could lie at depth. An increase in the alkalinity as well as in the oxygen fugacity of the argentiferous mineralizing solutions is made evident by the precipitation of abundant native silver following acanthite.

The mineralogical assemblages show a three-stage temporal evolution of the composition of the mineralizing fluids. The first stage is characterized by the deposition of Cu, Zn and Pb sulfides in a gangue of siderite. The sphalerite is iron-rich. During the second stage, the deposition of gold and the main deposition of Ag-bearing- and Ni–Co-bearing minerals in a gangue of ferroan rhodochrosite and quartz took place. The sphalerite formed at this stage shows enrichment in Mn, Cd, Ge and As, and galena, in Bi, As, Hg and Cd. Stage III is characterized by the deposition of Te-bearing minerals in a gangue of calcite and quartz. Only galena of the third stage is enriched in Te. Despite the lack of ¹⁸O isotopic data, we contend that the mineralizing solutions that formed the Caldera, Tigre and Cerro Negro deposits had an important component of meteoric water.

From a lithotectonic point of view, the ore deposits on the eastern side of the Famatina Range seem to be restricted to the back-arc basin of the Tertiary magmatic arc, and are directly related to the silicic to intermediate magmatism of Pliocene age. These deposits formed in tensional cracks that appeared following the main stage of compression, late in the subduction phase of the orogenic cycle.

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