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Ore mineralogy, fluid inclusion, and stable isotopic characteristics of stratiform copper deposits in the coastal Cordillera of northern Chile

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Abstract Late-Jurassic stratiform copper deposits in the coastal range of northern Chile (Susana-Lince and Buena Vista of the Carolina de Michilla district, and Mantos de La Luna) are hosted in an andesite-dominant volcanic pile of the Jurassic La Negra Formation which is extensively intruded by gabbroic to granodioritic plutons and dikes. Primary copper mineralization is characterized by chalcocite ($\sim\text{Cu}_{1.90}\text{S}$) + digenite + bornite \pm chalcopyrite + hematite. Supergene alteration of these minerals has produced chalcocite (djurleite), covellite, atacamite, chrysocolla and copper oxides (copper wad). Fluid-inclusion data indicate a variable temperature of formation (200 to 380 °C) and a wide range of fluid salinities (7 to 34 wt% NaCl). Carbon and oxygen isotopic compositions of calcite from the Susana-Lince deposit ($\delta^{13}\text{C} = -2.6$ to -3.6‰ , $\delta^{18}\text{O} = 13.7$ to 18.7‰) combined with the thermometric data suggest that the fluid responsible for the calcite mineralization derives from mixing of high-temperature meteoric water with cooler basinal brines. These data imply that the stratiform copper deposits of the coastal Cordillera are epigenetic and formed from non-magmatic, moderately oxidized hydrothermal solutions.

Keywords Chile · Coastal Cordillera · Stratiform copper · Fluid inclusions · Stable isotopes

Introduction

In northern Chile, stratiform copper deposits are widely distributed along the coastal range between Tocopilla and Taltal, forming an important cupriferous metallogenic belt (Ruiz et al. 1965, 1971). The deposits are hosted within a thick sequence of andesite to basaltic andesite of Jurassic age named the La Negra Formation (García 1967; Buchelt and Tellez 1988; Pichowiak 1994). The volcanic sequence is extensively intruded by Jurassic to Early-Cretaceous plutons of gabbroic to granodioritic composition. Numerous geological and geochemical studies on this type of copper deposits have been undertaken over the years (e.g., Ruiz et al. 1965, 1971; Losert 1973; Palacios 1974; Espinoza 1981, 1982; Espinoza and Palacios 1982; Sato 1984; Soto and Dreyer 1985; Palacios 1986, 1990; Boric et al. 1990; Wolf et al. 1990; Espinoza et al. 1996; Vivallo and Henríquez 1998), yielding various ideas on their metallogeny. These studies primarily focused on the following questions: are the stratiform deposits syngenetic (volcanogenic) or epigenetic and, in the latter case, which (La Negra Formation or the plutons) was the source of the metallic components (i.e., copper).

In spite of such significant discussions, fundamental studies on physico-chemical conditions, such as temperature and redox state of ore mineralizations, have scarcely been carried out for the stratiform copper deposits of this coastal range. The temperature of the primary mineralization was estimated only for the Buena Esperanza deposit near Tocopilla, using fluid-inclusion data (Nisterenko et al. 1973; Palacios 1990). In particular, no systematic studies on fluid inclusions combined with ore mineralogy have been carried out. Thus, the aim of this study is to investigate ore mineralogy and fluid-inclusion properties of several typical stratiform copper deposits (Susana-Lince and Buena Vista of the Carolina de Michilla district, Mantos de La Luna) located along the coastal Cordillera in the northern province of Antofagasta, Chile, with the

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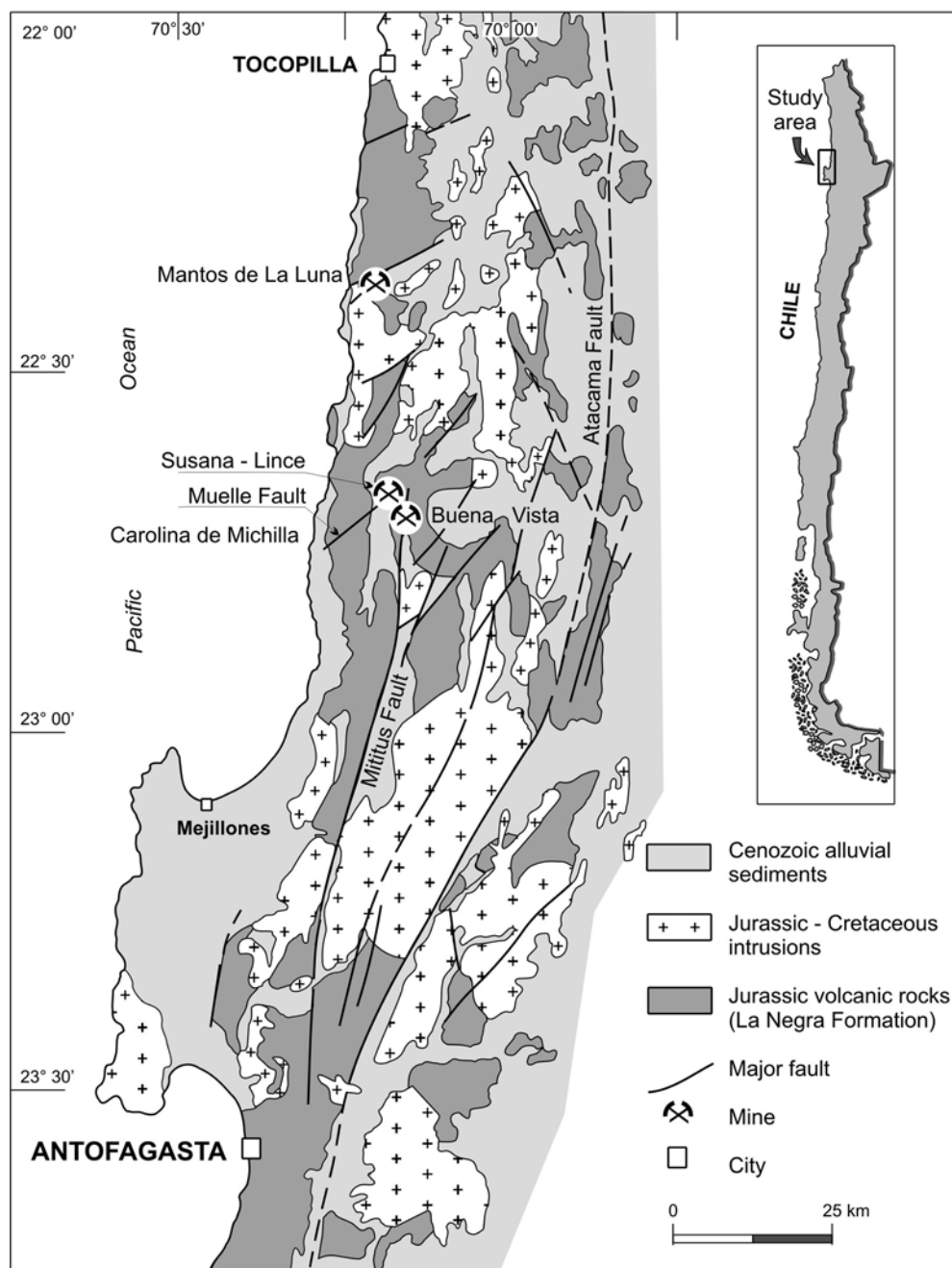
objective to infer conditions of primary copper formation. In addition, preliminary data on the isotopic composition of calcite associated with primary copper sulfides at the Susana-Lince deposit are reported to specify the source of the hydrothermal fluid.

Outline of geology and ore deposits

The geology of the northern coastal area of Antofagasta is characterized predominantly by the La Negra Formation of Jurassic age, Late-Jurassic to Early-Cretaceous plutonic rocks which intrude the La Negra

Formation, and Cenozoic alluvial sediments (Fig. 1). The La Negra Formation consists mostly of monoclinical andesitic to basaltic andesite lavas and variable amounts of tuff breccias, sandstone and limestone (García 1967; Astudillo 1983; Buchelt and Tellez 1988; Muñoz et al. 1988; Boric et al. 1990; Venegas et al. 1991). The formation has a total thickness of at least 7.4 km (Muñoz et al. 1988). Rb-Sr absolute ages of 186 ± 14 Ma and 173 ± 19 Ma have been obtained on basaltic andesite lava near the Mantos de La Luna deposit (Rogers 1985) and andesitic lava in the Carolina de Michilla district (Venegas et al. 1991), respectively. The La Negra Formation has experienced variable degrees of propylitic

Fig. 1 Location map showing the stratiform copper deposits studied and the general geology of the coastal range of northern Chile (after Boric et al. 1990; Vivallo and Henríquez 1998)



alteration, and it has the typical mineral association of albite, chlorite, epidote, sericite and calcite (Espinoza et al. 1996). In addition, extreme sodium metasomatism and calc-silicate (grandite, clinopyroxene, sphene) alteration are reported for the early alteration stages (Wolf 1990; Wolf et al. 1990). Furthermore, prehnite and pumpellyite typical of low-grade burial metamorphism are locally observed in the formation (Losert 1974; Palacios 1977).

Intrusive rocks consist of holocrystalline gabbroic to granodioritic rocks of the magnetite series of the calc-alkaline suite (Ishihara and Ulriksen 1980; Palacios and Espinoza 1982; Ishihara et al. 1984). These intrusions have various absolute ages ranging mostly from 168 to 133 Ma (Palacios and Definis 1981; Astudillo 1983; Rogers 1985; Venegas et al. 1991). Some porphyritic stocks and dikes of different ages are observed in the study area, of which the younger ones cut primary mineralization zones.

The structural framework of the area is dominated by two major faults, the Atacama and the Mititus Faults (Fig. 1). The Atacama Fault runs in a NS to NNE direction and is considered to be a sinistral strike-slip fault formed during transtensional oblique subduction in the Jurassic to Early Cretaceous (e.g., Scheuber and Andriessen 1990). In general, the stratiform deposits of the coastal range are located on the western side of the Atacama Fault, and are closely related to younger fault systems with ENE–EW orientation (see Fig. 1).

All of the stratiform deposits studied correspond to the “stacked tabular type” defined by Sato (1984), and occur as numerous tabular orebodies (mantos) in the La Negra Formation. Primary copper mineralization occurs preferentially in the porous parts of the host rocks such as amygdale fillings, veinlets and disseminations, and they generally exhibit epigenetic features (Sato 1984; Soto and Dreyer 1985; Espinoza et al. 1996; Definis and Bello 2000). Based on our fieldwork and previous studies, the characteristic features of each deposit are briefly summarized as follows.

The *Carolina de Michilla district* is located about 120 km north of Antofagasta, and is the largest mining area of the coastal Cordillera, producing more than 147,000 tonnes (t) of copper ore per month with an average grade of $\sim 1.2\%$ Cu. The district has many stratiform and vein-type deposits, among which the *Susana-Lince deposit* ($22^{\circ}40.2'S$, $70^{\circ}09.8'W$) is the biggest of the stratiform type, producing more than 60,000 t/month with an average grade of 0.6–1.0% Cu and 25–26 g/t Ag. The district is composed of a monoclinical volcanic sequence at least 1,000 m thick, and has a $N65^{\circ}E$ trend with dips varying from 35 to $40^{\circ}NW$. The Susana-Lince orebodies display a vertical zonal arrangement with increasing depth from a secondary copper oxide zone to the copper sulfide zone via the transitional (mixed) zone (Acevedo et al. 1997). In the central part of the deposit, a barren breccia zone termed the “Susana Breccia” (Soto and Dreyer 1985) occurs surrounding an unmineralized gabbro-dioritic

stock (154 ± 8 Ma; Astudillo 1983). Mineralized breccia zones, composed of rock fragments of andesitic and intrusive rocks, are distributed outside the Susana Breccia (Wolf et al. 1990; Acevedo et al. 1997). These features demonstrate that the brecciation associated with the gabbro-dioritic intrusion is a post-mineralization event. In the deeper level, the gabbro-dioritic intrusion cuts a diorite porphyry which is accompanied with mineralized intrusive breccias (Acevedo et al. 1997). Following these events, the Susana-Lince area was strongly fractured by the dextral-normal Muelle Fault which has a $N65^{\circ}E$ trend with $55^{\circ}SE$ dip (Fig. 2A).

The *Buena Vista deposit* ($22^{\circ}42.2'S$, $70^{\circ}09.6'W$), situated approximately 4 km southeast of the Susana-Lince deposit, is a small stratiform deposit producing 5,000 t/month with an average grade of $\sim 2.5\%$ Cu and 7 g/t Ag. This deposit is hosted in andesitic lavas exhibiting porphyritic, aphanitic and amygdaloidal textures, similar to the host rocks at the Susana-Lince deposit. The lava sequence, which trends $N50-60^{\circ}E$ with dips of $20-25^{\circ}NW$, is irregularly intruded by medium-grained dioritic stocks and dikes, and it is locally brecciated (Alvarez 1999). The copper-mineralized zone is composed of irregular-shaped mantos which developed concordantly outside the main stock separated by a meter-wide, barren zone. The mineralized zone is locally fractured, occasionally taking the form of hydrothermal breccias at depth (Fig. 2B).

The *Mantos de La Luna mine* is situated about 30 km south of Tocopilla ($22^{\circ}22.7'S$, $70^{\circ}12.7'W$), producing 60,000 t/month copper ore with an average grade of $\sim 1.7\%$ Cu. This deposit consists of three small orebodies termed Bloque Norte (Capacho), Bloque Central and Bloque Sur, of which the Bloque Central is currently the biggest copper producer. The boundaries between Bloque Norte – Bloque Central and Bloque Central – Bloque Sur are marked by an EW-trending fault (Albornoz Fault) and a NWW-trending fault (Sur Fault), respectively. The mineralized bodies occur within a nearly monoclinical volcanic sequence striking $N10^{\circ}E$, dipping $30^{\circ}E$, and showing aphanitic, amygdaloidal and porphyritic textures (Greiner 1982; Definis and Bello 2000). Copper mineralization in the Mantos de La Luna deposit occurs preferentially in the lower levels of the amygdaloidal and porphyritic horizons. The northernmost part of the Bloque Norte is cut by an unmineralized granodioritic dike emplaced along the NEE-trending Capacho Fault, and the dike is fractured by a NWW-trending fault (Rincon Fault).

Methods of investigation

For each deposit, a subset of 34 to 43 samples were selected from specimens collected in the field, and prepared for microscopic and fluid-inclusion studies. The samples were collected from drill cores in underground levels and in the open pits of the Susana-Lince and Buena Vista deposits (Fig. 2), and from the walls of the main adits

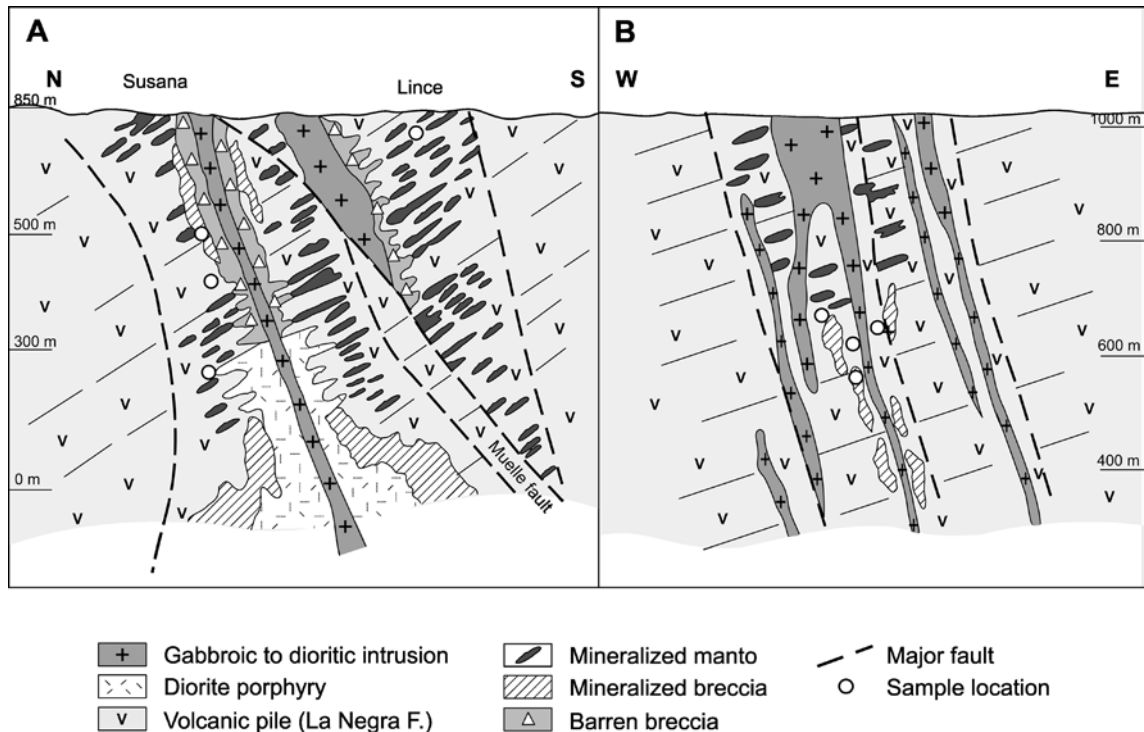


Fig. 2 Geologic cross sections of the Susana-Lince (A) and Buena Vista (B) deposits, showing copper orebodies (Acevedo et al. 1997; Alvarez 1999) and the locations of samples used for fluid-inclusion analysis

of the Bloque Central and Bloque Norte of the Mantos de La Luna deposit. Textural relationships of the ore minerals were examined using polished sections and thin sections, and the compositions of hypogene chalcocite and digenite were determined using a JEOL JXA-8600 electron microprobe at the Universidad de Concepción with wavelength-dispersive spectrometers. The analyses were performed under an accelerating voltage of 20 kV for Cu, Fe, Ag and S, using metallic copper, chalcopyrite and argentite as standard materials, and the data were processed using a ZAF correction method.

Primary fluid inclusions in calcite and quartz (including amethyst) of the primary hydrothermal stage from the three deposits were examined to obtain data of their homogenization temperatures (T_h) and NaCl wt% equivalent salinities, using a Linkam THMSG 600 heating-freezing stage connected to TMS 93 – LNP programmable controllers. All samples were prepared as doubly polished thin sections approximately 0.1 to 0.5 mm thick. The salinities of the fluid inclusions were indirectly estimated from the measured ice melting point for the liquid-vapor inclusions or from the halite disappearance temperature for polyphase inclusions (Sternner et al. 1988; Bodnar 1993). Heating rates of 1 to 3 °C/min were used for homogenization temperature measurements, and rates of 0.2 to 0.4 °C/min were adopted for ice melting temperature. The data obtained are reproducible to $\pm 0.4^\circ$ for the heating runs, and $\pm 0.1^\circ$ for the freezing runs.

Carbon and oxygen isotope analyses were made on six calcite specimens from the Susana-Lince deposit. These calcites were carefully separated and powdered, and CO_2 was liberated using phosphoric acid at 25 °C under vacuum condition (Morishita and Matsuhisa 1984). Isotopic measurements were carried out using a Finnigan MAT 252 mass spectrometer at Tohoku University. All data obtained are given as per mil (‰) relative to PDB for $^{13}\text{C}/^{12}\text{C}$ and VSMOW for $^{18}\text{O}/^{16}\text{O}$, with reproducibility better than $\pm 0.1\text{‰}$. The oxygen isotopic fractionation factor of CO_2 gas liberated from calcite at 25 °C was taken as 1.01025 (Friedman and O'Neil 1977).

Ore mineralogy

Based on careful macroscopic and microscopic observations, the mineralization at the three deposits is divided into the following three stages: primary hydrothermal stage, secondary enrichment stage, and oxide alteration stage. The primary hydrothermal stage is further subdivided into early and main hydrothermal substages. The early substage is characterized by magnetite + pyrite + chalcopyrite with a typical propylitic alteration assemblage of albite + chlorite + epidote + sericite. The main substage is characterized by hypogene chalcocite + digenite + bornite \pm chalcopyrite + hematite, locally with small amounts of native silver and native copper in the case of the Susana-Lince deposit. The secondary enrichment stage involved sulfide replacement by supergene chalcocite + covellite with small amounts of hematite, whereas secondary copper minerals such as atacamite, chrysocolla, cuprite and copper oxide aggregate (copper wad) formed in the oxide alteration stage. Lesser amounts of calcite and quartz (including amethyst) are observed as gangue minerals in the primary hydrothermal stage, and goethite and gypsum occur in the oxide alteration stage.

Hypogene mineralization

Small concentrations of magnetite and pyrite as early substage minerals usually occur as polyhedral discrete grains, and the former frequently contain fine lamellae of hematite as a result of martitization. As mentioned above, copper mineralization in the main hydrothermal

substage is characterized by the association of chalcocite + digenite + bornite \pm chalcopyrite + hematite. In particular, an intimate association between chalcocite and bornite is usually observed in the Carolina de Michilla samples (Fig. 3A, B). The typical myrmekitic intergrowth of chalcocite and bornite, which has been recognized in the Susana-Lince samples (Wolf et al. 1990), has also been found in several samples from the Buena Vista deposit (Fig. 3B). Digenite and chalcopyrite occur locally as exsolution products in chalcocite and bornite, respectively. Fine lamellae of chalcopyrite in bornite have been sporadically observed in samples from the three deposits. Frequently, coarse-grained chalcocite exhibits lamellar twinning suggestive of high-low inversion. In the Susana-Lince deposit, digenite is associated locally with native silver, and rarely includes tiny spherical inclusions or veinlets of native silver. In the main hydrothermal substage, hematite occurs as discrete grains with columnar habits or in radial aggregates, and is closely associated with primary chalcocite and bornite (Fig. 3A). This type of hematite is locally replaced by colloform goethite in the latest stage. As stated above, hematite also occurs as fine lamellae in magnetite.

Supergene mineralization

Secondary enrichment

The secondary enrichment stage is characterized by the formation of fine-grained aggregates of supergene chalcocite and covellite. These minerals replace primary chalcocite, digenite and chalcopyrite, and are themselves locally replaced by goethite. Recently, Apablaza (2001) has reported, based on X-ray powder diffraction analy-

sis, that the supergene chalcocite (blue chalcocite) corresponds to djurleite as a low-temperature mineral phase. Covellite occurs as fibrous aggregates or networks on the periphery and along cleavages of primary chalcocite and digenite crystals (Fig. 3C).

Oxide alteration

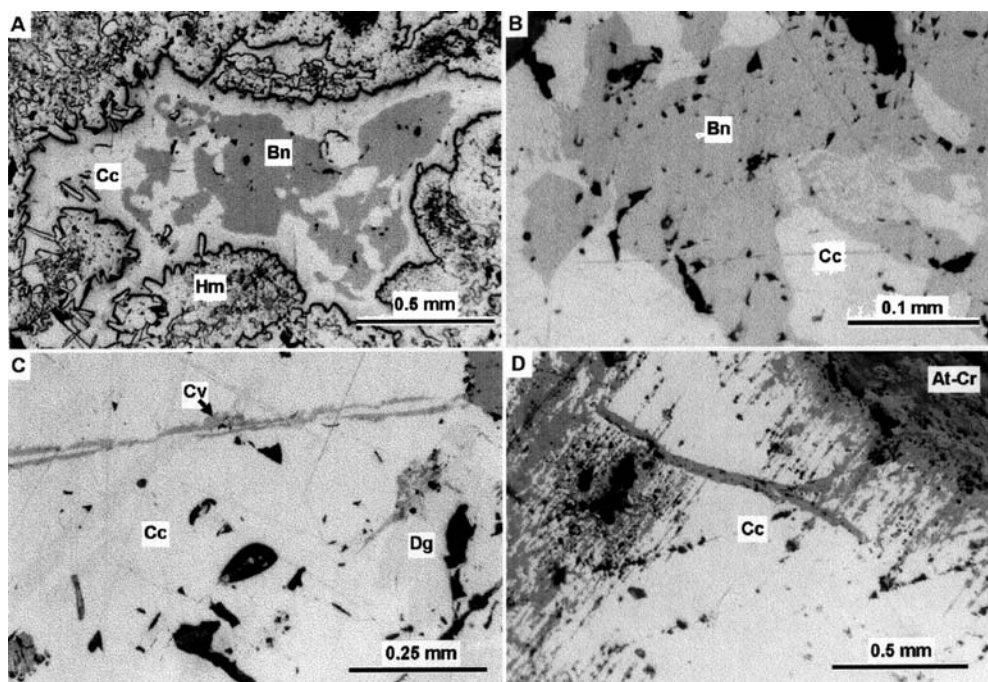
In the three deposits, atacamite and chrysocolla occur abundantly as oxide alteration stage minerals. Both minerals developed as amygdale infillings in the andesitic rocks, and generally chrysocolla appears to have formed slightly later than atacamite. These minerals frequently replace the edges of hypogene chalcocite and digenite (Fig. 3D), and also supergene chalcocite and covellite. In this stage, copper oxide minerals (copper wad) occur in close association with atacamite and chrysocolla in the Susana-Lince deposit.

The paragenetic sequences are very similar in the three deposits, and thus the whole sequence is summarized as illustrated in Fig. 4. However, certain differences are recognized in the occurrence of quartz and calcite. Quartz occurs predominantly in the primary hydrothermal stage in the Susana-Lince and Buena Vista deposits. Calcite is observed in the primary hydrothermal stage in the Susana-Lince deposit and in a slightly later stage in the Mantos de La Luna deposit. However, no observable amount of calcite occurs in the Buena Vista deposit.

Analytical results

Hypogene chalcocite from the Susana-Lince and Buena Vista deposits averages $\text{Cu}_{1.90}\text{S}$ in composition, a value

Fig. 3A–D Photomicrographs showing paragenetic relations among copper minerals, taken under plane-polarized reflected light. **A** Chalcocite and bornite rimmed by fine aggregates of hematite, Susana-Lince deposit. **B** Myrmekitic intergrowth of bornite and chalcocite, Buena Vista deposit. **C** Chalcocite and digenite replaced by fibrous aggregates and veinlets of covellite, Mantos de La Luna deposit. **D** Atacamite and chrysocolla replacing primary chalcocite, Susana-Lince deposit. *Cc* Chalcocite, *Bn* bornite, *Dg* digenite, *At* atacamite, *Cr* chrysocolla, *Hm* hematite



Mineral	Primary hydrothermal stage		Secondary enrichment stage	Oxide alteration stage
	Early substage	Main substage		
Albite	-----			
Sericite	-----			
Epidote	-----			
Chlorite	-----			
Quartz				
Calcite	-----	Susana - Lince	Mantos de La Luna	
Gypsum				-----
Pyrite				
Magnetite				
Chalcopyrite	-----			
Bornite			(Djurleite)	
Chalcocite				
Digenite		Susana - Lince		
Native copper		Susana - Lince		
Native silver				
Covellite				Buena Vista
Hematite				
Atacamite				-----
Chrysocolla				-----
Cuprite				Susana - Lince
Copper wad				-----
Goethite				-----

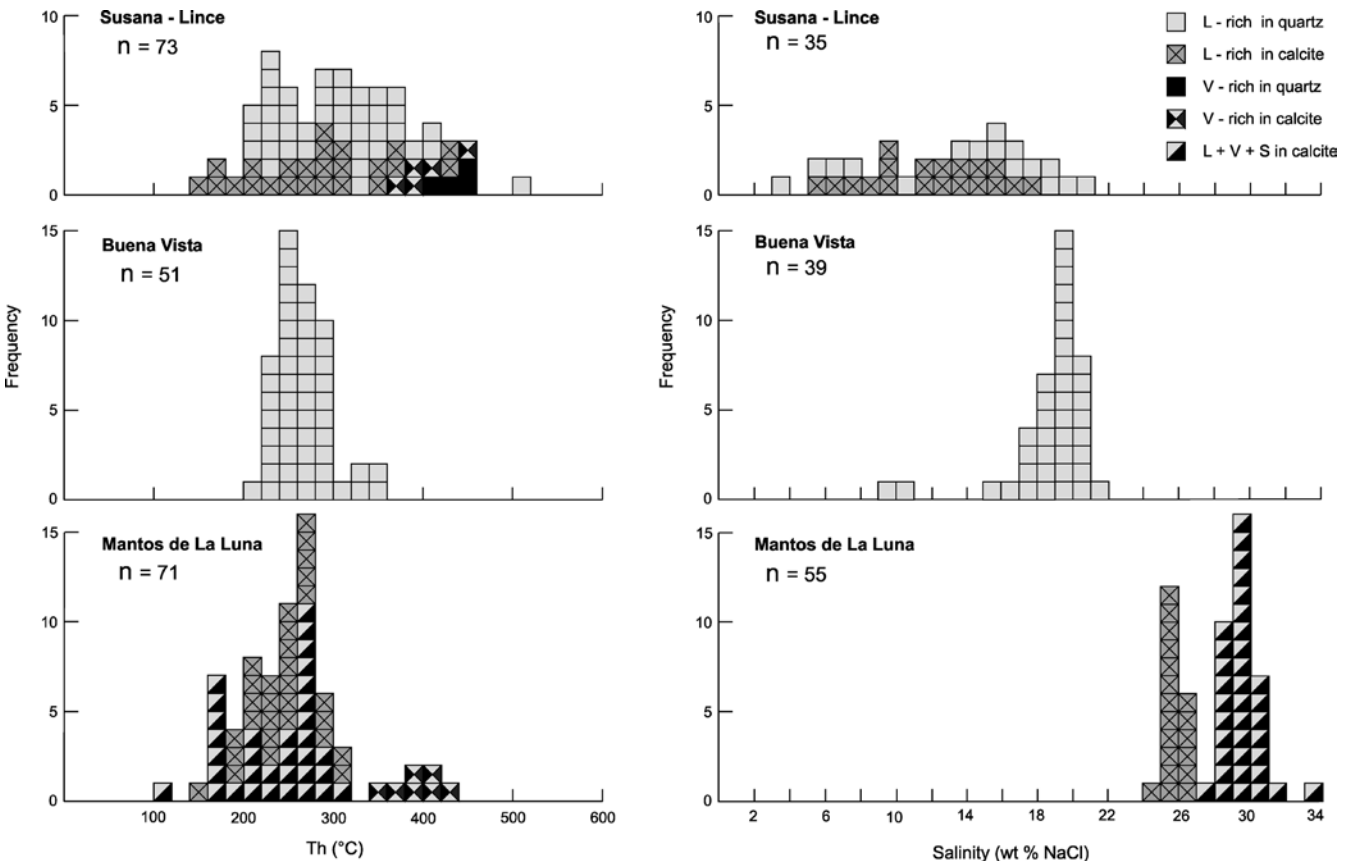
Fig. 4 Paragenetic sequence of ore and gangue minerals observed in the stratiform copper deposits studied

similar to that reported by Wolf et al. (1990). The digenites have compositions varying between $Cu_{1.783}S$ and $Cu_{1.844}S$ (58 point analyses), with trace amounts of Fe (~0.1 wt%) and Ag (0.03 to 0.12 wt%). Digenite from the Mantos de La Luna deposit scarcely contains Fe.

All primary fluid inclusions examined correspond to two-phase or polyphase inclusions with a halite crystal, and display no evidence of necking or leaking. Polyphase inclusions were observed only in the Mantos de La Luna calcites. No liquid CO_2 or clathrate was observed in any of the inclusions studied. The size of the inclusions range from 6 to 113 μm , and the coexistence of vapor-rich and liquid-rich inclusions is locally observed in samples from the Susana-Lince and Mantos de La Luna deposits, with no relation to sample depth. By contrast, no vapor-rich inclusions were observed in the Buena Vista samples. All the data obtained are summarized in Fig. 5.

The Th values of fluid inclusions in quartz and calcite from the Susana-Lince deposit range widely from 151 to 509 $^{\circ}C$, with most values distributed in the 200 to 380 $^{\circ}C$ range. In general, the vapor-rich inclusions display relatively higher temperatures than the liquid-rich inclusions (see Fig. 5), suggesting that liquid-gas immiscibility occurred during the primary inclusion formation; a similar tendency is also recognized in the Manto de La Luna inclusions. The Susana-Lince inclusions have relatively low salinities from 3.7 to 20.5 wt% NaCl (mostly 9 to 17 wt% NaCl). By contrast, fluid inclusions in quartz from the Buena Vista deposit have

Fig. 5 Histograms of homogenization temperature and of salinity in equiv. wt% NaCl of primary fluid inclusions in calcite and quartz from the Susana-Lince, Buena Vista and the Mantos de La Luna deposits



moderately narrow ranges of Th (214 to 360 °C) and salinity (mostly 16 to 21 wt% NaCl). The latter is higher than that of the Susana-Lince inclusions.

In the Mantos de La Luna inclusions studied, temperature of vapor disappearance was always above that of halite dissolution, so that the former was adopted as the Th value. The Th values of fluid inclusions in calcite from the Mantos de La Luna deposit are lower than those in calcite and quartz from the Carolina de Michilla district, ranging between 163 and 350 °C. Conversely, the Mantos de La Luna inclusions are considerably saline (25 to 34 wt% NaCl), having much higher salinities than those obtained for the Susana-Lince and Buena Vista deposits. The Th -salinity relationships of fluid inclusions in the three deposits are compared in Fig. 6, and a slight negative correlation of Th and salinity was observed.

The isotopic compositions of calcite, primary sulfides (chalcocite, pyrite) and copper sulfide concentrate from the Susana-Lince deposit and those of calcite from the Mantos de La Luna deposit are listed in Table 1. All the Susana-Lince calcites analyzed are isotopically fairly homogeneous, with $\delta^{13}C$ and $\delta^{18}O$ values ranging from -2.6 to -3.6‰, and 13.7 to 18.7‰, respectively. All the

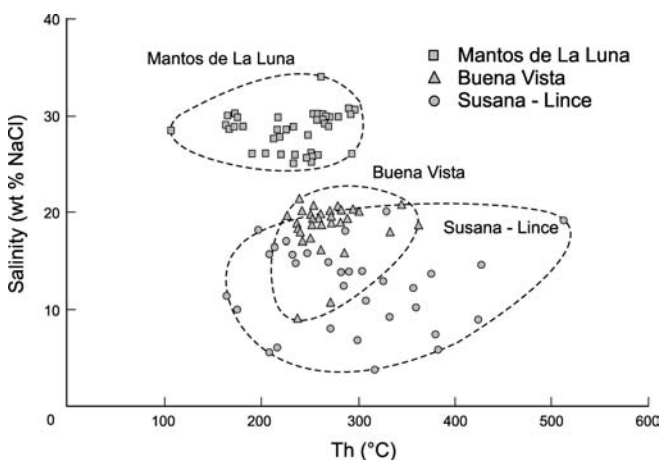


Fig. 6 Relationship between homogenization temperature (Th) and salinity (equiv. wt% NaCl) of primary fluid inclusions in calcite and quartz

primary sulfides show negative $\delta^{34}S$ values (Sasaki et al. 1984; Vivallo and Henríquez 1998).

Ore-forming conditions

The lower temperature limit of hypogene mineral formation can be inferred by applying the compositional data of the hypogene chalcocite to the phase diagram of the Cu-S system constructed by Roseboom (1966) and Barton (1973). The diagram demonstrates that the minimum temperature for the stability of high digenite, below which phase separation of hexagonal chalcocite from high digenite occurs, depends on the bulk composition of the high-digenite solid solution. The pressure effect on this change is not considered here, because the temperature of the transition from high digenite (cubic chalcocite) to hexagonal chalcocite (~435 °C) is scarcely affected by pressure in geologically important ranges (Grace and Cohen 1979). As mentioned above, the precipitation of calcite and/or quartz in the Susana-Lince and Buena Vista deposits is regarded to have occurred in the primary hydrothermal stage, and thus we can compare the temperature values determined from fluid inclusions with those estimated from the bulk chalcocite composition. The average composition of the chalcocites from the Susana-Lince and Buena Vista deposits (~Cu_{1.90}S) suggests a minimum temperature of ~200 °C, which is similar to the minimum Th values of fluid inclusions.

Because the Buena Vista fluid inclusions do not show evidence of boiling, a pressure correction is required for the Th data. The minimum lithostatic pressure is estimated to be ~160 bar for the Buena Vista deposit, assuming a solution of ~360 °C and 20 wt% NaCl (Bischoff and Pitzer 1989). This pressure corresponds to a thickness of ~630 m for the overlying La Negra Formation, with an average density of ~2.6 (Minera Michilla S.A., unpublished data). Judging from the analytical results including the Th data, we estimate 200 to 380 °C as a reasonable range for the primary formation temperature. Due to absence of certain sulfidation state-indicator minerals, it is difficult to estimate exactly the range of sulfur fugacity (f_{S_2}) or redox state for the

Table 1 List of isotopic compositions of calcite ($\delta^{13}C$, $\delta^{18}O$) and primary sulfides ($\delta^{34}S$) from the Susana-Lince and Mantos de La Luna deposits

Deposit	Mineral	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	$\delta^{34}S$ (‰)	Source ^a
Susana-Lince	Calcite	-2.6	13.8		a
		-2.6	13.8		a
		-3.3	16.6		a
		-3.6	16.0		a
		-3.5	18.6		a
		-3.6	18.7		a
	Chalcocite			-3.0	b
			-4.1	b	
			-5.1	b	
	Concentrate			-2.1	c
Mantos de La Luna	Calcite	-0.8	15.3		b
		-4.4	11.7		b

^aData sources: a, this study; b, Vivallo and Henríquez (1998); c, Sasaki et al. (1984)

above temperature range. Nevertheless, the intimate association of hematite and hypogene chalcocite ($\sim\text{Cu}_{1.90}\text{S}$) and the local stability of native silver indicate moderately oxidized and low f_{S_2} conditions.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the hydrothermal fluid can be inferred using the isotope data in Table 1, and the isotopic fractionation factors for carbon between calcite and CO_2 (Bottinga 1968) and for oxygen between calcite and water (O'Neil et al. 1969; Golyshev et al. 1981). The calculated range of $\delta^{13}\text{C}_{\text{CO}_2}$ is from -0.4 to -3.2‰ , and that of $\delta^{18}\text{C}_{\text{H}_2\text{O}}$ is from 4.8 to 15.2‰ at $T=200\text{--}360\text{ °C}$, the average formation temperatures of the Susana-Lince calcite. In the case of the Mantos de La Luna calcite formed at $T=160\text{--}300\text{ °C}$, $\delta^{13}\text{C}_{\text{CO}_2}$ is from 1.0 to -5.1‰ , and $\delta^{18}\text{C}_{\text{H}_2\text{O}}$ is from 0.3 to 10.2‰ . Because the Susana-Lince and Mantos de La Luna inclusions show evidence of boiling (see above), its effect on oxygen and carbon isotopic compositions of calcite should be considered.

The effect of boiling on the oxygen isotope composition is small at temperatures higher than 100 °C , whereas fluid boiling near neutral pH conditions could induce a considerable increase in $\delta^{13}\text{C}$ values of precipitating calcite, owing to a large removal of CO_2 into the gas phase leading to a higher concentration ratio of $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ (Matsuhisa 1986). Consequently, the $\delta^{13}\text{C}$ value of the mineralizing fluid is inferred to have been more negative than the estimated $\delta^{13}\text{C}_{\text{CO}_2}$ values of 1.0 to -5.1‰ . Thus, igneous carbon of $\delta^{13}\text{C}=-5$ to -8‰ (Deines and Gold 1973; Kyser 1986) or the limestone in the La Negra Formation of $\delta^{13}\text{C}=-4.8\text{‰}$ (Venegas et al. 1991) is regarded as the source of the calcite carbon. On the other hand, the estimated range of $\delta^{18}\text{C}_{\text{H}_2\text{O}}=0.3$ to 15.2‰ includes typical magmatic water with a value of $7.5\pm 2\text{‰}$ (Sheppard 1986). However, the estimated range of $\delta^{18}\text{C}_{\text{H}_2\text{O}}$ is much wider, suggesting a contribution of $\delta^{18}\text{O}$ -poor meteoric water and $\delta^{18}\text{O}$ -rich sedimentary rock, like the La Negra Formation limestone ($\delta^{18}\text{O}=20.8\text{‰}$; Venegas et al. 1991).

The negative correlation in the Th – salinity relations of the fluid inclusions (Fig. 6) cannot be explained by a magmatic-meteoric hydrothermal model involving mixing between hot, saline fluid and cooler, surficial water. Instead, the distribution pattern suggests mixing of a high-temperature meteoric fluid (which caused propylitic alteration) with a cooler basinal brine in the sedimentary sequence of the La Negra Formation. This is compatible with the above estimate on $\delta^{13}\text{C}_{\text{CO}_2}$ and $\delta^{18}\text{C}_{\text{H}_2\text{O}}$. It is therefore concluded that the mineralizing fluid was generated mostly from non-magmatic oxidized solutions, although a magmatic heat source is likely. The source of the sulfide sulfur with slightly negative $\delta^{34}\text{S}$ values (Table 1) is uncertain, since isotopic data on igneous sulfur of the area have not yet been obtained.

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