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Sn–Ge–Cd–Cu–Fe-BEARING SULFIDES AND SULFOSALTS FROM THE BARQUILLA DEPOSIT, SALAMANCA, SPAIN

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ABSTRACT

Sn–Ge–Cd–Cu–Fe mineralization is observed in the Fuentes Villanas mine, which exploits the hydrothermal vein deposit of Barquilla, Salamanca, Spain. Two associations are present, one consisting of cassiterite, černýite, greenockite, tetrahedrite, herzenbergite and minor chalcopyrite, Ag–Pb–Bi-bearing sulfosalts, galena and native bismuth, in the veins; the other involves chalcopyrite, stannite, stannoidite, mawsonite, tetrahedrite, cadmian briartite, bornite, mohite, native bismuth, bismuthinite and digenite in the altered host-rock close to the veins. The first one crystallized before an intense episode of sericitic alteration, whereas the second is contemporaneous with it. The crystallization sequence of Sn-bearing minerals proposed is: cassiterite → herzenbergite → černýite → stannoidite → mawsonite. Available experimental data suggest that these minerals crystallized in a sequence controlled by the increase of S fugacity or decrease of temperature (or both). The germanium content of cadmian briartite probably was picked up from the host rocks by migrating fluids.

Keywords: Sn–Ge–Cd–Cu–Fe-bearing sulfides, sulfosalts, hydrothermal deposit, Barquilla, Spain.

SOMMAIRE

Le gisement filonien de Barquilla (Salamanque, Espagne) présente dans la mine de Fuentes Villanas une minéralisation originale Sn–Ge–Cd–Cu–Fe. Deux associations sont présentes. L'une dans les filons contient l'assemblage cassitérite, černýite, greenockite, tétraédrite, herzenbergite et, comme phases mineures, chalcopyrite, sulfosels à Ag–Pb–Bi, galène et bismuth natif. L'autre, située dans la roche encaissante altérée, contient chalcopyrite, stannite, stannoïdite, mawsonite, tétraédrite, briartite cadmifère, bornite, mohite, bismuth natif, bismuthinite et digénite. La première association a cristallisé avant le processus intense de séricitisation, alors que la seconde est contemporaine de celui-ci. La séquence proposée de cristallisation des minéraux contenant de l'étain est cassitérite → herzenbergite → černýite → stannoïdite → mawsonite. Les données expérimentales font penser que cette succession témoigne d'une augmentation de la fugacité du soufre ou d'une diminution de la température (ou des deux facteurs). La teneur en Ge de la briartite cadmifère provient probablement des roches encaissantes, sujettes à la migration des fluides.

Mots-clés: sulfures de Sn–Ge–Cd–Cu–Fe, sulfosels, gisement filonien, Barquilla, Espagne.

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INTRODUCTION

The Barquilla deposit, located in the southwestern part of Salamanca, Spain, is unusual in the development of rare sulfides and sulfosalts of Sn–Ge–Cd–Cu–Fe. These ore minerals occur in cassiterite – montebrasite – apatite – albite – quartz – mica veins and in their intensely sericitized host-rocks.

The importance of this work does not reside only in the extreme rarity of this sulfide assemblage, but in the fact that all these minerals form an inherent part of the Barquilla deposit and, therefore, they can supply information about conditions required for its formation. For this reason, we sought to determine: a) the identity and paragenesis of the sulfides and sulfosalts, b) their spatial variations throughout the veins and the altered host-rocks, c) the compositions of sulfides and nature of the solid solutions in each sulfosalt series, and d) the interpretation of trends in mineral composition, in order to gain a better knowledge of this complex assemblage of minerals.

GEOLOGY OF THE BARQUILLA DEPOSIT

Three differents lithologies outcrop in this area (Corretgé & López Plaza 1976) (Fig. 1): Recent detrital deposits, low-grade metamorphic rocks of pre-Ordovician age (Schist–Greywacke Complex) and granitic

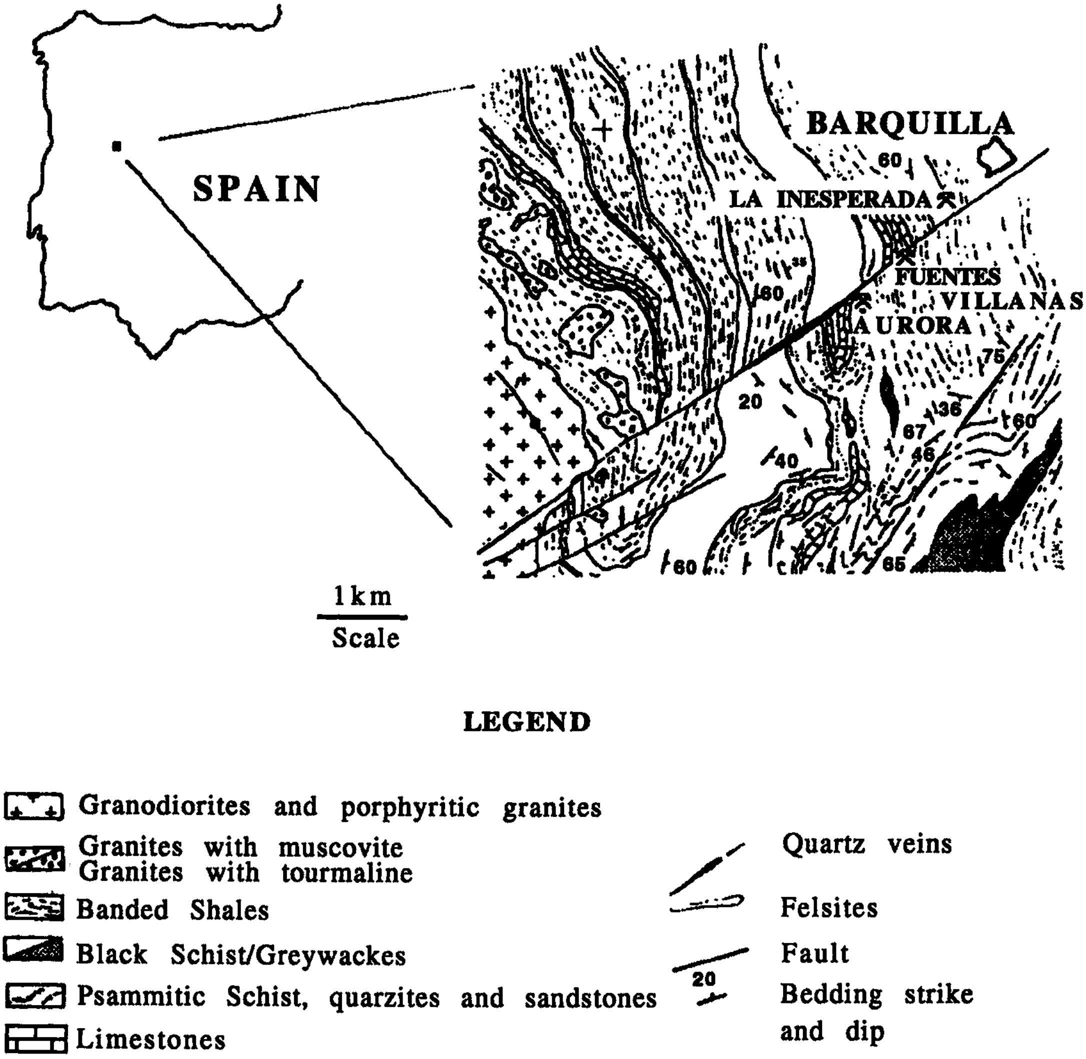

FIG. 1. Geographic location of the Barquilla deposit (Spain) and geological map showing location of the Aurora, La Inesperada and Fuentes Villanas mines (from Corretgé & López Plaza 1976).

rocks that form the eastern zone of the Guarda batholith in Portugal (Corretgé & López Plaza 1977).

The Barquilla deposit is exploited in three mines: Aurora, La Inesperada and Fuentes Villanas. This vein-type deposit has been worked since 1930, producing lithium and tin. The veins trend N–S to N70°E, dip 5–80°SE, and their width ranges from a few centimeters to one meter. There is commonly wedging and bifurcation in the veins. The host rocks are impure limestone in the Fuentes Villanas mine, and greywacke, conglomerate and schist in the Aurora and La Inesperada mines. Sericitic alteration, developed along the borders of the veins, rarely extends a meter into the host rocks. A comparison of mineral assemblages in the three mines enables us to group these into two groups: Aurora – La Inesperada and Fuentes Villanas (Murciego *et al.* 1992a, Pascua 1993).

The mineral assemblage in veins at Aurora and La Inesperada are cassiterite, apatite, albite, montebrasite, quartz and sericite, with minor proportions of a columbite–tantalite-group mineral and microlite. Murciego *et al.* (1992b) separated two generations of cassiterite (I and II); the first one cristallized at an early stage of mineralization, and the second one is related to sericitization. Cassiterite I, montebrasite, apatite and albite are corroded in the first place by quartz and, later, by sericite. The vein – host rock contact in both mines is marked by a narrow black band of cassiterite II. In the altered host-rocks, the following mineral association has been recognized: sericite – apatite – fluorite – cassiterite II.

The ore minerals studied in the present work occur, locally, in veins and in altered host-rocks of the Fuentes Villanas mine (Fig. 2); cassiterite II is absent there. In the veins, the sulfides and sulfosalts are restricted to the border, where they corrode and fill fissures in albite and cassiterite I, as well as enclose apatite, microlite and manganocolumbite. All of them are corroded by quartz and sericite. The vein – host rock contact is marked by a white band that consists mainly of apatite with minor sericite, quartz, sulfides and sulfosalts. The altered host-rocks close to the veins are formed by fluorite, sericite and apatite as gangue minerals, and sulfides and sulfosalts that are widespread in the sericite, and that surround and fill fissures in the fluorite.

Sampling and Analytical Procedures

About fifty samples from the walls and pits of the Fuentes Villanas mine of the Barquilla deposit and

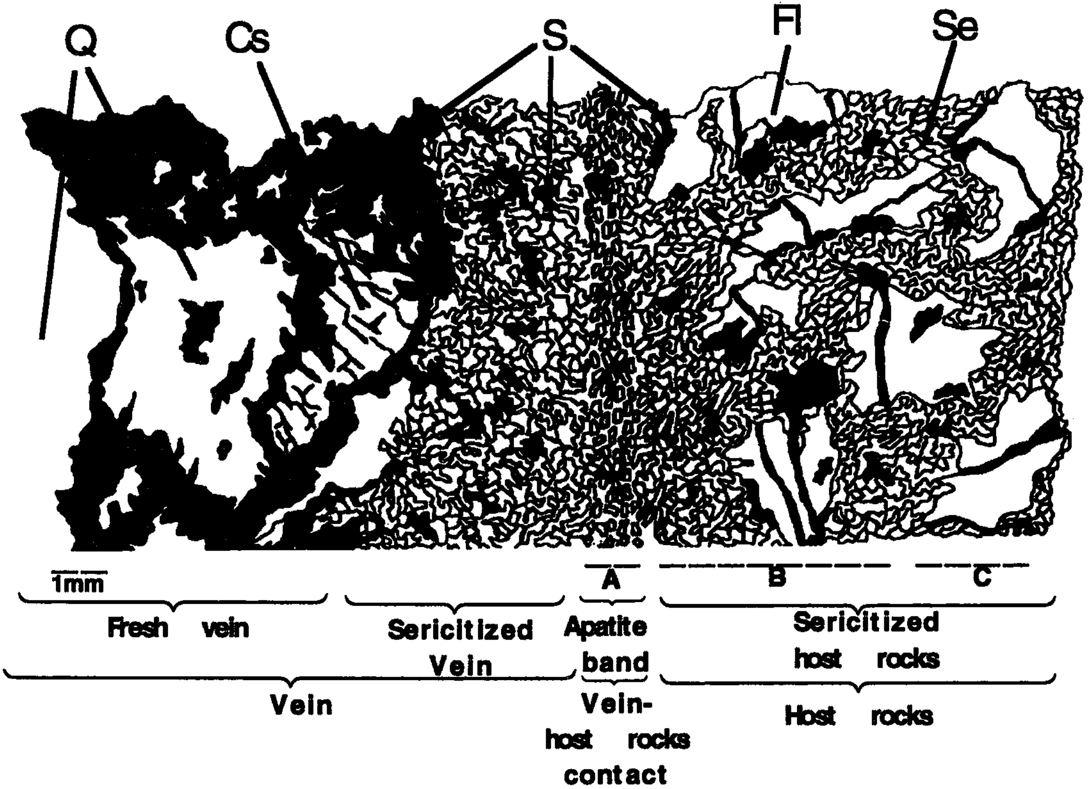

FIG. 2. Schematic cross-section of the vein and the altered host-rock from the Barquilla deposit (Q: quartz; Cs: cassiterite; S: sulfides and sulfosalts; Fl: fluorite; Se: sericite). Location of the subassociations A, B and C are indicated.

TABLE 1. SULFIDES, SULFOSALTS AND NATIVE ELEMENTS: FORMULAE, LOCATION AND RELATIVE ABUNDANCE

Name	Formulae	Vein	Altered zone
ANTIMONPEARCEITE	$(Ag,Cu)_{16}(Sb,As)_2S_{11}$		*
ARSENOPYRITE	$FeAsS$		*
BISMUTHINITE	Bi_2S_3		*
NATIVE BISMUTH	Bi	*	*
BORNITE	Cu_5FeS_4		°
BRIARTITE	Cu_2CdGeS_4		°
CHALCOPYRITE	$CuFeS$	*	°
ČERNÝITE	Cu_2CdSnS_4	°	*
COVELLITE	CuS	*	*
DIGENITE	Cu_9S_5		°
STANNITE	Cu_2FeSnS_4		°
STANNOIDITE	$Cu_8Fe_2(Fe,Zn)Sn_2S_{12}$		°
GALENA	PbS	*	
GREENOCKITE	CdS	°	*
HERZENBERGITE	SnS	°	
MATILDITE	$AgBiS_2$	*	
MAWSONITE	$Cu_6Fe_2SnS_8$		°
MOHITE	Cu_2SnS_3		°
PYRARGYRITE	Ag_3SbS_3		*
TETRAHEDRITE	$(Cu,Ag)_{10}(Fe,Zn,Cd)_2(Sb,As)_4S_{13}$	°	°

(° Principal mineral, * minor phase)

cores from the boreholes drilled in the area have been studied. The optical observations were complemented with an electron-microprobe analyzer. Electron-probe micro-analyses were performed at the Microanalysis Service, Université de Nancy I (France), on a CAMECA SX–50 operating at 20 kV and 20 nA. Standards and X-ray lines used were: PbS (Pb*M*α), AsFeS (As*L*α), ZnS (Zn*K*α), CuFeS (S*K*α; Cu*K*α), SnO_2 (Sn*L*α), FeS_2 (Fe*K*α), Sb_2S_3 (Sb*L*α), CdS (Cd*L*α), MnS (Mn*K*α), GaAs (Ga*K*α) and pure metals (Ag*L*α, Bi*M*α, Ge*K*α).

SULFIDES AND SULFOSALTS: MINERAL ASSEMBLAGES, TEXTURAL RELATIONSHIP AND PARAGENESIS

Two different assemblages of sulfides and sulfosalts, in the veins and in the altered host-rocks of the Fuentes Villanas mine, have been defined. From now on, we incorporate information on the vein – host rocks contact with information on the altered host-rocks. Table 1 shows the different mineral phases found, their theoretical chemical formulae, distribution and relative abundance. Some of these minerals are rare and, therefore, will be described in future detailed studies.

The first assemblage consists of černýite, greenockite, tetrahedrite, herzenbergite and, in minor

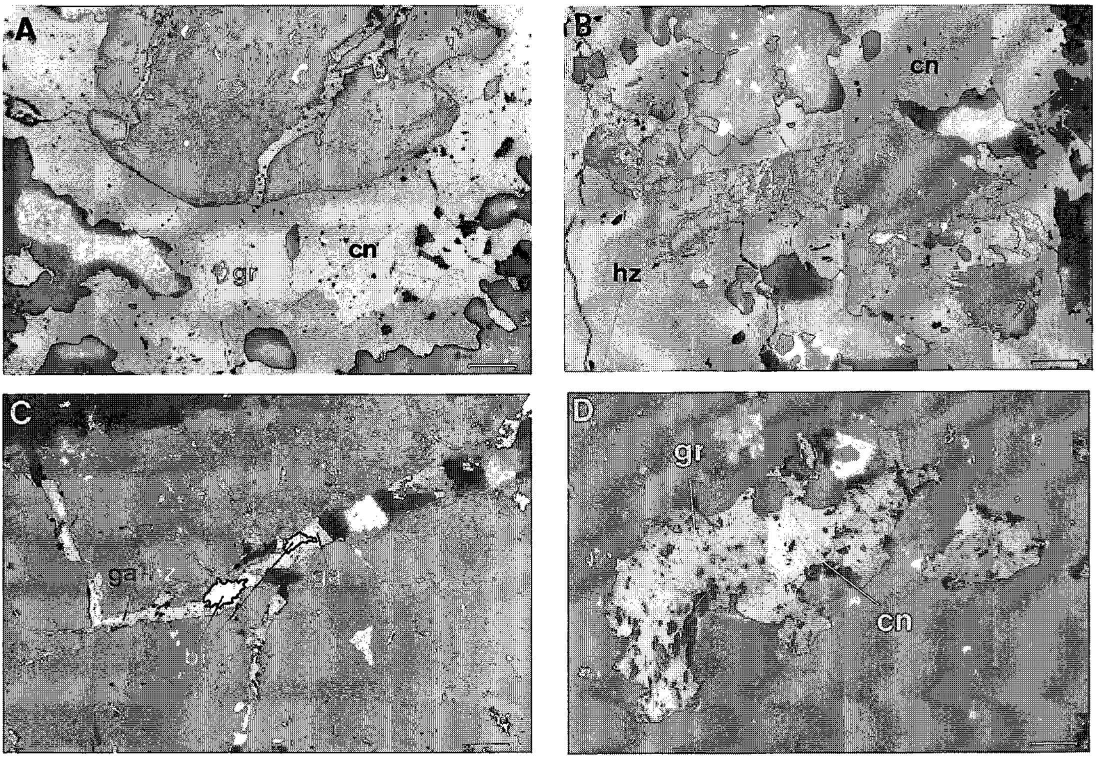

FIG. 3. Microphotographs in reflected light of the mineral phases in the veins (the scale bar indicates 50 μm): A. Intergrowth of coexisting černýite (cn) and greenockite (gr). Fractures in cassiterite (cs) are filled with černýite. Black grains are gangue. B. Cassiterite (cs), partly replaced by herzenbergite (hz), surrounded by černýite (cn). Black grains are gangue. C. Native bismuth (bi) surrounded by galena (ga) and by the mixture galena + herzenbergite (ga + hz) penetrating into cassiterite (cs) along small fractures. D. Greenockite (gr) and černýite (cn) embayed by sericite.

quantity, chalcopyrite, galena, native bismuth, covellite and Ag–Bi–Pb–Cu-bearing sulfosalts. The most abundant phase is černýite (Fig. 3A). There are irregular bands of tetrahedrite and greenockite within the černyite (replacement?). Greenockite appears in the borders and inside grains of černýite, seldom in contact with cassiterite because černýite forms a reaction rim between them. Herzenbergite appears to replace cassiterite I in borders and fissures; as well, it is included in černýite (Fig. 3B).

Tiny inclusions are widespread in the černýite and, less commonly, in the greenockite. These inclusions have similar features: micrometric size, more or less oval shape, white color and high reflectivity. Generally, they are Bi–Ag–Pb–Cu-bearing sulfosalts and, more rarely, galena, pyrargyrite or herzenbergite. Native bismuth seems to be included in černýite and fills fissures in cassiterite, generally surrounded by galena or by intermediate members of the galena – herzenbergite solid-solution series (Fig. 3C).

Commonly, chalcopyrite and tetrahedrite seem to be associated in the veins; both can be surrounded by černýite as well as fill fissures in černýite and greenockite. Chalcopyrite may be present as a thin discontinuous rim around the černýite.

Covellite occurs sporadically and has probably developed as a result of the supergene alteration of chalcopyrite.

In the altered vein, černýite and greenockite are disseminated within the sericite gangue, where corroded relics of cassiterite I are common. Černýite, the most abundant phase, and greenockite occur as isolated small crystals corroded by sericite (Fig. 3D).

In the second assemblage, a banded zonal distribution of sulfides and sulfosalts has been recognized. Each band has a variable width (millimeter scale), and there is a gradual transition from one to the next.

From the altered zone in the vein toward the unaltered host-rocks, the following subassociations appear (Fig. 2). Band A consists of černýite – stannoidite – tetrahedrite (Fig. 4A). This subassociation is better developed where the apatite – sericite – quartz band (vein – host rocks contact) is thicker (1 millimeter). Stannoidite is present as single crystals, although it commonly surrounds černýite, and occurs intergrown with tetrahedrite. Černýite fills transverse cracks in the vein (evidence of remobilization?). Band B consists of chalcopyrite – tetrahedrite – mawsonite – cadmian briartite

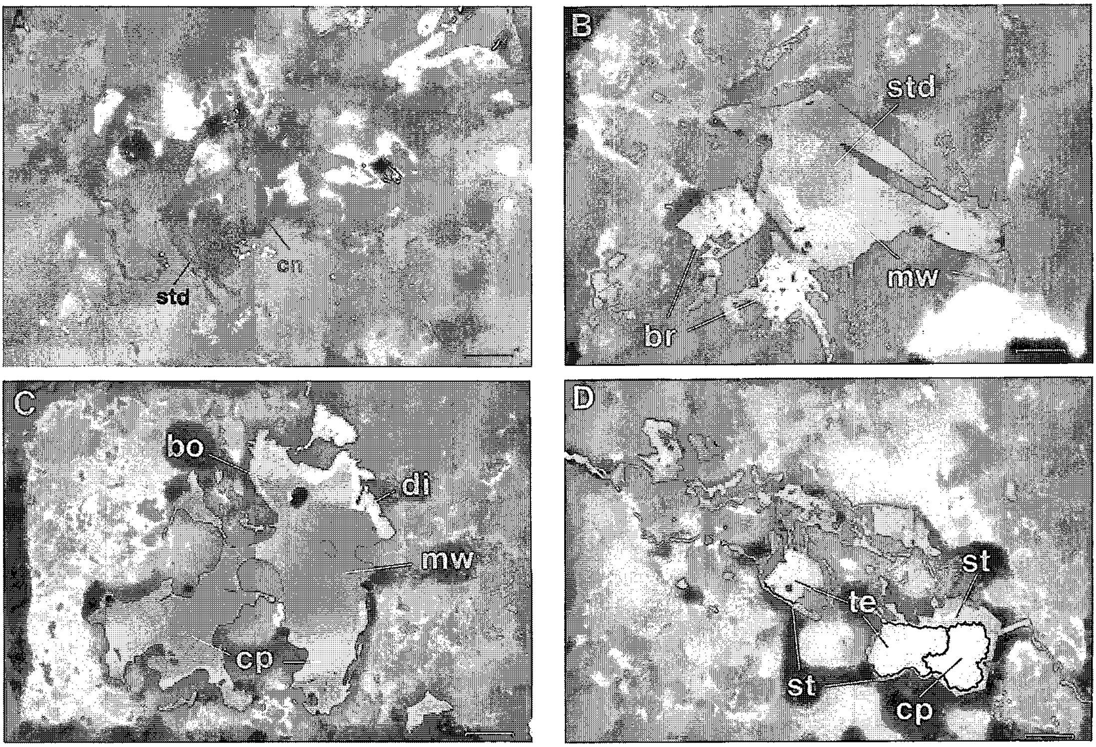

FIG. 4. Microphotographs in reflected light of the mineral phases in the altered host-rock (the scale bar indicates 50 μm): A. Černýite (cn) partly surrounded by stannoidite (std). Apatite and sericite constitute the gangue. Crossed nicols. B. Intergrowth of mawsonite (mw) and stannoidite (std) in contact with cadmian briartite (br). C. Mawsonite (mw) in contact with bornite (bo) and chalcopyrite (cp). The two latter sulfides are rimmed by digenite (di). D. Chalcopyrite (cp) partly replaced by stannite (st) and tetrahedrite (te). Stannite surrounds tetrahedrite.

– mohite – antimonpearceite – bornite – stannoidite – stannite – native bismuth – bismuthinite – arsenopyrite (Figs. 4B, C, D). These phases surround flakes of mica and fill interstices among them in the altered host-rocks. In some cases, they appear to have crystallized within small geodes, as the sulfide grains have a shape controled by euhedral quartz and apatite crystals. Chalcopyrite is the most abundant sulfide in this band. It occurs: (a) intergrown with mawsonite, cadmian briartite, tetrahedrite and bornite, and shows a granular texture, probably as a result of simultaneous crystallization, (b) corroded by mohite, tetrahedrite, antimonpearceite and stannite, and (c) as oval or rounded micro-inclusions in stannite crystals, in which they could represent exsolution lamellae. Stannoidite occurs associated with mawsonite (commonly, stannoidite is replaced by mawsonite) or in contact with chalcopyrite and tetrahedrite.

Cadmian briartite has an irregular distribution in band B, in which sulfides and sulfosalts are present as xenomorphic crystals; cadmian briartite commonly presents a characteristic laminar habit that helps in its identification. It is commonly in contact with tetrahedrite and chalcopyrite, even though it has been found with bornite, mawsonite, stannite, stannoidite and digenite. It commonly contains inclusions of tetrahedrite. Mohite replaces chalcopyrite or is between chalcopyrite and tetrahedrite grains. Mohite may be overlooked because of its similarity to stannoidite; for this reason, it could be more abundant than we currently indicate. Bornite generally seems to be in contact with chalcopyrite, mawsonite and tetrahedrite. It contains exsolution lamellae of chalcopyrite and, in some cases, a rim of digenite. Antimonpearceite corrodes chalcopyrite and presents complex intergrowths with stannite surrounding the chalcopyrite. Native bismuth is a minor phase that appears as simple grains surrounded by bismuthinite.

Band C consists of chalcopyrite + digenite. Both minerals are disseminated in a sericite gangue. Chalcopyrite usually presents a rim of digenite.

Mineral deposition in the Fuentes Villanas mine occurred in three stages: the first one is represented by crystallization of cassiterite I, columbotantalite, microlite and gangue minerals like albite, montebrasite and quartz in the veins; in the second, the vein sulfide and sulfosalt assemblage crystallized, and during the last stage, sulfide and sulfosalts of the altered host-rocks were deposited. Stages I and II are separated by an episode of deformation, and stages II and III, by the episode of intense hydrothermal alteration (sericitization) (Fig. 5).

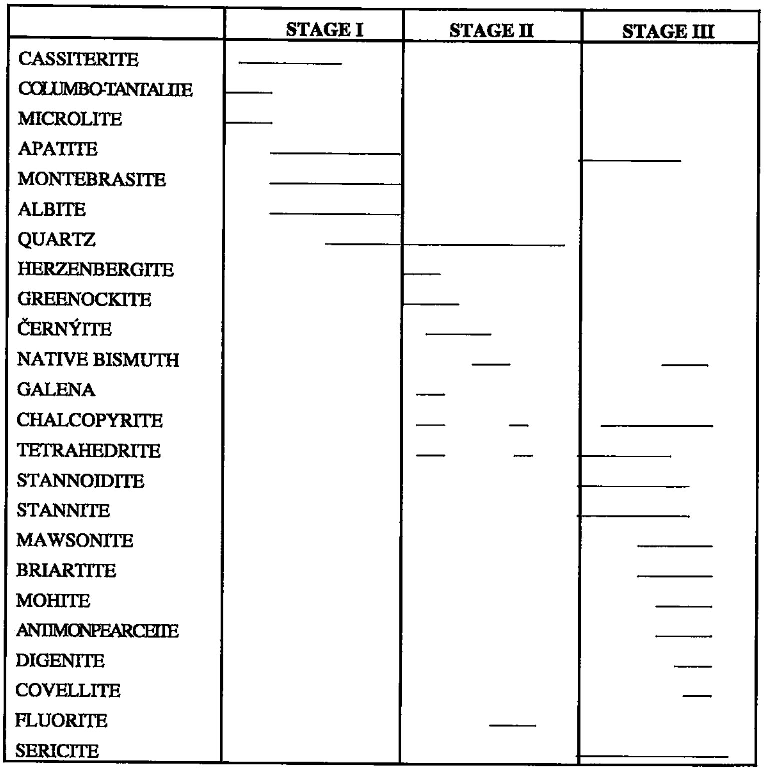

FIG. 5. Paragenetic sequence of deposition of ore and gangue minerals in the Barquilla deposit.

TABLE 2. REPRESENTATIVE CHEMICAL COMPOSITION OF TETRAHEDRITE

					WEIGHT PERCENT							
Sample	Cu	Ag	Zn	Fe	Mn	Cd	Sb	As	Bi	Ge	S	Total
VEIN	36.37	1.96	2.39	1.96	n.d.	4.71	27.98	0.97	0.16	n.d.	23.40	99.90
	36.38	1.93	2.56	1.92	n.d.	4.65	28.27	0.91	0.20	n.d.	22.75	99.57
	34.93	3.51	2.00	2.11	n.d.	4.83	27.63	1.11	0.18	n.d.	23.30	99.60
	34.72	3.89	1.75	2.01	n.d.	4.97	27.21	1.08	0.38	n.d.	23.49	99.50
	35.12	2.84	1.77	2.11	n.d.	5.12	27.43	1.03	0.29	n.d.	23.27	98.98
ALTERED ZONE	38.18	0.74	1.32	1.44	0.83	6.03	22.07	5.34	0.37	-	24.62	100.94
	38.46	0.94	-	5.02	-	0.77	28.67	1.03	-	-	24.65	99.77
	38.05	2.75	1.47	1.39	-	3.51	25.03	1.45	0.80	0.72	24.09	99.26
	34.98	2.09	0.35	0.79	-	10.96	24.85	2.24	-	0.27	23.56	100.09
	36.38	2.38	1.94	2.50	1.87	2.53	25.60	1.39	0.54	-	25.14	100.27
	35.66	1.12	0.77	0.60	-	9.60	22.97	2.05	3.69	-	22.84	99.30
	39.10	0.47	2.86	2.09	-	1.86	22.61	5.06	1.04	-	25.21	100.30
					ATOMIC PROPORTIONS (TOTAL ATOMS=29)							
	Cu	Ag	Zn	Fe	Mn	Cd	Sb	As	Bi	Ge	S	
VEIN	9.90	0.31	0.63	0.61	n.d.	0.72	3.97	0.22	0.01	n.d.	12.62	
	10.00	0.31	0.68	0.60	n.d.	0.72	4.06	0.21	0.02	n.d.	12.39	
	9.59	0.57	0.53	0.66	n.d.	0.75	3.96	0.26	0.02	n.d.	12.67	
	9.54	0.63	0.47	0.63	n.d.	0.77	3.90	0.25	0.03	n.d.	12.79	
	9.68	0.46	0.47	0.66	n.d.	0.80	3.95	0.24	0.02	n.d.	12.71	
ALTERED ZONE	9.99	0.11	0.34	0.43	0.25	0.89	3.01	1.18	0.03	-	12.76	
	10.15	0.15	-	1.51	-	0.11	3.95	0.23	-	-	12.90	
	10.26	0.44	0.39	0.43	-	0.53	3.52	0.33	0.07	0.17	12.87	
	9.62	0.34	0.09	0.25	-	1.70	3.57	0.52	-	0.06	12.84	
	9.54	0.37	0.49	0.75	0.57	0.37	3.50	0.31	0.04	-	13.06	
	10.01	0.19	0.21	0.19	-	1.52	3.37	0.49	0.31	-	12.71	
	10.13	0.07	0.72	0.62	-	0.27	3.06	1.11	0.08	-	12.94	

(n.d.: not determined; -: not detected)

CHEMICAL COMPOSITION OF SULFIDES AND SULFOSALTS

Sulfosalts

We have recognized and provide data for three separate solid-solution series: tetrahedrite–tennantite, pearceite–antimonpearceite, and pyrargyrite–proustite.

Tetrahedrite is the only member of the tetrahedrite–tennantite solid-solution series present; it occurs in the veins and in the altered host-rocks. The Sb/(Sb + As) value (Table 2) remains almost constant (0.96) for tetrahedrite in the veins, whereas it ranges from 0.75 to 0.90 for tetrahedrite of the host rocks. A high and uncommon content of Bi has been detected in this phase (up to 3.69 wt.%). Only minor quantities of Ge (up to 0.72 wt.%) have been detected in some grains of tetrahedrite; this could be due to contamination during the microprobe analyses, because those grains are very small inclusions in briartite.

The main cation within the series, Cu, has a well-defined reciprocal relation with Ag (Fig. 6): as copper decreases (from 35.29 to 29.63 at.%), the silver content rises (from 0.31 to 6.47 at.%). Shikazono & Kouda (1979) and Miller & Craig (1983) found similar trends.

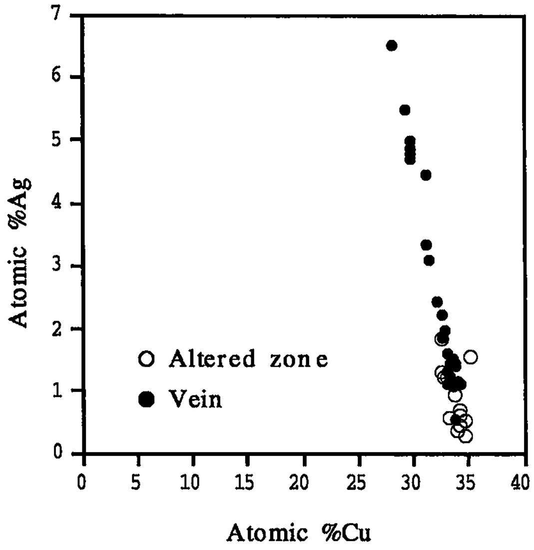

FIG. 6. Plot of Cu content of tetrahedrite *versus* its Ag content, showing data from Table 2 as well as others of the same deposits (atomic%).

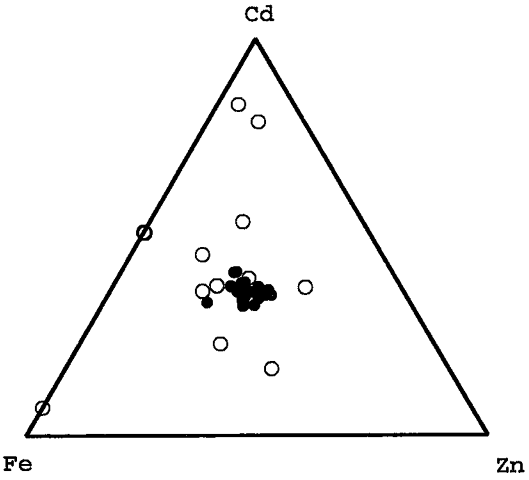

FIG. 7. Triangular plot (atomic) showing compositions of tetrahedrite from the Barquilla deposit: (●): vein, (○): altered zone.

TABLE 3. REPRESENTATIVE CHEMICAL COMPOSITION OF ANTIMONPEARCEITE

Sample	Cu	Ag	Fe	Cd	Sb	As	Bi	S	Total
				WEIGHT PERCENT					
1	11.61	60.03	-	0.51	11.33	0.29	-	15.48	99.25
2	8.89	65.81	-	0.57	9.53	0.21	-	15.18	100.19
3	8.95	64.20	-	0.52	9.61	0.32	-	16.22	99.82
4	9.16	63.39	-	0.67	9.96	0.28	-	16.08	99.54
				ATOMIC PROPORTIONS (TOTAL ATOMS=29)					
	Cu	Ag	Fe	Cd	Sb	As	Bi	S	
1	4.02	12.30	-	0.10	2.04	0.09	-	10.54	
2	3.10	13.50	-	0.11	1.73	0.07	-	10.40	
3	3.02	12.99	-	0.10	1.71	0.09	-	11.04	
4	3.14	12.86	-	0.15	1.79	0.09	-	10.90	

(-: not detected)

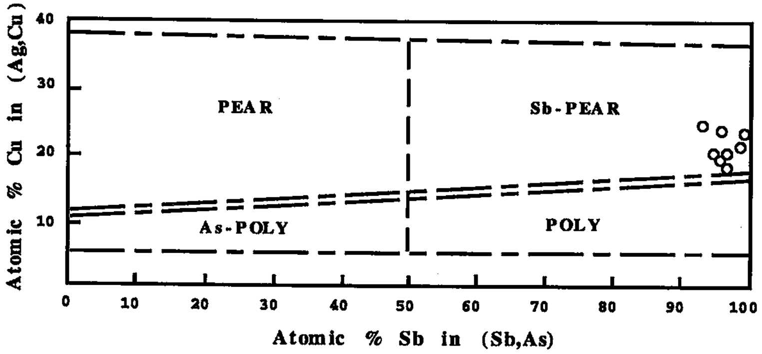

FIG. 8. Classification scheme based on compositional ranges, for polybasite–arsenopolybasite and antimonpearceite–pearceite solid-solution series (after Hall 1967).

TABLE 4. REPRESENTATIVE CHEMICAL COMPOSITION OF PYRARGYRITE

Sample	Cu	Ag	Fe	Cd	Sb	As	Bi	S	Total
				WEIGHT PERCENT					
1	-	58.60	-	0.44	23.23	0.43	-	16.67	99.37
2	0.62	60.92	-	0.39	20.41	0.45	0.67	17.00	100.46
				ATOMIC PROPORTIONS (TOTAL ATOMS=7)					
	Cu	Ag	Fe	Cd	Sb	As	Bi	S	
1	-	3.00	-	0.00	1.06	0.06	-	2.89	
2	0.05	3.06	-	0.00	0.93	0.05	0.00	2.90	

(-: not detected)

In the same plot, it is shown that the tetrahedrite of the veins is richer in Ag.

There are clear differences between the tetrahedrite in veins and host rocks in relation with the content in Cd, Fe, Zn (Fig. 7). The former have constant amounts of these elements; however, the second group exhibits wide compositional ranges in terms of these elements. Note that although the most homogeneous tetrahedrite is found in veins, tetrahedrite with the highest Cd content (10.96 wt.%) is located in the altered host-rocks. The highest Cd contents of natural tetrahedrite recorded in the literature seem to have been: 11.70 wt.% (Pattrick 1978) and 5.81 wt.% (Voropayev *et al.* 1988).

The manganese content has not been checked in the samples from veins. One grain of tetrahedrite from altered host-rocks contains a significant amount of this

TABLE 5. REPRESENTATIVE CHEMICAL COMPOSITION OF Ag-Pb-Bi-BEARING SULFOSALTS

					WEIGHT PERCENT				
Sample	Cu	Ag	Fe	Cd	Sb	Pb	Bi	S	Total
1	0.77	19.07	-	-	0.78	28.69	35.00	15.68	100.20
2	0.86	21.46	-	-	0.64	20.14	39.81	16.46	99.50
3	0.13	28.73	-	-	-	-	54.11	17.67	100.74
				STRUCTURAL FORMULA (S=2)					
	Cu	Ag	Fe	Cd	Sb	Pb	Bi	S	
1	0.04	0.73	-	-	0.04	0.57	0.32	2	
2	0.04	0.78	-	-	0.04	0.39	0.35	2	
3	0.00	0.98	-	-	-	-	0.44	2	

(-: not detected)

TABLE 6. REPRESENTATIVE CHEMICAL COMPOSITION OF STANNITE-GROUP MINERALS

					WEIGHT PERCENT					
Sample	Cu	Ag	Zn	Fe	Mn	Cd	Sn	Ge	Ga	S	Total
STANNITE	28.07	-	1.39	6.55	0.38	8.86	26.17	-	-	28.05	99.47
	28.24	-	1.73	6.46	0.27	8.51	26.24	-	-	28.03	99.48
	30.10	0.46	-	10.26	0.58	1.01	27.79	-	-	29.09	99.29
ČERNÝITE	27.30	-	-	0.84	0.58	20.66	23.90	0.00	n.d.	26.32	99.60
	25.95	1.60	1.52	1.19	n.d.	18.51	24.21	n.d.	n.d.	26.98	99.96
	27.57	-	0.76	2.78	n.d.	16.46	24.57	n.d.	n.d.	27.54	99.68
BRIARTITE	31.16	0.93	-	3.37	-	19.51	-	14.80	-	29.28	99.05
	29.45	0.92	-	0.49	0.71	23.02	-	15.76	-	29.22	99.57
	29.75	-	-	0.52	0.25	24.03	-	16.07	-	29.02	99.64
STANNOIDITE	39.23	-	0.71	11.99	-	0.75	18.01	-	-	29.30	99.99
	38.59	-	2.74	9.90	-	0.71	18.17	-	-	29.36	99.47
	39.43	-	2.98	9.93	-	0.75	18.12	-	-	28.93	100.14
MAWSONITE	44.47	-	-	13.09	-	-	13.33	-	-	29.15	100.04
	42.40	-	-	15.35	-	0.21	11.69	-	-	29.50	99.15
	43.83	-	-	13.07	-	-	13.92	-	-	29.18	100.00
					ATOMIC PROPORTIONS (TOTAL ATOMS=8,25,17)						
	Cu	Ag	Zn	Fe	Mn	Cd	Sn	Ge	Ga	S	
STANNITE	2.00	-	0.09	0.55	0.05	0.36	1.00	-	-	3.95	
	2.00	-	0.14	0.55	0.00	0.36	1.00	-	-	3.95	
	2.08	0.00	-	0.80	0.04	0.04	1.02	-	-	4.02	
ČERNÝITE	2.07	-	-	0.10	0.05	0.87	0.96	-	n.d.	3.95	
	1.98	0.05	0.10	0.10	n.d.	0.77	0.96	n.d.	n.d.	4.05	
	2.01	-	0.05	0.23	n.d.	0.70	0.98	n.d.	n.d.	4.02	
BRIARTITE	2.13	0.04	-	0.26	-	0.74	-	0.87	-	3.96	
	2.02	0.04	-	0.04	0.04	0.88	-	0.97	-	4.00	
	2.07	-	-	0.04	0.00	0.92	-	0.97	-	4.00	
STANNOIDITE	8.11	-	0.13	2.75	-	0.13	1.96	-	-	11.91	
	7.98	-	0.52	2.36	-	0.13	1.96	-	-	12.04	
	8.16	-	0.53	2.37	-	0.13	1.97	-	-	11.84	
MAWSONITE	6.04	-	-	2.16	-	-	0.95	-	-	7.85	
	5.75	-	-	2.35	-	0.00	0.87	-	-	8.02	
	6.01	-	-	2.00	-	-	1.05	-	-	7.93	

(n.d.: not determined; -: not detected)

element (1.87 wt.%). This can be considered as an example of slightly manganoan–cadmian tetrahedrite, reported previously by Dobbe (1992).

The compositional variability of tetrahedrite from the altered host-rocks may reflect, in part, their secondary character, as indicated by textural relationships. Most of the Fe, Cd and Zn contents could have been incorporated during replacement of pre-existing minerals, such as chalcopyrite and greenockite.

Pearceite–antimonpearceite is the second most abundant solid-solution series. The chemical composition of these phases is shown in Table 3. On the basis of the classification scheme devised by Hall (1967), all samples from the Fuentes Villanas mine consist of antimonpearceite (Fig. 8).

The identified phases within pyrargyrite–proustite series are antimonian end-members (Table 4), and they fit the ideal formula.

Compositional variations among sulfosalt minerals have been examined using Sb/(Sb + As) and Ag/(Ag + Cu) values. Owing to the scarcity and small size of pyrargyrite and antimonpearceite samples, the number of analyses is less representative than in the case of tetrahedrite. The Sb/(Sb + As) values do not vary significantly among phases, with the exception of the host-rock tetrahedrite.

Other Pb–Bi–Ag-bearing sulfosalts, with a composition intermediate between galena and matildite, are intergrown with galena (Table 5) and show wide variations in Pb contents. Sulfosalts with similar compositions have been reported by Bortnikov *et al.* (1987) and can be considered intermediate members in the galena–matildite solid-solution series.

Minerals of the stannite group

Five minerals of this group have been recognized in the Fuentes Villanas mine. They are represented by the general formula A_2BCS_4, (A: Cu, Ag; B: Fe, Zn, Cd, and C: Sn, Ge): stannite (Cu_2FeSnS_4), černýite (Cu_2CdSnS_4) and briartite [$Cu_2(Fe,Zn,Cd)GeS_4$], as well as stannoidite and mawsonite. There is a wide range in extent of substitutions for Fe and Cd in stannite, černýite and briartite, as summarized in Table 6; the Zn content of these minerals is low.

Experimental studies on the pseudobinary system Cu_2ZnSnS_4 – Cu_2CdSnS_4 (kesterite–černýite) (Osadchii 1991) revealed the existence of a solid-solution series between them, but in the case of the stannite–černýite series, the limits of the solid solution have not been experimentally determined. The range of the solid solution between stannite and černýite is wide in Barquilla and Tanco deposits (Kissin *et al.* 1978); there is quite an important range of substitution of Cd for Fe (and Zn) in stannite and of Fe and Zn for Cd in černýite (Fig. 9). Černý & Harris (1978) found a positive correlation between Zn and Cd contents in stannite from the Tanco granitic pegmatite. This trend is not suggested for stannite from Barquilla.

In the same way as černýite, briartite presents a wide variation in its chemical composition (Table 6). Examples of briartite from Tsumeb and Kipushi (Francotte *et al.* 1965, Viaene & Moreau 1968, Ottenburgs & Goethals 1972, Geier & Ottemann 1972) are Zn end-members, whereas samples from this orebody are Cd end-members as well as intermediate members between Cd and Fe end-members (Fig. 10), showing the possible existence of a new Cd–Fe solid-solution series with total absence of Zn (Babkine *et al.* 1990). We are in the process of determining the structure of this phase to confirm that it is a new species.

On the other hand, although experimental studies (Moh 1975) have shown that the existence of a solid solution series between Sn and Ge end-members (cadmian briartite – černýite) is possible, evidence for it has not been found in the Barquilla deposit.

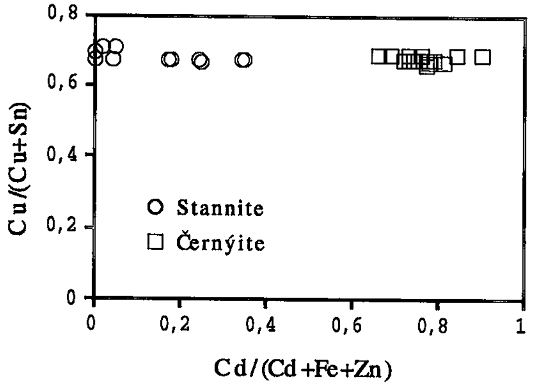

FIG. 9. Composition of stannite and černýite in the Cu/(Cu+Sn) – Cd/(Cd+Fe+Zn) diagram.

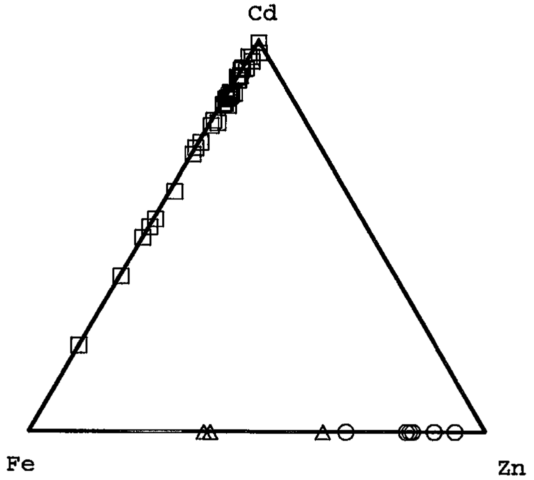

FIG. 10. Compositions of briartite in terms of Cd–Fe–Zn: □: Barquilla, ○: Tsumeb, and △: Kipushi.

TABLE 7. REPRESENTATIVE CHEMICAL COMPOSITION OF DIGENITE

	WEIGHT PERCENT					ATOMIC PROPORTIONS (TOTAL ATOMS=14)			
Sample	Cu	Ag	Fe	S	Total	Cu	Ag	Fe	S
1	69.44	2.83	4.26	23.03	99.56	8.16	0.22	0.22	5.39
2	74.14	3.44	0.70	21.77	100.05	8.71	0.22	0.00	5.06

(-: not detected)

TABLE 8. REPRESENTATIVE CHEMICAL COMPOSITION OF MOHITE

	WEIGHT PERCENT								
Sample	Cu	Ag	Fe	Mn	Cd	Sn	Sb	S	TOTAL
1	36.75	0.53	0.74	0.34	-	30.61	3.03	27.55	99.55
2	36.52	0.47	0.77	0.33	-	30.55	3.27	27.60	99.51
3	35.33	-	2.02	-	0.44	32.67	-	28.79	99.25
4	35.42	-	1.89	-	0.58	33.09	-	28.65	99.63
5	35.50	1.29	-	0.44	-	31.04	-	28.34	96.61
	ATOMIC PROPORTIONS (TOTAL ATOMS=6)								
	Cu	Ag	Fe	Mn	Cd	Sn	Sb	S	
1	2.01	0.00	0.03	0.03	-	0.90	0.69	2.98	
2	1.97	0.00	0.03	0.03	-	0.90	0.10	2.97	
3	1.89	-	0.13	-	0.00	0.94	-	3.03	
4	1.91	-	0.10	-	0.00	0.95	-	3.03	
5	1.96	0.03	-	0.00	-	0.91	-	3.09	

(-: not detected)

The chemical composition of stannoidite fits the ideal formula: $Cu_8Fe_2^{3+}(Fe^{2+},Zn)Sn_2S_{12}$ (Shimizu & Shikazono 1987). The Fe^{2+}/Zn value inferred, obtained by their method of calculation, varies between 0.6 and 6.

Mawsonite is compositionally homogeneous and does not deviate from its ideal formula.

Simple sulfides

Digenite contains significant amounts of Fe and Ag, up to 4.26 wt.% and 3.4 wt.%, respectively (Table 7).

The composition of several grains of mohite deviates significantly from its ideal formula: Cu_2SnS_3 (Table 8), although it has high Fe, Sb and Ag contents, minor quantities of Mn, and traces of Ge, As, Ga, Zn and Bi. Sb and Ag contents of the mohite that is in contact with tetrahedrite range from 3.03 to 3.27 wt.% and from 0.53 to 0.25 wt.%, respectively. Mohite coexisting with chalcopyrite contains high concentrations of Fe (3.57–3.28 wt.%). The compositional variability may reflect, in part, their secondary character, indicated by textural relationships.

Herzenbergite shows low Cu, Sb, Ag and Fe contents and traces of Ga, Mn, Bi and Zn. Various intermediate members o the herzenbergite–galena solid-solution series have been analyzed (Table 9).

Galena shows limited substitution of Bi, Ag for Pb. Only one grain contains a significant amount of Cu (1.91 wt.%). The composition of galena, plotted in the Pb–Bi–Ag diagram, plots to the right of the galena–matildite joint (Fig. 11). Various investigators (Czamanske & Hall 1975, Karup-Møller 1977, Paar *et al.* 1980, Makovicky & Karup-Møller 1984, Pattrick 1984) have shown that the composition of the galena component of the matildite–galena intergrowths plots on or very close to the galena–matildite joint, whereas galena directly associated with Pb–Bi–Ag sulfosalts is enriched in Bi relative to Ag, as observed in the Barquilla deposit. Ag and Bi contents in galena are explained by the coupled substitution $Ag^+ + Sb^{3+}(Bi^{3+}) \rightarrow 2Pb^{2+}$ (Karup-Møller 1977, Karup-Møller & Pauly 1979, Jeppson 1987, Gaspar *et al.* 1987).

Analytical data for the greenockite show substitution of Zn and Mn for Cd (up to 6.19 and 1.00 wt.%, respectively).

DISCUSSIONS AND CONCLUSION

This study of sulfides, sulfosalts and a native element from the Fuentes Villanas mine shows that not only are there mineralogical differences between the vein and the altered host-rocks, but also important compositional differences.

Tin is an element that is present in the veins and in the altered host-rocks. Cadmium in the veins forms its own sulfides (černýite and greenockite) and is concentrated in tetrahedrite. Gouanvic & Babkine (1985) described the occurrence of Cd-bearing sulfosalts in the mineralized veins from the Monteneme deposit, but no mineral containing essential Cd has been found. In the altered host-rocks, Cd is incorporated in cadmian

TABLE 9. REPRESENTATIVE CHEMICAL COMPOSITION OF MEMBERS OF THE GALENA-HERZENBERGITE SOLID-SOLUTION SERIES

				WEIGHT PERCENT					
Sample	Cu	Ag	Fe	Pb	Sn	Sb	Bi	S	Total
1	0.64	-	-	38.34	41.31	-	1.16	17.34	98.79
2	-	-	-	40.81	39.06	0.22	0.77	16.94	97.80
				STRUCTURAL FORMULA (S=2)					
	Cu	Ag	Fe	Pb	Sn	Sb	Bi	S	
1	0.02	-	-	0.33	0.64	-	0.02	1	
2	-	-	-	0.38	0.62	0.00	0.00	1	

(-: not detected)

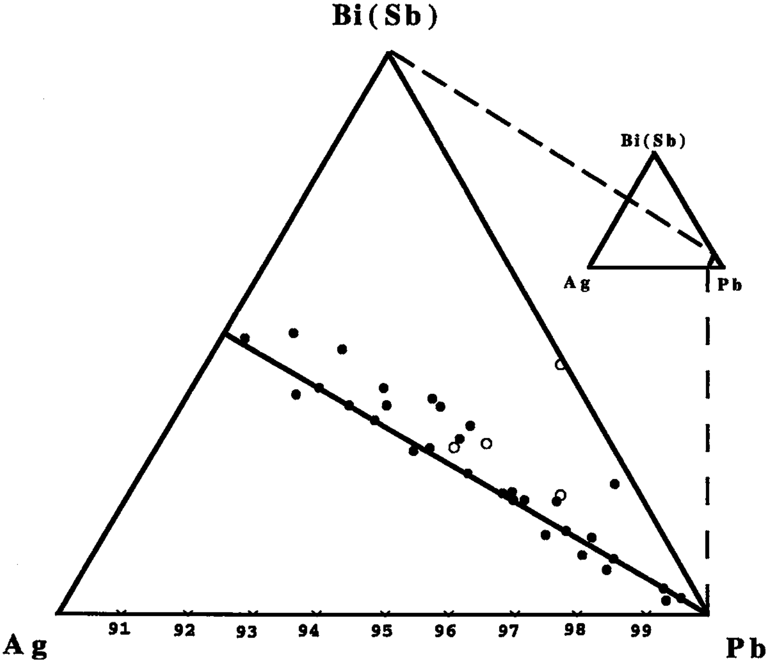

FIG. 11. Triangular plot (atomic) showing a portion of the system Pb–Ag–Bi(Sb) and composition of galena analyzed in this study, as well as selected data from the literature. Open circles are from the Barquilla deposit; solid circles are from Foord & Shawe (1989).

briartite, tetrahedrite and, to a minor extent, in minerals of the stannite group. Ge has been detected only in sulfides from the host rocks; the highest concentrations of Ge occur, chiefly, in briartite (from 12.09 to 16.07 wt.%) and, to a minor extent, in tetrahedrite (up to 0.72 wt.%) and stannite (0.69 wt.%).

In unmetamorphosed sulfide ore deposits, at high activity of S, Ge will form its own sulfides, such as briartite, renierite or germanite if the Ge concentration is sufficient, or else it will substitute for As, Sn or other metals in sulfosalts (Bernstein 1985). These factors have allowed the formation of one of the sulfides of this element, cadmian briartite, in the Barquilla deposit.

Ge in hydrothermal fluid either derives from enrichment during the fractional crystallization of a magma, or is due to the incorporation of Ge from the country rocks: the frequent associations of Ge-bearing sulfides and sedimentary host-rocks enriched in organic material (*e.g.*, Tsumeb and Kipushi) could be due, in part, to this mechanism (Bernstein 1985). The very high content of Ge (16.7 ppm) in the unmineralized calc-silicate host-rocks of the Fuentes Villanas mine lead us to think of a possible leaching of Ge from the host rocks. This hypothesis would explain the presence of Ge in the host rocks and its absence in the vein.

Cu, Fe and Zn are concentrated in sulfides in the host rock, whereas Ag is concentrated in sulfosalts in the veins (tetrahedrite and pyrargyrite). Bi is scarce in the veins of the Barquilla deposit; it is concentrated at low levels in matildite, native bismuth, tetrahedrite and galena. Foord & Shawe (1989) reported that if Ag and Bi are available to substitute for Pb, the substitution will occur readily, particularly in systems with low contents in Cu, Sb and Zn. On the other hand, if Ag and Sb are available at the moment of crystallization and Bi is rare, a complete solid-solution series could form between galena and matildite. However, if Cu, Zn and other metals are present, Ag and Sb will be incorporated into minerals as a tetrahedrite–tennantite-group mineral, and only a limited amount will substitute for Pb in galena, as it does in Fuentes Villanas mine.

The ratio of fugacity of sulfur to fugacity of oxygen governs the crystallization of Sn-bearing sulfides or cassiterite: where there is a high ratio of sulfur to oxygen, tin sulfides will be generated, and if cassiterite appears, it will be associated with Sn–Fe-bearing sulfides. This type of deposit is rare and, in most examples, Cu (as well as Fe, Cd, Zn) is present, leading to the formation of stannite-group minerals (Moh 1974), as occurs at the Fuentes Villanas mine.

Textural relationships among sulfides and cassiterite at the Fuentes Villanas mine suggest the existence of a first stage with low ratio of sulfur to oxygen fugacity, leading to the formation of cassiterite I in the three mines. Afterward, there was a local inversion of this ratio, that is to say, an increase in sulfur fugacity, recorded only at the Fuentes Villanas mine, which explains the deposition of sulfides and sulfosalts. In the veins, the presence of cassiterite corroded first by herzenbergite and later by černýite, suggests a progressive change of this ratio. Diman & Nekrasov (1966) noted that SnS precipitates under reducing conditions from solutions relatively low in S. Crystallization took place before the sericitic alteration.

The sequence of crystallization observed in the altered zone is černýite → stannoidite → mawsonite. Stannite does not occur associated with these minerals, but instead with chalcopyrite (exsolution?) and with chalcopyrite + tetrahedrite (replacement). Mawsonite commonly replaces and corrodes grains of stannoidite. Similar textures have been found in synthetic samples (Lee *et al.* 1975) and in other natural samples (Markham & Lawrence 1965, Imai *et al.* 1975, Manning 1983). Lee *et al.* (1975) demonstrated that the formation of mawsonite is favored by an increase in S fugacity as well as by a reduction in temperature. This fact suggests that the mawsonite formed by the increase of sulfur fugacity or reduction in temperature (or both). Furthermore, this increase is reflected by the decomposition of native bismuth to give bismuthinite, extensively reported in various assemblages, formed together with the sericitic alteration.

The following sequence of crystallization of the Sn-bearing minerals may be proposed:

cassiterite → herzenbergite → černýite → stannoidite → mawsonite.

This sequence involves a progressive increase of the metal/S, Fe^{3+}/Fe^{2+} and Cu/Sn values in these minerals, which is consistent with the drop in temperature expected from the veins to the altered host-rocks.

Minerals like cadmian briartite, mohite, antimonpearceite and chalcopyrite seem have been generated simultaneously.

The crystallization of sulfides and sulfosalts in the Barquilla deposit seems to have taken place in an unusual chemical system, because these minerals are not present in most ordinary hydrothermal sulfide assemblages; furthermore, they show an unusual range of compositions, that leads, in extreme cases, to the formation of rare mineral species such as herzenbergite, černýite, mohite and cadmian briartite.

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