A CONTRIBUTION TO THE KNOWLEDGE OF THE MINERALIZATION AT MINA CAPILLITAS, CATAMARCA

Hubert PUTZ, Werner H. PAAR and Dan TOPA

Department of Materials Engineering and Physics (Division of Mineralogy), University of Salzburg, Austria;
Email: hubertputz@yahoo.de

ABSTRACT

The Capillitas deposit is part of the Farallón Negro Volcanic Complex, Catamarca Province, northwestern Argentina. The epithermal mineralization is related to the Capillitas diatreme, a volcanic pipe composed of intrusive and volcanoclastic rocks of rhyolitic to dacitic composition of Miocene age which is located in the granitic basement block of the Sierra de Capillitas. The deposit consists of numerous mineralized veins which crosscut the diatreme volcanics and the adjacent Capillitas granite. The different geological environments, the alteration features and the ore mineralogy enable to distinguish between high- and intermediate-sulfidation environments, which are overprinted by supergene processes. The first group is accompanied by advanced argillic alteration and silicification and in the second rhodochrosite and quartz are the predominant gangue minerals. The polymetallic character of the Capillitas epithermal deposit is clearly emphasized by its complex Cu-Pb-Zn-Fe-Mn-As-Sb paragenesis, with minor W, Bi, Sn, Te, Ag and Au and traces of Ge, Cd, In, V, Ni and Tl, present in more than 150 different minerals. Additionally, Capillitas represents the type locality for the two new mineral species putzite and catamarcaite. The hydrothermal vein system at Capillitas was formed under strongly changing p-T-X conditions. Cu, As, Te, Sn, Bi and Au represent the key metals of the high-sulfidation stage whereas the metal association Zn-Pb-Ag is typical for the intermediate-sulfidation stage. Based on fluid inclusion studies, the Capillitas deposit can be characterized by temperatures of ore formation mostly below 300 °C and low salinities (< 6 wt. % NaCl equivalent).

Keywords: *Capillitas diatreme, Epithermal veins, High-sulfidation, Intermediate-sulfidation, Bornite.*

RESUMEN: *Aportes al conocimiento de la mineralización de mina Capillitas, Catamarca.* El yacimiento Capillitas pertenece al Complejo Volcánico Farallón Negro, provincia de Catamarca. La mineralización del tipo epitermal está relacionada con la diatrema Capillitas, una chimenea volcánica ubicada en el bloque de basamento de la sierra de Capillitas y constituida por rocas intrusivas y volcaniclásticas del Mioceno de composición riolítica a dacítica. Se reconocieron numerosas vetas mineralizadas que se encuentran encajadas en las rocas volcánicas y en el granito adyacente. En base a las diferentes litologías, los tipos de alteración y los minerales de mena se puede distinguir pulsos mineralizantes de alta sulfuración y de sulfuración intermedia, transformados por procesos supergénicos. El primer grupo está acompañado por silicificación y alteración arcillosa avanzada; en el segundo, rodocrosita y cuarzo son los minerales de ganga predominantes. El carácter polimetálico del yacimiento epitermal Capillitas está bien documentado por su paragénesis compleja de Cu-Pb-Zn-Fe-Mn-As-Sb, con W, Bi, Sn, Te, Ag y Au como elementos menores y Ge, Cd, In, V, Ni y Tl como elementos traza. Además, Mina Capillitas representa la localidad tipo de las nuevas especies minerales putzita y catamarcaíta. El sistema hidrotermal de Capillitas está caracterizado por condiciones variables de P-T-X. Los elementos Cu, As, Te, Sn, Bi y Au representan los metales característicos del estadio de alta sulfuración. La asociación Zn-Pb-Ag es muy típica para el estadio de sulfuración intermedia. Basado en estudios de inclusiones fluidas, el yacimiento Capillitas muestra temperaturas de formación generalmente por debajo de 300°C y bajas salinidades (< 6 % en peso de NaCl equivalente).

Palabras clave: *Diatrema Capillitas, Vetas epitermales, Alta sulfuración, Sulfuración intermedia, Bornita.*

INTRODUCTION

The Capillitas epithermal vein-type deposit (lat. 27° 20' 30" S, long. 66° 23' W) is located in the Andalgalá's Department, Catamarca province, north-western Argentina, at elevations between 2,800 and 3,400 m above sea level. It is well-known for its famous mining history (Stelzner 1885, 1924, Kittl 1925, 1940, Angelelli *et al.* 1974, Márquez-Zavalía 1988, 1999). Local *indios* are considered to have been the first miners of gold from the alluvial deposits and outcrops. Later on, during the 17th and 18th centuries, Jesuit priests successfully mined gold. Since approximately 1850, private companies from Argentina and England were active in the district, and mined for copper, with gold and silver recovered as by-products. The mining for base and precious metals terminated during the first decades of the 20th century as the rich portions of the veins were exhausted. Additionally, signi-

ficant problems in beneficiation were encountered with the remaining complex ores at deeper levels of the veins. However, the Capillitas district still remains the source of magnificent and gem-quality rhodochrosite, which had been mined for more than fifty years.

Capillitas' rhodochrosite was firstly reported by Stelzner (1873) and, since then, many contributions were devoted to different aspects of this carbonate (i.e., Radice 1949, Angelelli *et al.* 1974, Saadi and Grasso 1988, Cassedanne 1998 and Lieber 2000). From a mineralogical point of view, Capillitas is one of the most interesting mineral deposits of Argentina. During the last two decades, the central part of the Capillitas deposit was the subject of intensive mineralogical research by Márquez-Zavalía (1988, 1999) who described more than 100 mineral species from there. However, with exception of the sector Ortiz, the mineralogy and ore geology of the granite-hosted veins in the vicinity of the Capillitas diatreme was not comprehensively studied. Thus, a detailed investigation of the mineralization of the Capillitas deposit, with the emphasis on the La Argentina, Nueva Esperanza, La Grande, La Rosario and Bordón veins, was carried out as part of the project "Contributions to the Tertiary metallogeny of structurally controlled and precious metal-bearing mineralizations of NW-Argentina" of the Austrian Science Foundation (FWF). The full results can be found in Putz (2005) and a short compilation is presented here.

GEOLOGICAL SETTING

Mina Capillitas is part of the Farallón Negro Volcanic Complex, which is located at the interface between the Sierras Pampeanas and the Puna physiographic and tectonic provinces. The oldest rocks exposed in this area are metamorphic rocks of Precambrian and Early Paleozoic age such as migmatitic and amphibolitic gneisses of the Sierra Aconquija Complex and metapelites of the Lower

Cambrian Suncho Formation (Aceñolaza *et al.* 1982). They were intruded by various Paleozoic granitoids, defined as the peraluminous Capillitas Batholith (Toselli *et al.* 1996). Granitic magmatism took place from the Ordovician to the Silurian and thus belongs to the Famatinian magmatic cycle (Aceñolaza *et al.* 1982, Toselli *et al.* 1996). Tertiary continental red beds of the El Morterito Formation locally overlie the crystalline basement (Aceñolaza *et al.* 1982).

According to Sasso (1997) and Sasso and Clark (1998), the Farallón Negro Volcanic Complex, covering an area of approximately 700 km², is interpreted as a deeply eroded remnant of a stratovolcano with small outlying intrusive and/or volcanic centers of Miocene age. Several steps in the evolution of this volcanic complex can be divided (Sasso and Clark 1998). The early volcanic history of the area, from 12.6 to 8.5 Ma, was characterized by the eruption of basalts, basaltic andesites and dacites from several volcanic centers. The main Farallón Negro stratovolcano construction commenced at ca. 8.5 Ma, covering the precursor extrusive centers with thick andesitic to dacitic flows and breccias. Stratocone evolution was accompanied and followed by intrusive and hydrothermal activity, extending from 8.5 to 5.5 Ma. The emplacement of dacite and rhyolite dikes marked the termination of magmatic activity in the region. A cluster of polymetallic, but Cu- and Au-dominated hydrothermal deposits is temporally and spatially associated with the Farallón Negro Volcanic Complex. They comprise both porphyry Cu-Au deposits (e.g., Bajo de la Alumbrera and Agua Rica) and epithermal vein-type deposits (e.g., Capillitas and Farallón Negro - Alto de la Blenda).

The Capillitas district itself is composed of the Sierra de Capillitas, an uplifted basement block of the Capillitas Batholith, the NE-oriented Cuesta de Capillitas and the Capillitas diatreme. Within the Cuesta de Capillitas, several units of andesitic volcanics of an early extrusive stage in the history of the Farallón Negro Volca-

nic Complex overly the sediments of the El Morterito Formation (Breitenmoser 1999). The Capillitas diatreme, a funnel shaped volcanic pipe composed of extrusive and intrusive rocks of rhyolitic to dacitic composition, is exposed several hundred meters west of the small settlement Capillitas. It is oval in shape (1,600 m by 900 m) and elongated in a NE direction (Fig. 1). The main lithologies are lapilli tuff, ignimbrite, rhyolite porphyry, lithic tuff and dacite porphyry (Breitenmoser 1999, Hug 1999, Márquez-Zavalía 1988, 1999). Basaltic melanocratic dykes and leucocratic dykes of rhyolitic composition are exposed north and west of the diatreme. Based on geochronological data, 5.16 ± 0.05 Ma (Ar-Ar on K-feldspar) for the dacite porphyry (Sasso 1997), the Capillitas diatreme postdates the andesitic volcanics deposited in the Cuesta de Capillitas. Two minor intrusive bodies are exposed a few kilometers west of the Capillitas diatreme: Bajo El Estanque and Alto El Estanque. They are composed of hydrothermally altered rocks of andesitic and rhyolitic composition (Breitenmoser 1999). Clastic sediments of Quaternary age cover most of the andesitic volcanics in the Cuesta de Capillitas and the granitic basement in the Campo del Arenal, a shallow basin situated to the north of Capillitas (Breitenmoser 1999).

CAPILLITAS EPITHERMAL DEPOSIT

The Capillitas deposit has a pronounced polymetallic character and consists of numerous mineralized veins which crosscut the diatreme volcanics and the adjacent Capillitas granite north and west of the Capillitas diatreme (Fig. 1). Two preferred orientations of the veins are observed (Fig. 1): ENE (*e.g.*, La Grande, Luisita, La Rosario, La Argentina and Nueva Esperanza veins) and WNW to NNW (*e.g.*, Capillitas, Nueve, Restauradora, Ortiz and Bordón veins). They are either hosted in granite (*e.g.*, Ortiz and Bordón veins), in rhyolite dykes within granite (*e.g.*, La Grande, Luisita, La Ar-
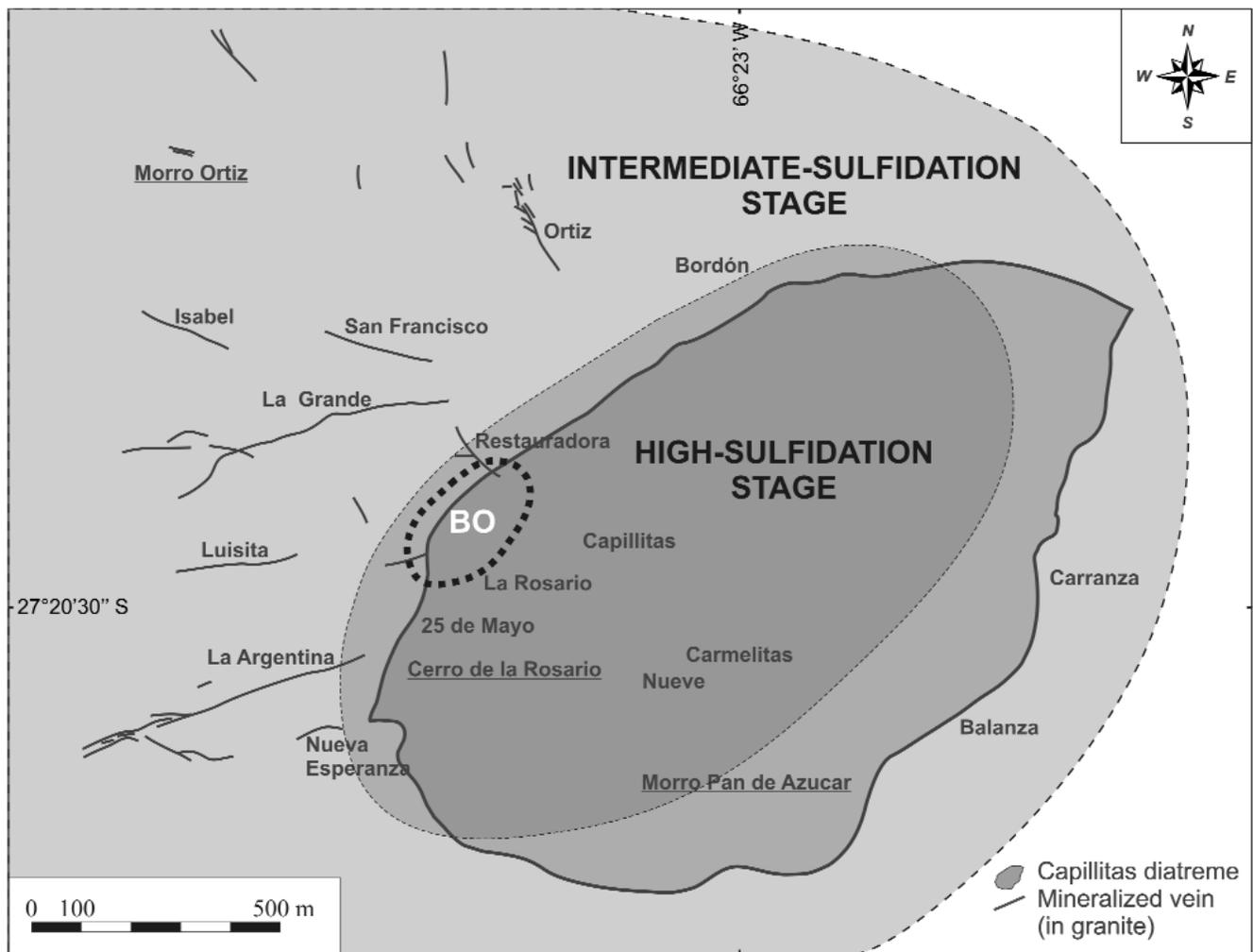
Figure 1: Simplified geologic map and estimated zonation of the epithermal mineralization at the Capillitas deposit. The high-sulfidation stage mineralization was overprinted by the intermediate-sulfidation stage mineralization; BO = bornite-chalcocite-digenite-rich ores.

gentina and Nueva Esperanza veins) or in the diatreme volcanics (mainly in ignimbrite and rhyolite porphyry; *e.g.*, Capillitas, Carmelitas and Nueve veins). The ENE-oriented veins are commonly steeply (70° to 85°) dipping to the S or, less frequent, to the N; the WNW to NNW-oriented veins are mainly dipping to the SW, averaging between 60° and 80°. At the surface, the veins are easily observed because they form pronounced silicified outcrops with dark brown to black color (*e.g.*, La Argentina vein). The veins can be traced along strike from a few meters up to 800 m; their vertical extent is unknown but estimated to be more than 500 m. The major veins consist of numerous lenticular to tabular ore bodies of variable length and width that pinch, swell and

anastomose. Similar to other epithermal vein-type deposits, the distribution of these *bonanzas* is very irregular, both along strike and dip. The thickness of the mineralized veins is ranging from a few cm up to more than 2.5 m (*e.g.*, Capillitas and La Rosario veins), averaging at 50 to 70 cm (Angelelli and Rayces 1946).

Hydrothermal Alteration
In the Capillitas area, at a late stage of the diatreme history, hydrothermal activity caused alteration and subsequent mineralization of the diatreme volcanics, granite and granite-hosted dykes. The alteration types and their intensities mainly depend on the host rock lithology. Hydrothermal alteration overprint of the diatreme volcanics encompasses silicifi-

cation, advanced argillic alteration, argillitization and pyritization (Angelelli and Rayces 1946, Márquez-Zavalía 1988, 1999). The melanocratic dykes hosted in granite typically show propylitization whereas the leucocratic dykes show sericitization, argillitization (feldspar destructive alteration) and, more rarely, pyritization. If the leucocratic dykes constitute the host rock of the mineralized veins they are strongly silicified, sometimes leading to a pervasive replacement of the whole rock (*e.g.*, La Argentina vein). The granitic basement is altered around the Capillitas diatreme (halo of several tens of meters) and in the vicinity of the dykes and epithermal veins (up to several meters in width). In general, argillic alteration occurs as wallrock altera-

tion around the granite- and rhyolite dyke-hosted veins, usually as small veinlets of clay minerals. Advanced argillic alteration typically accompanies high-sulfidation mineralization (*e.g.*, Nueva Esperanza vein).

Mineralization styles

The different geological environments, the alteration features and the ore mineralogy enable to distinguish between high- and intermediate-sulfidation environments, which are overprinted by supergene processes (Putz 2005). Many textures (*e.g.*, vugs and cavities, crustiform and colloform vein-filling, cockade breccias) are indicative for open space filling, which is typical for a mineralization in extensional structures. Structural reactivation is indicated by fault planes with slickensides and vein breccias. The polymetallic character of the Capillitas epithermal deposit is clearly emphasized by its complex Cu-Pb-Zn-Fe-Mn-As-Sb paragenesis, with minor W, Bi, Sn, Te, Ag and Au and traces of Ge, Cd, In, V, Ni and Tl, and the large number of more than 150 different mineral species (Márquez-Zavalía 1988, Putz 2005; Figs. 2, 3). Pyrite, sphalerite, galena, tennantite-tetrahedrite, chalcopyrite and enargite are the predominant mineral species comprising more than 95 % of the total sulfide content. Quartz, rhodochrosite and barite are the main gangue minerals. Additionally, several new mineral species were identified and characterized, for which Capillitas represents the type locality. Two of them, putzite - $(Cu_{4.7}Ag_{3.8})_{\Sigma 8}GeS_6$, and catamarcaite - Cu_6GeWS_8, have already been accepted by the IMA and published elsewhere (Paar *et al.* 2004, Putz *et al.* 2006b; Figs. 3b-c). The characterization of two further Ge-sulfides, unnamed $Cu_8Fe_2ZnGe_2S_{12}$ and a briartite-type phase (Putz 2005, Putz *et al.* 2006b; Figs. 3b-c), a Bi-sulfosalt (member of the cuprobismutite-homologous series; Fig. 2d) and several secondary phases, all of which possibly represent new mineral species, is in progress.

The **high-sulfidation stage assembla-ges** (*e.g.*, Nueva Esperanza and La Rosario veins) are typically composed of pyrite, enargite-luzonite, tennantite-tetrahedrite-goldfieldite, hübnerite, Bi-sulfosalts (*e.g.*, aikinite-bismuthinite, wittichenite), Sn-sulfides (*e.g.*, colusite-nekrasovite, stannoidite, mawsonite) and ± native gold, accompanied by advanced argillic alteration (quartz, kaolinite/dickite, alumino phosphate-sulfates, rutile) and vuggy quartz (Putz 2005; Figs. 2a-e). Goldfieldite and Te-bearing tennantite-tetrahedrite is characteristically associated with precious metal tellurides such as hessite, krennerite, calaverite, sylvanite and petzite (Márquez-Zavalía and Craig 2004, Putz 2005; Fig. 2c). Both the Sn-sulfides (especially the members of the colusite-nekrasovite series) and the members of the fahlore group (tennantite-tetrahedrite-goldfieldite series) usually show a very complex chemical zonation (Figs. 2a-b). This type of mineralization represents an early, high-temperature stage and is mainly restricted to the diatreme-hosted veins (Capillitas and Carme-litas sectors). It usually consists of disseminated ores that replace or impregnate leached country rock (granite, rhyolite dykes, diatreme volcanics). Massive to banded sulfide veins (mainly consisting of pyrite) locally occur in the deeper parts of the veins (*e.g.*, Capillitas, Nueve and Bordón veins).

The granite- and rhyolite dyke-hosted veins remote from the diatreme show typical **intermediate-sulfidation stage assemblages** (*e.g.*, La Argentina and Ortiz veins) which consist of galena, Fe-poor sphalerite, tennantite-tetrahedrite, chalcopyrite, pyrite, marcasite and ± native silver and Ag-sulfides (proustite, argyrodite, pearceite, acanthite) with rhodochrosite, quartz and barite as the predominant gangue minerals (Putz 2005; Figs. 3d-f). This type of mineralization is also found in the diatreme-hosted veins, but is distinctly separated from the older high-sulfidation assemblages. Open space filling and rhythmic banding (*e.g.*, the rhodochrosite-rich parts) are ubiquitous textural features (*e.g.*, Ortiz, La Argentina

and 25 de Mayo veins). Vein breccias are commonly observed and usually constitute cockade breccias (*e.g.*, Ortiz and La Argentina veins).

A significantly different mineral assemblage is represented by **bornite-digenite-chalcocite-rich ores** that are mainly restricted to the La Rosario sector (Figs. 2f, 3a-c). They are characterized by a very complex and unique mineralogy and two sub-types can be classified. (1) Massive bornite-digenite-chalcocite ore with subordinate hübnerite, pyrite, tennantite, wittichenite, sphalerite, mawsonite and thalcusite yielded several Ge-bearing sulfides: putzite, catamarcaite, unnamed $Cu_8Fe_2ZnGe_2S_{12}$ and a briartite-type phase (Paar *et al.* 2004, 2005, Putz 2005, Putz *et al.* 2002a, 2002b, 2006a, 2006b; Figs. 2f, 3a-c). (2) A disseminated to stockwork-like sub-type is characterized by the abundant deposition of Sn-bearing (mawsonite, colusite-nekrasovite, stannoidite) and Te-bearing minerals (goldfieldite, hessite). These ores are interpreted as remnants of a bornite-rich high-sulfidation mineralization which was overprinted by a late-stage supergene mineralization with the deposition of chalcocite, digenite and covellite.

Mineral and metal zonation

Mineral and metal zonation is clearly observable at the Capillitas deposit (Fig. 1). From top to bottom an oxidation, cementation and primary zone can be distinguished. The oxidation zone is developed throughout the deposit and restricted to the uppermost 40 to 50 meters of the veins (Angelelli and Rayces 1946). Mn- and Fe-oxides/-hydroxides, cuprite, malachite, azurite, brochantite, cyanotrichite, cerussite, anglesite and beudantite-osarizawaite occur as common phases. Supergene enrichment led to the development of a cementation zone, typified by the deposition of chalcocite, digenite and covellite at and near the water table. It is mainly restricted to the Cu-rich central part of the deposit. Especially in the La Rosario and Capillitas (former Restauradora I) veins it is well developed and
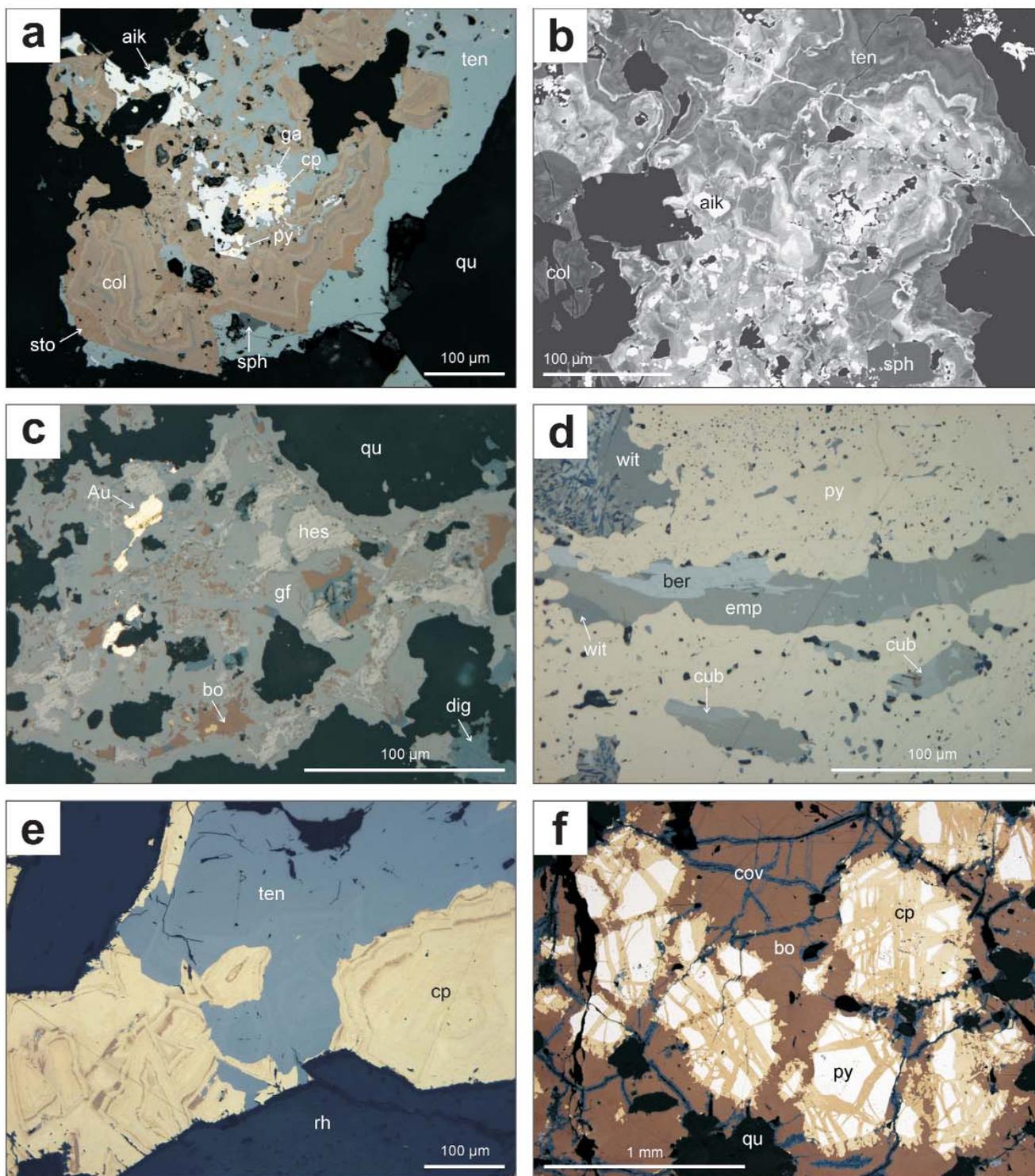
Figure 2: Ore mineralogy of high-sulfidation stage assemblages and bornite-rich ores. a) Inclusions of strongly zoned colusite-nekrasovite (col) with rims of stannoidite (sto) in tennantite (ten) and associated with aikinite (aik), galena (ga), chalcopyrite (cp), sphalerite (sph) and pyrite (py); qu is quartz. Nueva Esperanza vein. b) Bismuth-bearing tennantite (ten) with strong chemical zonation (the bright areas contain up to more than 15 wt.% Bi) and inclusions of zoned colusite-nekrasovite (col), aikinite (aik) and sphalerite (sph). Nueva Esperanza vein. c) Zoned aggregate of tellurian tennantite-golfieldite (gf) with inclusions of hessite (hes), native gold (Au), bornite (bo) and digenite (dig); qu is quartz. La Rosario vein. d) Pyrite (py) with inclusions of Bi-sulfo-salts: berryite (ber), emplectite (emp), a member of the cuprobismutite-homologous series (cub) and wittichenite (wit). Bordón vein. e) Tennantite (ten) is replaced by chalcopyrite (cp); note the complex zonation of chalcopyrite with brownish, As-rich bands; rh is rhodochrosite. Nueva Esperanza vein. f) Replacement relics of pyrite (py) and chalcopyrite (cp) in bornite (bo); covellite (cov) replaces bornite along irregular fractures; qu is quartz. La Rosario vein.
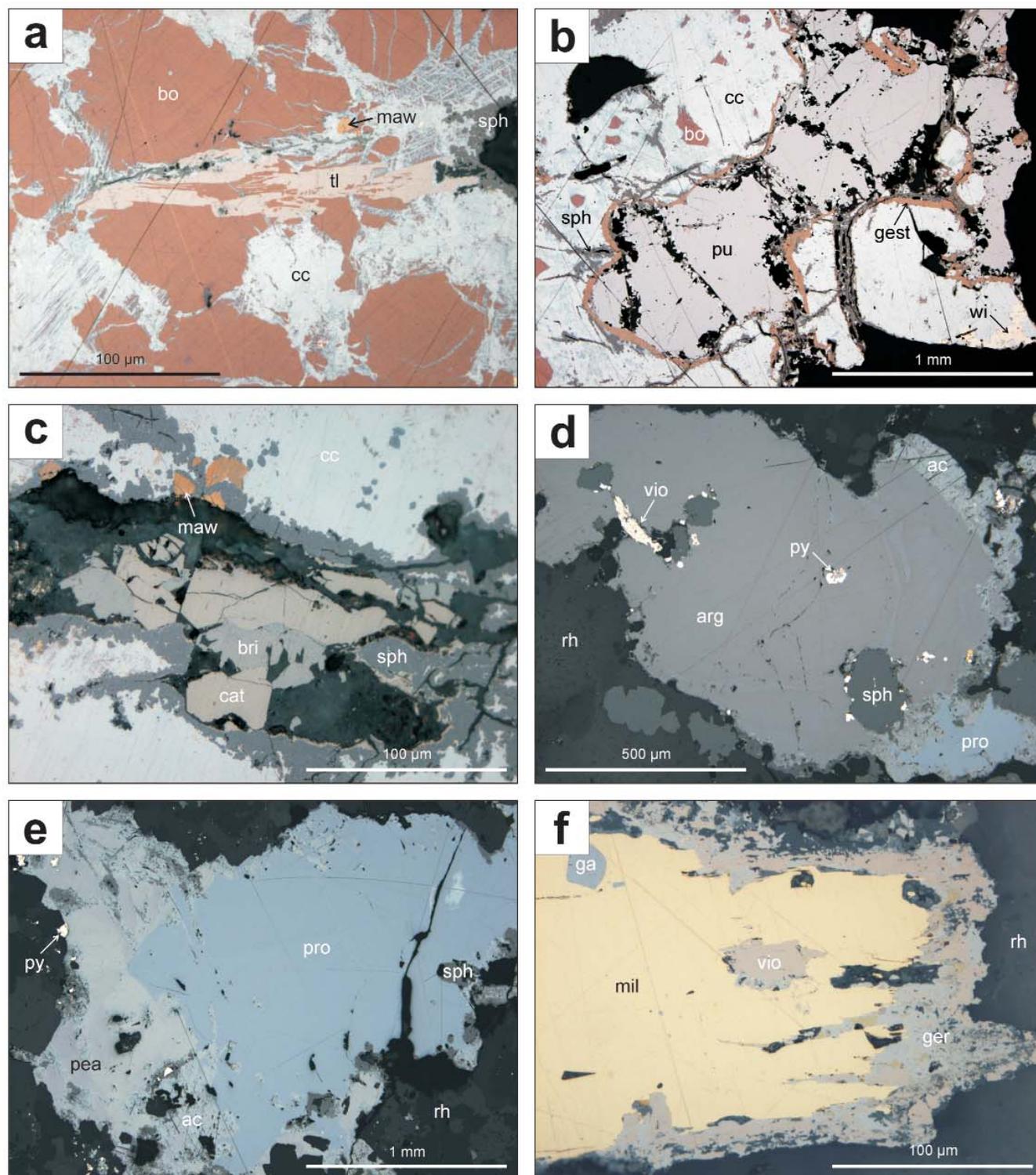
Figure 3: Ore mineralogy of bornite-rich ores and intermediate-sulfidation stage assemblages. a) Thalcusite (tl) as tabular inclusions in bornite (bo) and chalcocite (cc); sph is sphalerite, maw mawsonite. La Rosario vein. b) Large inclusion of putzite (pu) in chalcocite (cc) with unnamed $Cu_8Fe_2ZnGe_2S_{12}$ (gest), sphalerite (sph), wittichentite (wi) and relics of bornite (bo). La Rosario vein. c) Fractures in chalcocite (cc) are rimmed by sphalerite (sph) and filled with euhedral catamarcaite (cat) and anhedral grains of a briartite-type phase (bri); maw is mawsonite. La Rosario vein. d) Argyrodite (arg) is replaced by proustite (pro) and acanthite (ac); further associates are sphalerite (sph), pyrite (py) and violarite (vio); rh is rhodochrosite. La Argentina vein. e) Proustite (pro) is replaced by pearceite (pea) and acanthite (ac); sph is sphalerite, py pyrite, rh rhodochrosite. La Argentina vein. f) Millerite (mil) is replaced by violarite (vio) and gersdorffite (ger); rh is rhodochrosite, ga galena. La Argentina vein.

extends up to 150 m from the surface (Angelelli and Rayces 1946). Additionally, Stelzner (1885) and Kittl (1940) emphasized the richness of copper and precious metals (Au, Ag) in the ores of the ancient workings developed within the cementation zone, which are completely inaccessible nowadays.

The primary zone comprises both high- and intermediate-sulfidation stage ore. The Cu-rich high-sulfidation stage mineralization is mainly restricted to the central parts of the deposit (*e.g.*, Capillitas, La Rosario and Nueve veins). The Pb-Zn-rich mineralization of the intermediate-sulfidation stage overprints the former stage and is developed throughout the deposit (Fig. 1). Neither a vertical nor a horizontal zonation has been observed for the latter stage.

The high-sulfidation stage ore shows strong evidence of vertical zonation, especially in relation to the copper-bearing minerals. Angelelli and Rayces (1946) and Kittl (1940) emphasize the occurrence of bornite and chalcopyrite within the upper parts and enargite and tennantite within the intermediate parts of the veins in the Capillitas and Carmelitas sectors, whereas pyrite becomes the dominant mineral in the deeper parts. Another type of vertical zonation is reflected by the vein-textures of pyrite-enargite-luzonite-bearing assemblages. Massive, pyrite-dominated veins with thin veinlets of enargite-luzonite (*e.g.*, La Rosario vein) constitute a deep sequence whereas disseminated to vuggy pyrite-enargite-hübnerite ore corresponds to a shallow sequence (*e.g.*, Nueva Esperanza vein).

Exploration drilling has proven vein continuity at depth as a stockwork-like to disseminated mineralization composed of pyrite, sphalerite, quartz and rhodochrosite (Angelelli 1984). In analogy to other high-sulfidation systems such as the Nevados del Famatina mining district, La Rioja province (Losada-Calderón and McPhail 1996), where close temporal and spatial relationships between porphyry Cu and epithermal precious metal deposits have been demonstrated,

a porphyry-style mineralization can be inferred somewhat below the epithermal system. However, further exploration data are needed to prove this assumption.

Metal grades and ore reserves

The Capillitas epithermal deposit was mined for copper and precious metals (gold, silver) and the metal content mainly depended on the ore type. High-sulfidation assemblages were rich whereas intermediate-sulfidation assemblages were poor in copper. Massive bornite-digenite-chalcocite ore from the cementation zone of the La Rosario mine (25 % Cu on average) and chalcopyrite-tennantite-rich ores from the upper parts within the primary zone of the La Restauradora mine (18 % Cu on average) constituted the richest copper ore ever mined (Stelzner 1885, 1924). In both ore types the precious metal content was elevated and their respective copper ingots yielded up to 200 - 400 g/t Au and 5 - 6.3 kg/t Ag (Stelzner 1885, 1924). With increasing depth the proportion of Cu-sulfides decreased and thus the copper content of the primary zone diminished to less than 5 % (Angelelli and Rayces 1946). Although the upper levels of the Capillitas deposit - mainly developed within the cementation and upper primary zone - are mined out and practically inaccessible, it can be assumed that chalcocite, digenite, bornite and chalcopyrite constituted the main copper carriers of the ore.

The precious metal (Au, Ag) contents also show a clear dependence on the ore type and zonation (Putz and Paar 2003). Gold is significantly enriched within the oxidation zone where the ancient mining by the Jesuit monks was performed. Angelelli and Rayces (1946) mention the richness in gold of the oxidation zone of the Luisita vein (up to 265 g/t). The recent finding of native gold in platy aggregates up to 15 mm within a strongly oxidized outcrop in the area of the Nueva Esperanza vein ratifies this report (Putz 2005). Parts of the cementation zone are

also rich in gold. According to Stelzner (1885, 1924), the bornite-rich ores from the La Rosario vein sporadically yielded free gold. This was confirmed by microscopic investigations of bornite-chalcocite-rich ore from old dumps near the La Rosario shaft (in former times the La Rosario shaft has also been called Gold Shaft or "pique de oro"). Ores of the high-sulfidation stage usually show gold contents between 1 and 15 g/t (Putz 2005), rarely reaching up to more than 50 g/t (Angelelli and Rayces 1946). A decrease of gold with increasing depth has also been reported by Angelelli and Rayces (1946). In general, gold is lacking in ores of the intermediate-sulfidation stage (Putz 2005). Native gold, usually silver-bearing, is the main gold carrier of the ore whereas gold tellurides (krennerite, calaverite, sylvanite, petzite; Márquez-Zavalía and Craig 2004, Putz 2005) only occur in traces.

Silver is also an economically important element within the ores at Capillitas. It occurs throughout the deposit and its distribution is more uniform. The Cu-rich ores of the cementation zone and upper parts of the primary zone have also been rich in silver (Stelzner 1885, 1924). Ores of both the high-sulfidation and intermediate-sulfidation stage usually have silver contents in the range of 50 to 500 g/t (Putz 2005) and, similarly to gold, a decrease with increasing depth can be observed (Angelelli and Rayces 1946). Interestingly, several portions of the veins, especially those with base metal-rich intermediate-sulfidation mineralization, can be extremely enriched in Ag (*e.g.*, ore shoots of the La Argentina vein which yielded up to 10 kg/t Ag; Angelelli and Rayces 1946, Putz 2005).

In contrast to gold, the mineralogy of silver is more complex. Microscopic investigations and microprobe analyses yielded a wide range of (possible) silver carriers of the ore (Putz 2005). Due to their silver content (0.10 to 0.30 wt. % Ag) bornite, digenite and chalcocite represent the most important silver carriers of the Cu-rich cementation ores. In Cu-

rich high-sulfidation and intermediate-sulfidation ore, minerals of the tennantite-tetrahedrite series are the sole silver-bearing minerals. They have an average content of 0.10 wt. % Ag but the Bi- and Te-rich members carry up to more than 1 wt. %. Enargite/luzonite, chalcopyrite and sphalerite are virtually free of silver. The Ag-Bi-bearing galena of the late high-sulfidation stage has locally up to several wt. % silver (*e.g.*, Bordón vein). In contrary, Pb-Zn-rich intermediate-sulfidation ore is usually poor in Ag as galena does not contain any silver. Within the Ag-rich ore shoots of the La Argentina vein, the silver carriers are native silver, acanthite, proustite, pearceite and argyrodite (Putz 2005; Figs. 3d-e).

Based on the extensive exploration work in the late 1970's, a total of 387.000 tons of ore reserves (vein-type mineralization) was calculated. The average grades are: Au 2.6 g/t (1.006 kg Au), Ag 108 g/t (41.800 kg Ag), Cu 2.32 %, Pb 1.62 % and Zn 3.10 % (Angelelli 1984). From 1951 until 1979, a total of 2.513 tons of rhodochrosite has been mined; its remaining reserves were estimated at approximately 5.400 tons (Schalamuk *et al.* 1983).

GENETIC MODEL

Based on our extensive field work at Capillitas and the subsequent investigations at the Salzburg University, six episodes of mineralization can be distinguished. These are: 1) pre-mineralization or alteration stage, 2) early high-sulfidation stage (HS I), 3) late high-sulfidation stage (HS II), 4) early intermediate-sulfidation stage (IS I), 5) late intermediate-sulfidation stage (IS II), and 6) oxidation and supergene enrichment (Fig. 4, Putz 2005).

The homogenization temperature of enargite-hosted fluid inclusions of secondary(?) origin ranges from 215.5 to 237.5 °C (average Th 220.8 °C), with salinities between 2.57 and 4.80 wt. % NaCl equivalent (Putz 2005). These fluids probably belong to the tennantite-rich, late high-sulfidation stage that has overprinted enargite deposition at Capillitas. Fluid in-

clusions in sphalerite, rhodochrosite and quartz of the intermediate-sulfidation stage yielded homogenization temperatures from 130.0 to 270.5 °C, and salinities between 0.70 and 5.56 wt. % NaCl equivalent (Putz 2005). The highest Th and salinity values were found in iron-bearing sphalerite (202.0 to 270.5 °C; 2.41 to 5.56 wt. % NaCl eq.) and quartz (219.0 to 265.0 °C; 0.70 to 4.65 wt. % NaCl eq.) of the early IS stage. Iron-poor sphalerite (152.0 to 204.5 °C; 1.40 to 3.39 wt. % NaCl eq.), rhodochrosite (130.0 to 195.5 °C; 1.91 to 4.18 wt. % NaCl eq.) and quartz (164.0 to 207.4 °C; 1.22 to 3.06 wt. % NaCl eq.) of late IS stage assemblages show distinctly lower homogenization temperatures but very similar salinities (Putz 2005).

The genesis of the Capillitas epithermal deposit is strongly related to the geologic history of the Capillitas diatreme. The emplacement of the diatreme is structurally controlled and its volcanic evolution can be divided into three stages: pyroclastic stage (formation of a diatreme which is subsequently filled by lapilli tuff and ignimbrite), early intrusive stage (intrusion of the rhyolite porphyry and emplacement of the lithic tuff and the rhyolite dykes) and late intrusive stage (intrusion of the dacite porphyry) (Hug 1999). However, the temporal relationships between ore deposition and intrusion of the dacite porphyry remain unclear.

At a late stage of the diatreme history, highly acidic fluids produced advanced argillic alteration and silicification of the diatreme volcanics and granite-hosted dykes. Quartz, rutile, svanbergite-hinsdalite, members of the kaolinite group and pyrite are typical minerals of the pre-mineralization or alteration stage (Fig. 4). The leached volcanic rocks were subsequently mineralized by high-sulfidation stage minerals.

The early high-sulfidation stage (HS I; Figs. 2a-d, 4) is characterized by the precipitation of pyrite + enargite + hübnerite in a quartz-rich gangue. Luzonite, colusite-nekrasovite, kesterite, stannoidite and tellurian tennantite-goldfieldite crys-

tallized somewhat later (Fig. 2a). Goldfieldite is typically associated with precious metal tellurides such as hessite and calaverite-krennerite (Fig. 2c). The earlier formed tin sulfides are replaced by mawsonite and bismuth is incorporated in members of the bismuthinite series and in complex Cu-Ag-Pb-Bi sulfosalts (berryite, cuprobismutite-homologous and pavonite-homologous series; Fig. 2d). The crystallization of bismuth-rich tennantite, wittichenite, emplectite and matildite terminated this stage. This early HS stage mineralization either consists of disseminated ore that replaced or impregnated the leached country rocks or of massive pyrite veins.

Silver-poor members of the tennantite-tetrahedrite series and iron-poor sphalerite prelude the late high-sulfidation stage (HS II; Figs. 2e, 4). Chalcopyrite and galena crystallized later and frequently replaced the earlier formed sulfides (Fig. 2e). Native gold is typically associated with tennantite. Ag-Bi-bearing galena, lillianite homologues, tetradymite, stannite, vinciennite, roquesite, seligmannite, bournonite and semseyite formed during this stage but their exact position within the sequence is debatable. Massive to banded sulfide veins are a typical feature of this stage. Bornite crystallized at the end of the high-sulfidation stage in the central sector of the Capillitas deposit (sector La Rosario; Fig. 2f). It usually contains numerous inclusions of pyrite, colusite-nekrasovite, stannoidite, wittichenite, tennantite-tetrahedrite-goldfieldite, chalcopyrite and hübnerite, which belong to the HS I and HS II stages. Putzite, thalcusite, mawsonite and tiny droplets of wittichenite and galena probably formed co-genetically (Figs. 3a-b).

Reactivation of the existing structures (diatreme-hosted veins and rhyolite dyke-hosted veins within granite) and opening of new ones (granite-hosted veins) induced the ascent of "new", moderate to low-salinity ore-bearing fluids of intermediate-sulfidation state. Repeated brittle deformation events either caused brecciation or created openings. In
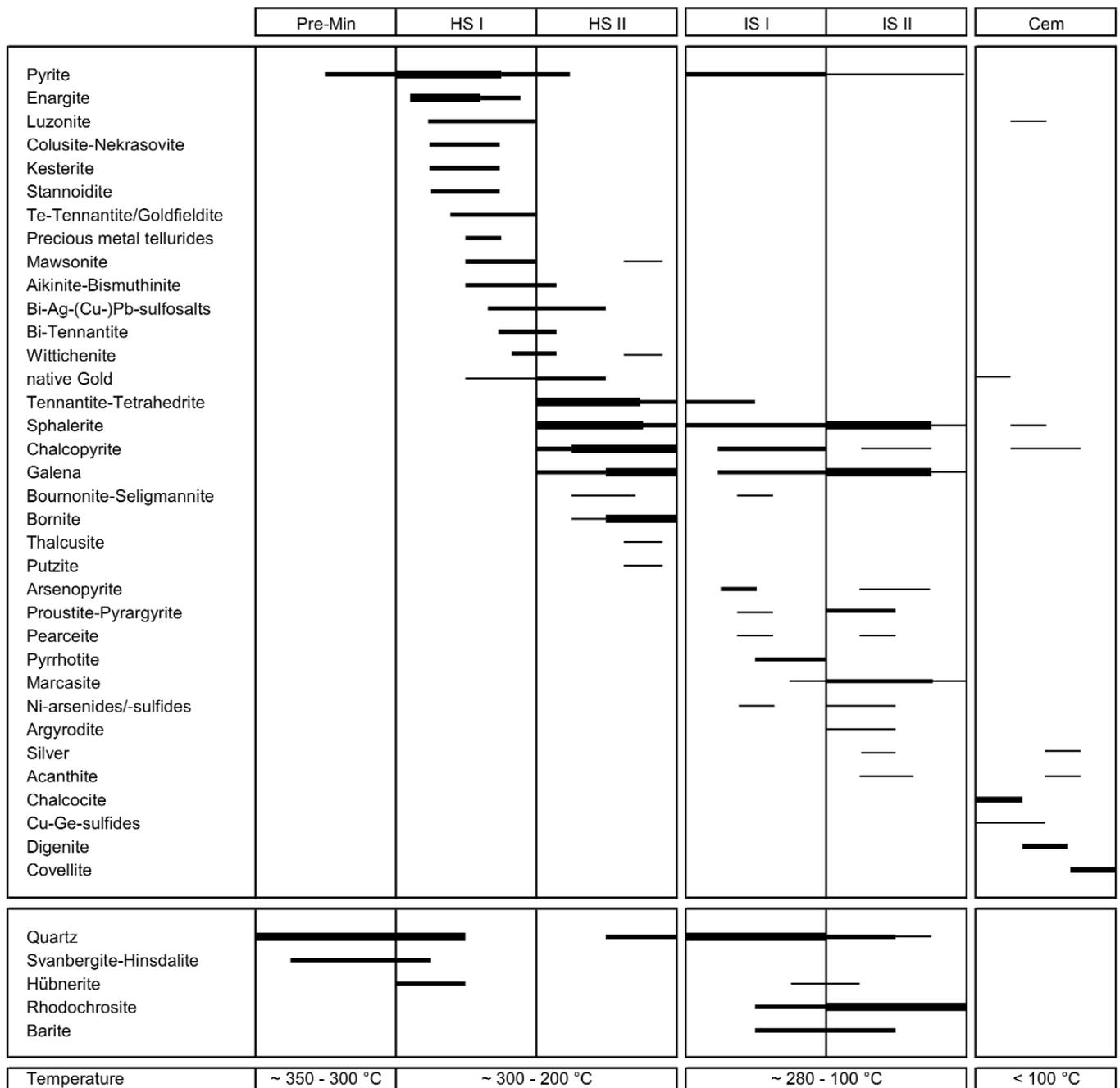
Figure 4: Paragenetic sequence of the Capillitas epithermal deposit; for explanation see text.

strong contrast to the high-sulfidation stage ore, the vein filling is crustiform to colloform, which is indicative for open-space filling. Silica and manganiferous carbonates are the predominant gangues. At the beginning of the early intermediate-sulfidation stage (IS I; Fig. 4), pyrite, dark brown, iron-bearing sphalerite, chalcopyrite, galena and minor tennantite were formed in a quartz-rich gangue.

Trace amounts of Ag- and Sb-sulfosalts (proustite-pyrargyrite, pearceite, diaphorite, Ag-tetrahedrite, Ag-tennantite, bournonite), arsenic, rammelsbergite, löllingite, arsenopyrite, hematite and hübnerite are typical for this stage. Pyrrhotite crystallized at the end of the IS I stage.

The late intermediate-sulfidation stage (IS II; Figs. 3d-f, 4) is characterized by the crystallization of greenish yellow to

honey-yellow, iron-poor to iron-free sphalerite and coarse-grained galena. Quartz, rhodochrosite and barite are the predominant gangue minerals; anhydrite and fluorapatite occur in traces. In several sectors of the granite-hosted veins, silver was significantly enriched during this stage (Figs. 3d-e). The supposed sequence of crystallization of the Ag-minerals is: argyrodite + proustite → pear-

ceite → argentite → native silver → acanthite. Millerite, gersdorffite, violarite, greenockite and chalcopyrite are rare associates of this assemblage (Fig. 3f). Pyrrhotite was altered to fine-grained intergrowths of marcasite and pyrite and hematite is replaced by magnetite. The last pulses are represented by the abundant deposition of banded rhodochrosite (including the famous stalactites) containing only trace amounts of sulfides (sphalerite, galena, pyrite, marcasite and chalcopyrite). Finally, Mn-Zn-Fe-bearing carbonates ("capillitite" and "oligonite") precipitated as the latest minerals of this stage. Soon after the emplacement of the Capillitas diatreme, the Sierra de Capillitas basement block was rapidly uplifted and exposed to erosion. Ongoing erosion resulted in the exposure of the epithermal veins and led to the formation of the oxidation and cementation zones (Fig. 4). Due to supergene processes, hypogene bornite was converted to chalcocite and digenite. The crystallization of catamarcaite, unnamed $Cu_8Fe_2ZnGe_2S_{12}$, a briartite-type phase, betekhtinite, and late generations of chalcopyrite, luzonite, sphalerite and native gold is probably related to this event (Figs. 3b-c). Additionally, but under meteoric conditions, chalcopyrite, bornite, chalcocite and digenite were transformed to covellite and "blue-remaining covellite".

CONCLUSIONS

The hydrothermal vein system at Capillitas was formed under strongly changing p-T-X conditions. Cu, As, Te, Sn, Bi and Au represent the key metals of the high-sulfidation (HS) stage whereas the metal association Zn-Pb-Ag is typical for the intermediate-sulfidation (IS) stage (Fig. 4). Sulfidation states (Einaudi *et al.* 2003) ranged from very high (early HS stage) to intermediate (late HS stage, IS stage), and pH conditions from highly acidic (pre-mineralization) to moderately acidic (HS stage, early IS stage) to nearneutral (late IS stage). Based on various phase relationships and fluid inclusion

studies, the temperatures of formation are estimated to be: 350 to 300 °C for the alteration stage, 300 to 200 °C for the high-sulfidation stage, 280 to 100 °C for the intermediate-sulfidation stage, and below 100 °C for the supergene enrichment (Fig. 4).

In general, the Capillitas deposit can be characterized by temperatures of ore formation mostly below 300 °C and low salinities (< 6 wt. % NaCl equivalent) as has been reported elsewhere for epithermal deposits (Hedenquist and Arribas 1999, Sillitoe and Hedenquist 2003). The common spatial and temporal association between high- and intermediate-sulfidation deposits strongly favors a close magmatic relationship (Sillitoe and Hedenquist 2003). Based on their mineralogy and fluid characteristics, they may be considered as being potentially transitional (Einaudi *et al.* 2003). This can be also assumed for the Capillitas deposit, where high- and intermediate sulfidation mineralization show strong evidence for a direct genetic relationship.

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