

Tellurium and precious-metal ore minerals at Mina Capillitas, Northwestern Argentina

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With 5 figures and 1 table

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Abstract: Mina Capillitas is an epithermal-type deposit located in Catamarca province of NW Argentina. Six separate stages of mineralization were identified in this complex Cu–Au–S–As–Sb–Pb–Zn association; the native elements (Au and Te) and Te minerals are concentrated in the fourth stage. Gold occurs as small grains with an average fineness of 920, hosted mainly by quartz and coexists with hübnerite and Bi minerals. Tellurium occurs locally in grains up to 10 µm in diameter, and is associated with the Te-bearing minerals of Au, Ag, Bi, Cu, and Ni. These Te minerals include krennerite, calaverite, sylvanite, petzite, hessite, stützite, goldfieldite, melonite, tetradymite, and possibly volynskite. The grains are generally arranged in larger polycrystalline aggregates. These minerals occur in quartz, generally accompanied by hübnerite, pyrite, chalcopyrite, and Bi- and Sn-bearing minerals.

The mineralizing fluids cooled gradually with the typical temperatures ranges characteristic of epithermal systems. Based on the preponderance of the different gangue minerals, we suggest that the pH of the environment became progressively more basic after the third stage of mineralization. This mineral assemblage together with the fluid inclusion homogenization temperature data indicate that the log f_{S_2} values declined as the fluids deposited the Te-bearing minerals. The absence of tellurium phases in the first three stages suggests that either the source of the tellurium had not yet been tapped or that the log f_{Te_2} lay below –10 to –17, the minimum activity for the Te phases present in stage IV to form.

Key words: telluride, gold, silver, goldfieldite, mineralogy, epithermal deposit, Argentina.

Introduction

Mina Capillitas (27° 27' S, 66° 30' W) is located on the northwestern edge of the Capillitas Range in Catamarca province of northwestern Argentina. It is an epithermal-type deposit related to high-K calcalkaline to shoshonitic magmas which were extruded along the inner magmatic arc of central Andean during Upper Miocene to Recent (VIRAMONTE et al. 1984).

The complex base and precious metal ores of the Mina Capillitas deposit contain a diverse group of Te-bearing minerals which were preliminary and shortly described (MÁRQUEZ-ZAVALÍA & CRAIG 1996, 2000). Although volumetrically small, the relative quantity of sulfide ores and their presence as isolated grains and polymineralic assemblages present an opportunity to examine the conditions of ore genesis. The aim of this paper is to describe the Te minerals and to determine the conditions of their formation.

Geological setting and mineralization

The rocks exposed in and around Mina Capillitas include the Paleozoic Capillitas granite (ACEÑOLAZA et al. 1982) and subordinate Cenozoic units: the terrigenous clastic El Morterito Formation, the Volcanic Complex, and the Quaternary cover deposits. The El Morterito Formation crops 3 km south out of Mina Capillitas where it overlies the Capillitas granite with unconformable contact; it consists of continental conglomerate, sandstone, and claystone lithologies of Miocene age. The volcanoclastics of the Volcanic Complex (GONZÁLEZ BONORINO 1950) overlies the El Morterito Formation. At this unit belongs the ellipsoidal diatreme (1500 by 900 m) placed in Mina Capillitas, infilled with a complex of andesitic breccia, rhyolite, rhyolitic and granitic breccia, dacite porphyry, and peripheral rhyolitic, trachytic and basaltic dykes. Two K/Ar dates from the Pan de Azúcar dacite porphyry and the rhyolite indicate a 5 ± 0.5 Ma age (JICA 1978–81). A Quaternary cover unconformably overlies these older units sporadically, consisting of unconsolidated conglomerate and sand sheets.

Mineralization at Mina Capillitas occurs along NE and NW striking veins that cut the rhyolite, rhyolitic breccia, and granite (Fig. 1), especially along the western margin of the diatreme. Silicification, advanced argillic alteration, and pyritization affect the west-central part of the diatreme, whereas sericitization and subordinate propylitization occur near the periphery.

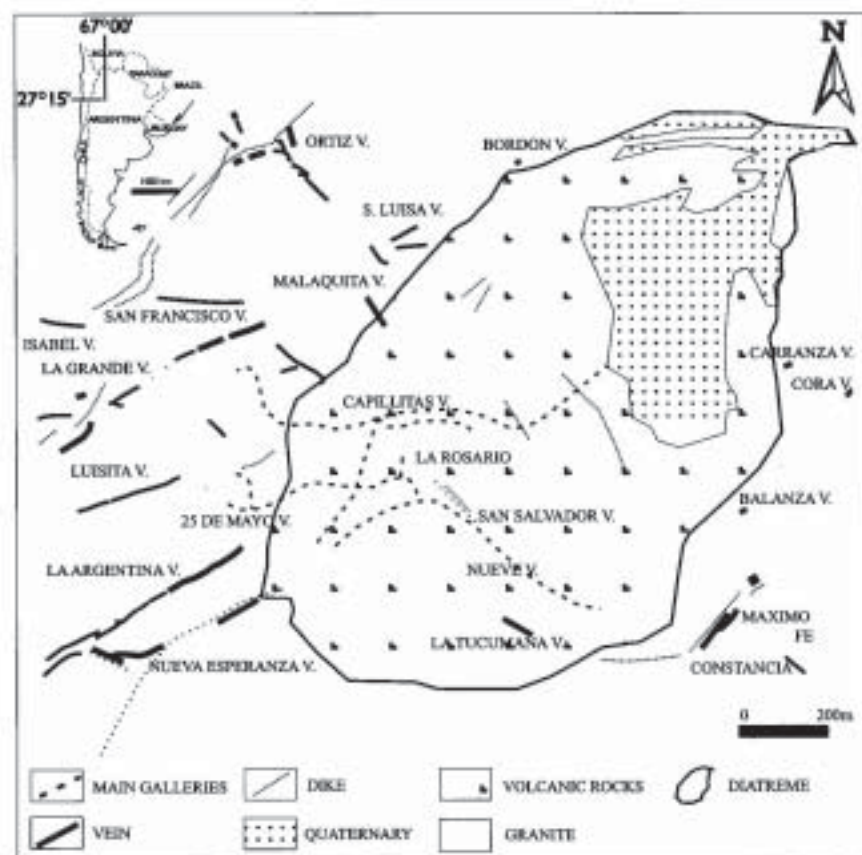


Fig. 1. Principal lithologic units and veins of Capillitas deposit.

MÁRQUEZ-ZAVALÍA (1988, 1999) recognized six stages of ore mineralization, followed by an episode of silica deposition each of which is separated by brecciation episodes. These six stages include: (I) dominant pyrite, quartz and alunite; (II) the major phases dominated by pyrrhotite, arsenopyrite and marcasite, with pyrite, galena and sphalerite, are accompanied by quartz and alunite; (III) copper mineralization, represented mainly by chalcopyrite, enargite, tetrahedrite, and tennantite; (IV) complex mineralization containing Au, Ag, W, Sn, Bi, Te, Ge, Ni, In, Ga and Cd which is associated with the ubiquitous base metal sulfides; (V) a stage of mineralization characterized by pyrite, sphalerite, marcasite and wurtzite; and (VI) scarce chal-

copyrite in a gangue of widespread rhodochrosite. The main gangue minerals in the first three stages of the mineralization are quartz and alunite while rhodochrosite prevails in the final three stages. The average homogenization temperature measured in primary two-phase liquid-vapor fluid inclusions is 250 °C (MÁRQUEZ-ZAVALÍA 1988).

The epithermal veins at Capillitas have a complex mineralogy with more than 120 different species recognized (MÁRQUEZ-ZAVALÍA 1988, 1990, 1999). The bulk of the ore mineralization (~80%) consists of pyrite, marcasite, galena, sphalerite, chalcopyrite, enargite, pyrrhotite, bornite and tetrahedrite-tennantite. The veins are lenticular to tabular, with an average thickness of 50–70 cm, a linear to sinuous architecture, and are sometimes anastomosing. They are generally forked, while thin pyrite veinlets connect the strands.

Many metres- to decimetres-scale structures are present in the deposit; the most widespread are massive, banded, brecciated and druse. One of the most characteristic features of the deposit is the banded nature of the vein mineralization which consists of a succession of layers of different minerals such as pyrite–chalcopyrite–rhodochrosite, or sphalerite–galena–tennantite–enargite–quartz; in some areas the mineralogy remains constant but displays diverse variations in color (e.g. rhodochrosite and/or capillite, the brown Fe–Zn-rich variety of rhodochrosite). Open spaces are surrounded on both sides by rhythmically banded crusts apparently formed during deposition from the mineralizing fluids which oscillate in composition and degree of saturation. Individual bands range from 1 to 40 mm and may be planar to mammilar in nature and are more massive in the areas where pyrite is abundant. Cavities, ranging from few mm up to 2 cm across, are common; some of them are filled with idiomorphic minerals such as galena, pyrite, enargite, hübnerite, quartz, and barite. Brecciated structures are common in the deposit; brecciated pyrite ore is cemented by younger minerals, especially galena, sphalerite, chalcopyrite, tennantite, quartz, rhodochrosite, and its brown variety, capillite. In other areas of the deposit, alunite commonly fills the open spaces and cements the fragments of the ore. In some veins of the deposit the druse structure is fairly common and crystals up to 5 mm in size, have been developed inside.

The surficial oxidation zone is less than 50 m thick; and is evidenced by copper sulfates and carbonates in the Cu-bearing ores, and by manganese oxides and limonite where rhodochrosite and iron sulfides are abundant. The supergene enrichment zone is, in some areas, up to 150 m thick. Al-

Table 1. Representative chemical analyses of native elements and Te-bearing minerals.

Mineral Sample #	Gold		Tellurium		Meloanite		Sylvanite		Krennerite		Calaverite		Stützite		Hessite		Volynskite		Tetradymite		Pezizite		Goldfieldite	
	SS-023	LR-O23	LR-O10	LR-O61	LR-G41	LR-B03	LR-L01	LR-G23	LR-G19	LR-G21	LR-M03	LR-G45	SS-C02	LR-O21	LR-M03	LR-G45	SS-C02	LR-O21	LR-M03	LR-G45	SS-C02	LR-O21	LR-M03	LR-G45
Te	N.A.	96.30	78.04	60.29	57.23	56.23	41.18	36.27	34.95	33.97	32.78	14.01	33.97	34.95	32.78	14.01	33.97	34.95	32.78	14.01	33.97	34.95	32.78	14.01
Sb	N.A.	0.74	0.46	0.47	0.48	0.43	0.21	0.39	0.91	0.27	0.29	3.23	0.27	0.91	0.29	3.23	0.27	0.91	0.29	3.23	0.27	0.91	0.29	3.23
As	N.A.	-	-	-	-	-	-	-	0.38	0.82	-	7.09	0.82	0.38	-	7.09	0.82	0.38	-	7.09	0.82	0.38	-	7.09
Se	N.A.	-	-	-	-	-	-	-	0.22	4.37	-	25.54	4.37	0.22	-	25.54	4.37	0.22	-	25.54	4.37	0.22	-	25.54
S	N.A.	-	0.13	0.17	0.08	-	0.21	0.28	3.22	-	-	-	-	3.22	-	-	-	-	-	-	-	-	-	-
Au	95.03	-	-	27.53	34.57	42.54	56.17	61.62	26.52	-	-	0.33	-	26.52	-	0.33	-	26.52	-	0.33	-	-	-	0.33
Ag	5.25	0.84	3.05	10.59	7.91	0.58	56.17	61.62	32.80	-	-	3.43	-	32.80	-	3.43	-	32.80	-	3.43	-	-	-	3.43
Bi	N.A.	-	-	-	-	-	-	-	2.53	-	-	46.10	-	2.53	-	46.10	-	2.53	-	46.10	-	-	-	46.10
Cu	0.39	-	0.32	0.85	-	-	0.48	0.80	-	-	-	0.41	-	-	-	0.41	-	-	-	-	-	-	0.41	
Fe	N.A.	-	-	-	-	-	-	-	-	-	-	0.16	-	-	-	0.16	-	-	-	-	-	-	0.16	
Zn	N.A.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Ga	N.A.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Ni	N.A.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Total	100.67	97.88	96.31	99.90	100.27	99.78	98.25	99.36	101.53	97.42	99.13	100.30	97.42	101.53	99.13	100.30	97.42	101.53	99.13	100.30	97.42	99.13	100.30	97.42
Atomic %																								
Te	-	98.18	68.30	64.48	63.82	66.32	37.60	32.31	32.93	38.50	32.66	6.18	38.50	32.93	32.66	6.18	38.50	32.93	32.66	6.18	38.50	32.66	6.18	38.50
Sb	-	0.78	0.45	0.55	0.57	0.45	0.23	0.34	0.84	0.28	0.25	1.48	0.28	0.84	0.25	1.48	0.28	0.84	0.25	1.48	0.28	0.25	1.48	0.28
As	-	-	-	-	-	-	-	-	0.60	1.45	-	5.31	1.45	0.60	-	5.31	1.45	0.60	-	5.31	1.45	-	5.31	1.45
Se	-	-	0.45	0.68	0.28	-	0.70	1.02	0.36	1.45	-	44.72	1.45	0.36	-	44.72	1.45	0.36	-	44.72	1.45	-	44.72	1.45
S	-	-	-	-	-	-	-	-	12.02	19.68	-	-	19.68	12.02	-	-	19.68	12.02	-	-	19.68	-	-	19.68
Au	89.76	-	-	19.13	24.93	32.48	60.65	64.96	29.57	-	15.12	0.17	-	29.57	-	15.12	-	29.57	-	15.12	-	-	-	15.12
Ag	9.12	1.04	3.12	13.38	10.40	0.75	60.65	64.96	18.87	-	48.54	0.93	-	18.87	-	48.54	-	18.87	-	48.54	-	-	-	48.54
Bi	-	-	-	-	-	-	-	-	4.81	-	2.41	40.73	-	4.81	-	40.73	-	4.81	-	40.73	-	-	-	40.73
Cu	1.12	-	0.56	1.78	-	-	0.82	1.37	-	-	-	0.07	-	-	-	0.07	-	-	-	-	-	-	0.07	
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Zn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ga	-	-	0.33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ni	-	-	26.79	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Note: Each analysis on the table corresponds to a single analysis, not to averages. N.A. = not analyzed; SS = San Salvador vein; LR = La Rosario vein.

though this zone has been mined away, it is inferred that the primary economic mineral was chalcocite.

Mineralogy

The complexity of the mineral associations in Capillitas vein network is reflected in the diversity of Te-bearing minerals, 11 species with Au, Ag, Bi, Cu and Ni. Table 1 summarizes the mineral species identified by optical and electron microprobe techniques. These minerals, recognized in three of the more than 20 veins and claims identified at Mina Capillitas, were formed during the fourth stage of the mineralization. The distributions and attitudes of the veins, hosted in granites, rhyolites and brecciated rhyolites, are clus-

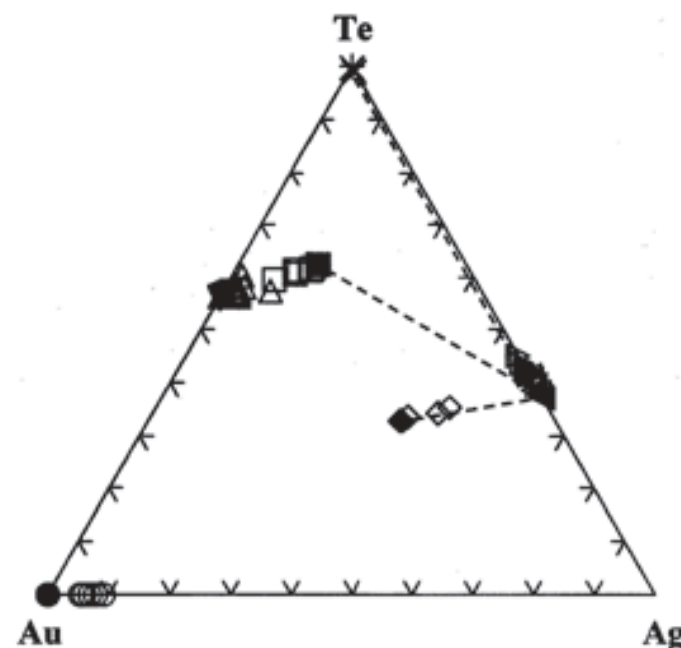


Fig. 2. Mineral phases of the Au-Ag-Te system encountered in this study. The first, filled symbol, indicates ideal compositions and the second, empty symbol, the data obtained in this study. \blacktriangle \triangle tellurium, \blacklozenge \lozenge gold, \times krennerite, \blacklozenge \lozenge calaverite, \blacksquare \square sylvanite, \blacktriangledown \triangledown pezizite, \bullet \circ hessite, \blacktriangleright \triangleright stützite. Coexisting mineral pairs are indicated by the heavy dashed line.

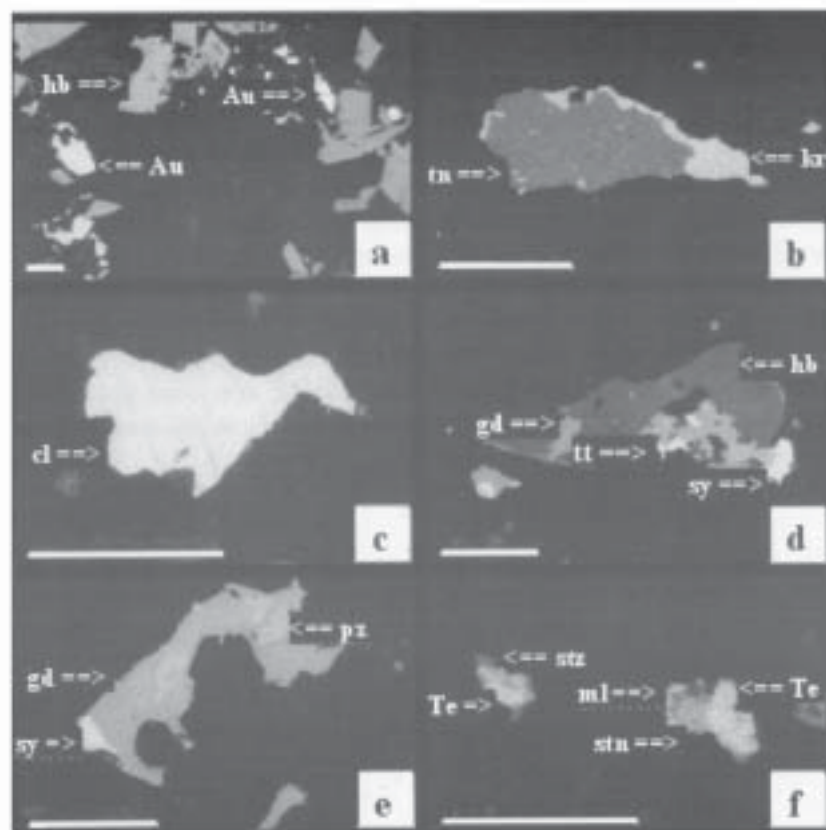


Fig. 3. Photomicrographs: *a.* Gold (Au) and hübnerite (hb) in quartz, San Salvador vein; *b.* Tennantite (tn) and krennerite (kr) in quartz, La Rosario vein; *c.* Calaverite (cl) in quartz, La Rosario vein; *d.* Goldfieldite (gd), sylvanite (sy) and tetradymite (tt) with hübnerite in quartz, La Rosario vein; *e.* Goldfieldite with petzite (pz) and sylvanite in quartz, La Rosario vein; *f.* Tellurium (Te) with stützite (stz), melonite (ml) and stannite (stn) in quartz, La Rosario vein. Scale bar = 20 μm .

tered about ENE and NW azimuths that probably reflect Neogene structural kinematics. The three veins hosting Te minerals are: La Rosario (strike N70°E, dip 50–75°S, length 245 m, thickness 0.90 m), San Salvador (strike N35°W, dip 65–75°S, length 180 m, thickness <0.20 m), and Nueva Esperanza (strike N80°E, dip 45°S, length 100 m, thickness 0.30 m).

Chemical analyses of the ore minerals were performed with a CAMECA SX-50 microprobe utilizing the following standards: Sb, Au, Ag, Bi, Ni, PbS, ZnS, CdS, CuFeS₂, PbTe, GaAs, MnSe, and InP. The analytical X-ray lines chosen were K α for S, Cu, Fe, Zn and Ni, L α for Te, Sb, As, Se, Ag, In, Cd, and Ga, and M α for Au, Bi, and Pb. Operating conditions included an accelerating voltage of 15 kV and a beam current of 20 nA. The analyses were performed at the Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA. Ore specimens were prepared as conventional polished sections. The chemical compositions of the Au–Ag–Te minerals and coexisting assemblages are plotted in Figure 2. Each structural formula was calculated using the method based on the total number of atoms, and unless it is specified, they correspond to single analysis, not to averages.

Gold

Gold occurs as small (20 μm on an average), irregular grains (Fig. 3 a). The fineness of the gold throughout the deposit varies between 830 to 970, whereas in the Te-bearing veins its fineness is 901 to 966. The formula obtained is $(\text{Au}_{0.90}\text{Ag}_{0.09}\text{Cu}_{0.01})_{\Sigma=1.00}$. The gold occurs primarily in quartz where it coexists with hübnerite, goldfieldite, chalcocopyrite and Bi-bearing minerals. Gold has also been observed as inclusions in goldfieldite, but is more abundant in those parts of the deposit where Te is absent.

Tellurium

Tellurium is rare, having been encountered in only two grains in a sample from La Rosario vein. It occurs as small (10 μm), anhedral grains, with goldfieldite, stützite and melonite, which are included in quartz (Fig. 3 f). The calculated structural formula is $(\text{Te}_{0.98}\text{Sb}_{0.01}\text{Ag}_{0.01})_{\Sigma=1.00}$. We suggest that the low total of the analysis of tellurium, which is consistent in all the points analyzed, may be the result of diffusion of Te at the point where the electron beam strikes the sample.

Melonite, NiTe₂

Also rare, melonite has been observed in a single grain, occurring in a thin rim (5 to 8 μm) that partly surrounds goldfieldite and coexists with stützite and tellurium, all of which are included in quartz (Fig. 3 f). Its formula is: $(\text{Ni}_{0.81}\text{Ag}_{0.09}\text{Cu}_{0.02}\text{Ga}_{0.01})_{\Sigma=0.93}(\text{Te}_{2.05}\text{Sb}_{0.01}\text{S}_{0.01})_{\Sigma=2.07}$. This analysis gives also a low total, which is attributed to the smallness of the single grain

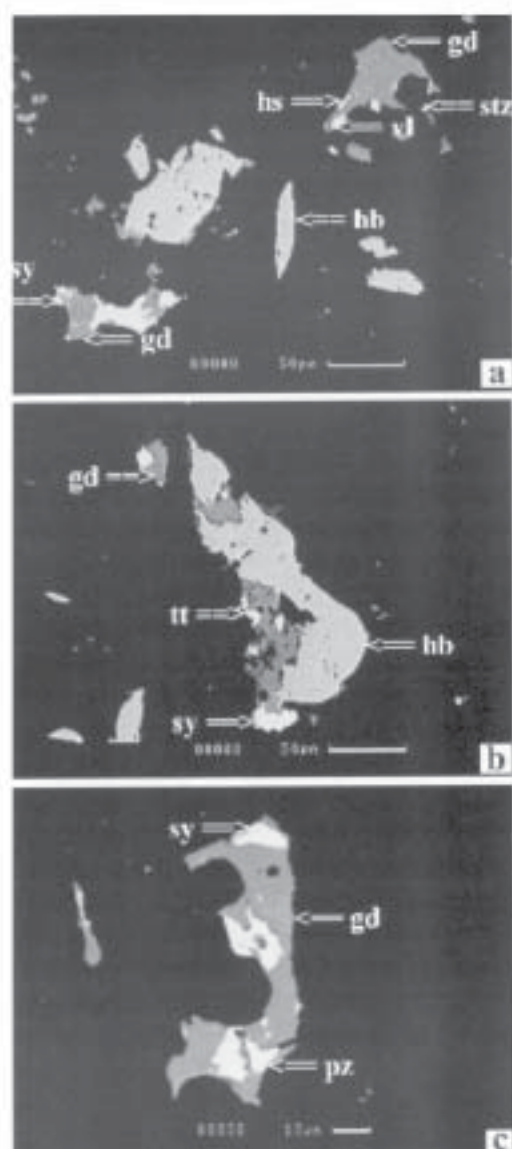


Fig. 4. BSE images: *a.* Goldfieldite (gd), sylvanite (sy), hessite (hs), stützite (stz) and volynskite (vl) in quartz, La Rosario vein; *b.* Goldfieldite, sylvanite and tetradyomite (tt) with hübnerite (hb) in quartz, La Rosario vein; *c.* Goldfieldite with petzite (pz) and sylvanite in quartz, La Rosario vein.

analyzed. The only two known nickel telluride minerals are melonite and imgreite, and the latter has more than twice the quantity of Ni (in wt.%) than the mineral from Mina Capillitas. This comparatively low Ni content, together with the diagnostic optical properties and the paragenesis, identifies the mineral as melonite, the low total notwithstanding.

Sylvanite, (Au,Ag)₂Te₄

Sylvanite, with a formula corresponding to $(\text{Au}_{1.15}\text{Ag}_{0.80}\text{Cu}_{0.11})_{\Sigma=2.06}(\text{Te}_{3.87}\text{Sb}_{0.03}\text{S}_{0.04})_{\Sigma=3.94}$, occurs as subhedral to anhedral grains up to 15 µm, always at the edge of goldfieldite grains included in quartz, (Figs. 3 d, e and 4 a, b, c). It is generally intergrown with hessite, chalcopyrite and hübnerite.

Krennerite, AuTe₂

Krennerite is less abundant than calaverite and since they are optically similar, thus frequently resulting in confusion in their identifications. Krennerite, however, is a bit less yellow and has cleavage. It occurs typically as coarse anhedral grains, which display at least one directions of cleavage. It is included in quartz and has been found in contact with goldfieldite, chalcopyrite, pyrite, tennantite, stannite and hübnerite. In some of the grains, krennerite borders tennantite (Fig. 4 b). The Te content ranges from 54.27 to 58.34 wt.%, Au ranges from 34.57 to 42.04 wt.%, and Ag from 1.34 to 7.91 wt.%. The structural formula was calculated using the analysis shown in Table 1: $(\text{Au}_{0.75}\text{Ag}_{0.31})_{\Sigma=1.06}(\text{Te}_{1.91}\text{Sb}_{0.02}\text{S}_{0.01})_{\Sigma=1.94}$.

Calaverite, AuTe₂

Calaverite is also rare, as are all the Te minerals in the Capillitas deposit. It occurs as anhedral to subhedral inclusions, generally smaller than 10 µm, included in quartz (Fig. 3 c), goldfieldite, and stannite. The contents of tellurium, gold and silver range from 55.62 to 56.81, from 41.14 to 43.64, and from 0.18 to 1.22 wt.% respectively. Atomic proportions in the formula vary between: $(\text{Au}_{1.00}\text{Ag}_{0.01})_{\Sigma=1.01}(\text{Te}_{1.98}\text{Sb}_{0.01})_{\Sigma=1.99}$ and $(\text{Au}_{0.95}\text{Ag}_{0.05})_{\Sigma=1.00}(\text{Te}_{1.99}\text{Sb}_{0.01})_{\Sigma=2.00}$.

Stützite, Ag₅₋₇Te₃

Like melonite, volynskite and tellurium, stützite is among the rarest Te-bearing minerals in Mina Capillitas. It occurs as irregular 10 to 15 µm grains in contact with goldfieldite (Fig. 4 a), tellurium, volynskite and melonite, all of which are included in quartz (Fig. 3 f). Te contents vary between 40.87

and 42.49 wt. percent and Ag between 54.90 and 56.17 wt. percent. The structural formula calculated is: $(\text{Ag}_{4.85}\text{Cu}_{0.06})_{\Sigma} = 4.91(\text{Te}_{3.01}\text{Sb}_{0.02}\text{S}_{0.06})_{\Sigma} = 3.09$.

Hessite, Ag_2Te

Hessite occurs as anhedral grains, smaller than $10\mu\text{m}$, which are included in goldfieldite and quartz (Fig. 4a) and intergrown with sylvanite, petzite and volynskite. Te content ranges between 36.27 and 39.09, and Ag between 55.06 and 61.62 wt. percent. The structural formula calculated, using the analysis shown in Table 1, is: $(\text{Ag}_{1.95}\text{Cu}_{0.04})_{\Sigma} = 1.99(\text{Te}_{0.97}\text{Sb}_{0.01}\text{S}_{0.03})_{\Sigma} = 1.01$.

Volynskite, AgBiTe_2

Volynskite, with a structural formula corresponding to: $\text{Ag}_{1.18}(\text{Bi}_{0.75}\text{Cu}_{0.19})_{\Sigma} = 2.12(\text{Te}_{1.33}\text{S}_{0.49}\text{Sb}_{0.03}\text{As}_{0.02}\text{Se}_{0.01})_{\Sigma} = 1.88$, was found as a single small ($8\mu\text{m}$) tabular crystal, included in goldfieldite (Fig. 4a), and coexisting with stützite and hessite. Its chemical composition is marginally different to typical volynskite quoted in the literature (ANTHONY et al. 1990), but we attribute this difference to the small size of the mineral in Mina Capillitas; it was impossible to find more grains of this mineral in order to obtain more analyses. The high Cu content is probably due to the host mineral: goldfieldite. That this mineral is indeed volynskite is also supported by the fact that it is the only Te-bearing mineral with bismuth and silver. A thin rim of another Ag and Te-bearing mineral surrounds this Mina Capillitas volynskite, but the results of the chemical analysis was insufficient for precise identification (80.90 wt. percent total).

Tetradymite, $\text{Bi}_2\text{Te}_2\text{S}$

Tetradymite occurs as very small, rare inclusions (5 to $10\mu\text{m}$) in hübnerite and in goldfieldite (Figs. 3d and 4b), and is compatible with the formula $\text{Bi}_2(\text{Te}_{1.93}\text{Se}_{0.07})_{\Sigma} = 2.00(\text{S}_{0.98}\text{Sb}_{0.02})_{\Sigma} = 1.00$.

Petzite, Ag_3AuTe_2

Petzite occurs as small grains (5 to $30\mu\text{m}$), irregularly distributed in goldfieldite (Figs. 3e and 4c), and as rare intergrowths with hessite. The measured amounts of Te, Ag and Au are 32.78 to 34.33, 41.20 to 47.01 and 15.60 to 25.40 wt.%, respectively. Petzite has a variable stoichiometry distribution between $(\text{Ag}_{2.92}\text{Au}_{0.91}\text{Cu}_{0.14})_{\Sigma} = 3.97(\text{Te}_{1.96}\text{Sb}_{0.01}\text{S}_{0.06})_{\Sigma} = 2.03$ and $(\text{Ag}_{3.27}\text{Au}_{0.59}\text{Cu}_{0.10})_{\Sigma} = 3.96(\text{Te}_{2.01}\text{Sb}_{0.01}\text{S}_{0.02})_{\Sigma} = 2.04$. Similar compositional ranges have been described by RUCKLIDGE & STUMPFL (1968), and more recently by

SPRY et al. (1997); these authors have suggested that a thermal and steep electric field gradient develop around the electron impact spot, thus resulting in the diffusion of Au during analysis.

Goldfieldite, $\text{Cu}_{12}(\text{Te}, \text{Sb}, \text{As})_4\text{S}_{13}$

The mineral present in Mina Capillitas can be considered goldfieldite, according to the definitions of KATO & SAKURAI and SPIRIDONOV (both in TRUDU & KNITTEL 1998), definitions that are coincident with the IMA rules, because Te is more abundant than the other three semimetals: Sb, As and Bi. In Mina Capillitas veins goldfieldite displays considerable variability: Te 10.02 to 14.85, Sb 2.82 to 11.57, As 0.75 to 8.07, S 24.04 to 25.75, Ag 0.01 to 1.86, Bi 1.13 to 7.67, Cu 42.01 to 47.08, Fe 0.03 to 2.23, and Zn 0.00 to 1.66 wt.%. The average composition is $(\text{Cu}_{11.68}\text{Ag}_{0.07}\text{Fe}_{0.14}\text{Zn}_{0.15})_{\Sigma} = 12.04(\text{Te}_{1.49}\text{Sb}_{1.10}\text{As}_{1.11}\text{Bi}_{0.29})_{\Sigma} = 3.99\text{S}_{12.97}$. Calculation was based on 20 analyses on 9 grains coming from 2 different veins. The calculated structural formula involved a unit cell consisting on 29 atoms, because all the Mina Capillitas goldfieldites have less than 2 atoms of Te per formula unit, and then no vacancies occur in the crystal structure (TRUDU & KNITTEL 1998).

Following the nomenclature of TRUDU & KNITTEL (op. cit.), all goldfieldites extracted from the San Salvador vein are stiboan-goldfieldites, while those in La Rosario vein consist of stiboan-goldfieldites and arsenoan-goldfieldites, which coexist.

Goldfieldite is the most common of the Te-bearing minerals in the Capillitas deposit. It includes or coexists with tellurium, calaverite, krennerite, hessite, petzite, sylvanite, stützite, melonite, volynskite and gold. It occurs as irregular grains of varying size (5 to $40\mu\text{m}$) that are mostly included in quartz, but are locally also hosted in hübnerite (Figs. 3d, e and 4a, b, c) and in chalcopyrite. Some grains exhibit an irregular zonation, with areas that are optically brighter and with a lighter blue hue than the rest of the crystal. Analyses of these zones reveal enrichment in Sb and depletion in Te and Cu up to 2 wt.%. Several tellurium-bearing tennantites and tetrahedrites were also analyzed, and are characterized by Te percentages that vary between 0.10 and 4.18.

Discussion

The temporal and spatial relationships of the Te-bearing minerals of Capillitas are similar to those observed in many other epithermal deposits (e.g. Ne-

vados del Famatina district, LOSADA-CALDERÓN & McPHAIL 1996; El Indio, JANNAS et al. 1990; Monte Negro deposit, MUNTEAN et al. 1990). Although constituting only a small proportion of the ores and occurring in small grains, their common association with precious metals could be significant both as an exploration tool as well as helping to define the conditions of ore formation. In the Mina Capillitas ores, Te-bearing minerals occur in the fourth stage of mineralization when temperatures were declining and the pH of the environment appears to have been less acid. In this stage tungsten-, bismuth-, tin-, indium-, and germanium-bearing minerals were also formed in small amounts.

Based on the textural evidence, we believe that goldfieldite was the first Te-bearing mineral formed in this deposit, followed by calaverite, krennerite, petzite, hessite, sylvanite, and tellurium. It is difficult to assign positions in the paragenetic sequence to the other Te-bearing minerals, because of their scarcity and because most occurs as very small inclusions only in goldfieldite, they lack evidence of textural relationships with the other minerals.

Observations show that the associations goldfieldite–hessite, goldfieldite–petzite and goldfieldite–sylvanite are the most common, and that each is usually accompanied by hübnerite and always included in quartz. Among all the Te minerals present in Capillitas, only goldfieldite has been observed in direct contact with gold; however, the gold, where it coexists with the other tellurium minerals, usually occurs in close proximity.

Even though calaverite and hessite coexist in the deposit, they do not appear to have been co-deposited. This observation agrees with MARKHAM's (1960), CABRI's (1965) and ZHANG & SPRY's (1994) studies that suggest these minerals cannot coexist stably at 250 °C.

Fluid inclusion homogenization temperatures, derived from primary two-phase liquid-vapor inclusions, indicate that the temperature during the major stages of mineralization ranged from about 275 °C in stage I to about 230 °C in stage V; thereafter, the temperature declined to about 150 °C in stage VI. The sulfide and tellurium mineral assemblages permit reasonable estimates of sulfur and tellurium activities. Figure 5 shows some relevant stability curves in terms of $\log f\text{Te}_2$ – $\log f\text{S}_2$ space (based on data from AFIFI et al. 1988 and BARTON & SKINNER 1979). The presence of pyrite as the only sulfide in stage I indicates that $\log f\text{S}_2$ exceeded –10 to –13, the lower limit of pyrite stability. The presence of pyrrhotite and arsenopyrite with pyrite in stage II places $\log f\text{S}_2$ at about –10 to –13, where all three

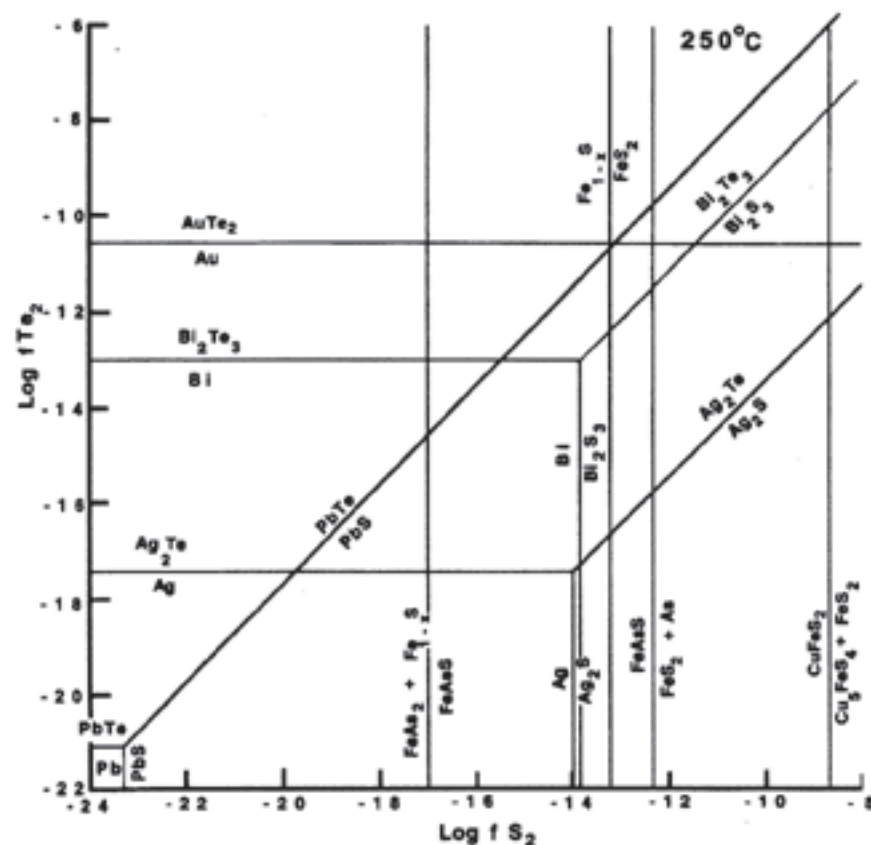


Fig. 5. $\log f\text{S}_2$ – $\log f\text{Te}_2$ plot of gold, silver, bismuth, and some other related Te mineral.

phases would be stable. Stage III contains chalcopyrite but lacks pyrrhotite and arsenopyrite and therefore would indicate that $\log f\text{S}_2$ was in the range of –10 to –13 until –8.5 to –10. The absence of tellurium phases in the first three stages suggests that either the source of the tellurium had not yet been tapped or that the $\log f\text{Te}_2$ lay below –10 to –17, the minimum activity where any of the tellurium phases present in stage IV could have formed. Stage IV contains the same major sulfide assemblage as stage III suggesting formation in the same realm of sulfur activity. The sudden appearance of several Te minerals suggests that some source of tellurium had been tapped

and that the activity rose, at least briefly, into the range of $\log f\text{Te}_2$ -10 to -11 under which conditions calaverite could have formed. Silver, observed in trace amounts in stage IV, could not exist under the high $\log f\text{Te}_2$ conditions of calaverite formation. Hence, whichever mineral formed first, it was apparently isolated from the later fluids and thus survived in its original form. It would also be consistent with the observation noted above that hesite and calaverite do not appear to have been co-precipitated. Accordingly, the presence of a high $f\text{Te}_2$ phase such as calaverite and a low $f\text{Te}_2$ phase such as silver in the same stage suggests that there were significant fluctuations (possibly pulses) in the activity of tellurium in the fluids during that stage.

All the preceding discussion could be summarized in the following next points, tending to frame the environmental conditions during the Te mineral deposition:

- Although there was a gradual cooling of the mineralizing fluids, the six stages of mineralization were always within temperatures characteristic of epithermal systems.
- Although the pH was not calculated, it is inferred that the environment possibly became progressively less acid as indicated by the preponderance of the different gangue minerals; rhodochrosite became the prevailing gangue mineral after the first three stages when quartz was dominant. This interpretation is consistent with more basic conditions.
- From the mineral assemblage and the fluid inclusion homogenization temperature data, we infer that the $\log f\text{S}_2$ values declined when the fluids deposited the Te-bearing minerals.
- The fluids were slightly Te-oversaturated, at least during a short period, because there was not only deposition of ditelluride minerals, but also tellurium, stützite and sylvanite. Gold was found as a native phase, and silver was observed in the deposit as very scarce and small grains (<10 μm) but never directly associated with the Te paragenesis.
- These considerations, and the fact that electrum was not found in this paragenesis, even when Ag and Au were available, indicate the influence of the Te concentration of the mineralizing fluids during Stage IV.

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