Cu, Mn, and Ag mineralization in the Quebrada Marquesa Quadrangle, Chile: the Talcuna and Arqueros districts

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Abstract The Quebrada Marquesa Quadrangle in Chile exhibits a series of mineralizations comprising manto-type manganese and copper deposits of Lower Cretaceous age, and copper and silver veins of Tertiary age. The deposits are hosted by volcanic and volcaniclastic units of the Arqueros (Hauterivian-Barremian) and Quebrada Marquesa (Barremian-Albian) Formations. Three episodes of manganese mineralization (Mn_{1-3}) are recognized within the study area. Hydrothermal activity leading to episodes 1 and 3 was of minor importance, while the second one (Mn_2) gave rise to major manto-type deposits of both manganese and copper in the Talcuna mining district. Extensional faulting during Tertiary time resulted in block faulting and the unroo®ng of the oldest andesitic volcanics and marine sediments (Arqueros Formation). This episode was accompanied by magmatic and hydrothermal activity leading to vein formation in the Arqueros (Ag) and Talcuna (Cu) districts. The latter veins cross-cut the previous manto-type copper deposits. Ore mineralogy is similar in both styles of mineralization (manto- and vein-type) and consists mainly of chalcopyrite and bornite, with variable amounts of galena, tetrahedrite (vein-related), chalcocite, sphalerite, pyrite, hematite, digenite and covellite. Alteration processes at Talcuna can be divided into two categories, those related to the Lower Cretaceous manto-type episode (LK alteration: chlorite-epidote-calcite-albite, prehnite, zeolite), and those associated with the locally mineralized normal faults of Tertiary age (Tt alteration: chlorite-calcite, sericite). The Arqueros silver veins display an ore mineralogy con-sisting of arquerite, argentite, native silver, polybasite, cerargyrite and pyrargyrite-proustite; associated altera-tion includes strong chloritization of the country rock. The manto-type deposits formed from fluids of salinity between 11 and 19 wt.% NaCl equivalent and temper-atures between 120 and 205 °C. Mineralizing fluids during the vein-type stage circulated at lower tempera-tures, between 70 and 170 °C, with salinity values in a wide range from 3 to 27 wt.% NaCl equivalent. This distribution of salinities is interpreted as the result of the complex interplay of two di•erent processes: boiling and fluid mixing; the former is considered to control the major mineralogical, textural and fluid inclusion features of the vein-type deposits. We suggest that the Lower Cretaceous mineralization (manto-type stage) developed in response to widespread hydrothermal activity (geo-thermal ®eld-type) involving basinal brines.

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Introduction

The early Cretaceous volcanic sequences from northern and central Chile host numerous stratabound copper mineralizations, many of them of economic importance. The Talcuna mining district belongs to this ˘600 km long N-S belt and is located at 29°53′S±70°55′W, some 50 km to the east of La Serena (Fig. 1). The district (Fig. 2) comprises eleven copper mines; Most operations are abandoned and only two are currently being mined (underground works): Coca-Cola (and its southern op-eration: Tambor) and 21 de Mayo-Socorro. Manganese is extracted from two mines, Balcanes and Placetas. Mining operations began around 1880 and concentrated on vein-type copper deposits of the district (e.g., Chile-na, Mercedes veins). The reserves amount to some 15 Mt at 1% Cu and 20 g/t Ag. Grades of up to 38% Mn have

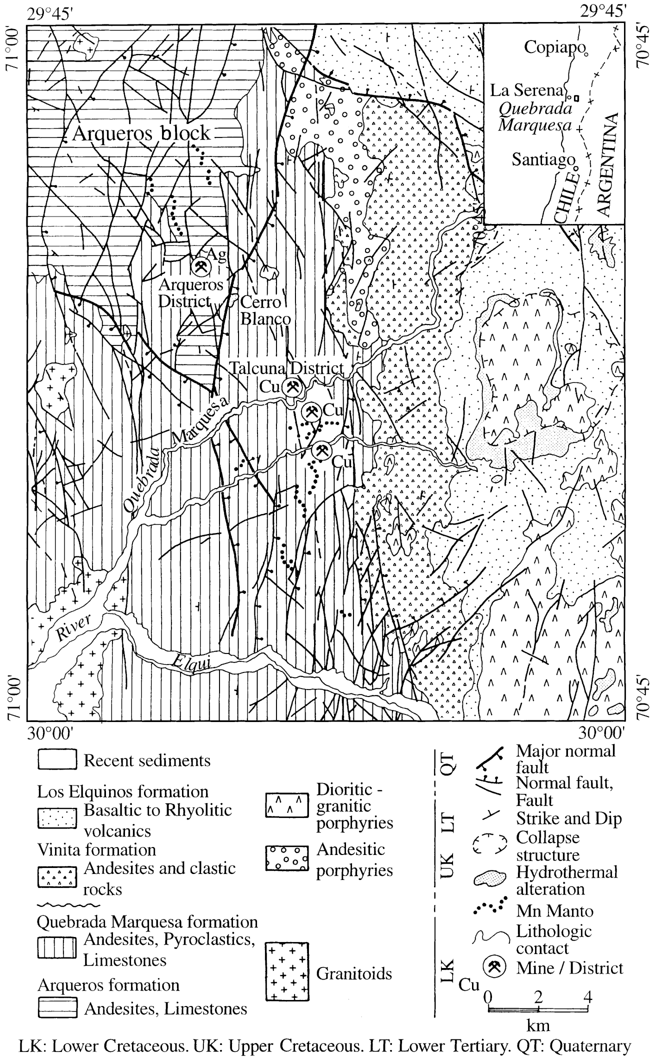

Fig. 1 The Quebrada Marquesa Quadrangle, geology and location of mineral deposits. Simpli®ed after Aguirre and Egert (1965), Boric (1985), and MaÂrquez et al. (1996)

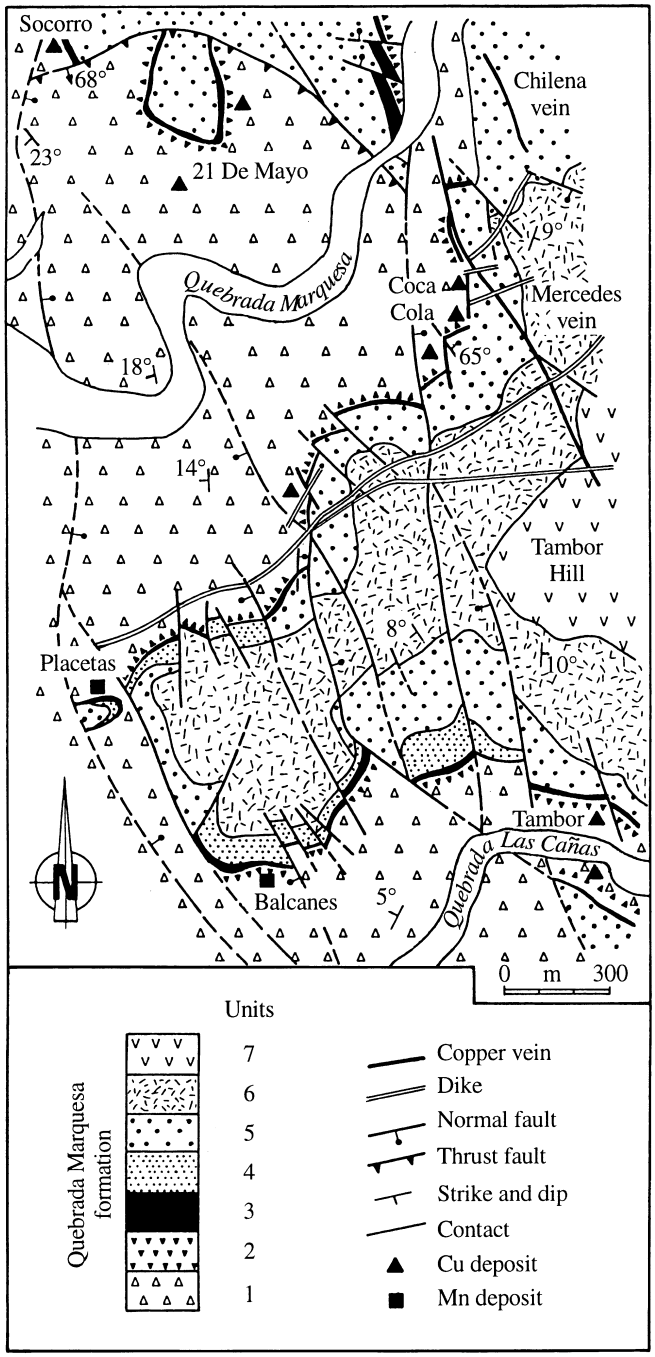

Fig. 2 The Talcuna district, geology and location of mineral deposits. Simpli®ed after Boric (1985). Unit 1: breccias, lapilli tu•s, andesites; Unit 2: Manto Talcuna, mineralized (Cu) andesitic pyroclastic fall deposits (bottom), and amigdaloidal andesites (top); Unit 3, manganese mineralizations, volcanic sandstones, shales and gypsum; Unit 4: ash fall deposits, sandstones and shales; Unit 5: breccias and andesites; Unit 6: shales and sandstones, ash and lapilli fall deposits and andesites; Unit 7: andesites

been reported from the manganese deposits (Boric 1985), however no information regarding reserves is available.

The copper deposits have been traditionally classified as either manto- or vein-type mineralizations, hosted by altered (regional and local propilitization) andesitic volcanic-volcaniclastic facies of the Quebrada Marquesa Formation (Barremian-Albian; Aguirre and Egert 1965; Boric 1985; Rivano and Sepulveda 1991). A closer inspection reveals that mineralization style is complex, including a close interplay between veining at very different scales and lateral, manto-type mineralization. Veins include a variety of textural assemblages ranging from banding to brecciation (hydraulic and collapse). The present mining operations of Coca-Cola-Tambor and 21 de Mayo-Socorro (Fig. 2) were chosen for this study because access to the abandoned mines is restricted.

The Arqueros vein-type epithermal deposits are located some 7 km to NW of Talcuna (Fig. 1) and comprise adularia-sericite type silver mineralizations (Cucurella et al. 1991). Although the Arqueros silver deposits cannot be regarded as an integral part of the

Talcuna district, their close proximity and geologic set-ting make them ideal for comparative studies. The Ar-queros mining district is currently inactive.

Geology

The Talcuna district (Figs. 1 and 2) is located at the centre of the Quebrada Marquesa Quadrangle (A Quadrangle is a formal 1: 50000 mapping unit in Chile). (29°30′–29°45′S/70°45′–71°00′W) which comprises the following volcanisedimentary units (Aguirre and Egert 1965; Boric 1985; Rivano and Sepúlveda 1991): (1) Arqueros Formation (Hauterivian-Barremian), a 1020 m thick unit comprising andesites and intercalations of marine limestones; (2) Quebrada Marquesa Formation (Barremian-Albian), 1500 m of andesites, tuffs and breccias, including some minor intercalations of marine limestones; (3) Viñita Formation (Upper Cretaceous), 1440 m of continental, clastic and volcanic (andesites) rocks unconformably lying on top of Quebrada Marquesa; and (4) Los Elquinos Formation (Lower Tertiary), 1850 m of lava flows, tuffs and breccias of basaltic to rhyolitic composition. The Arqueros and Quebrada Marquesa Formations can be ascribed to the Ocoite Group (Aguirre et al. 1989), a 3–13 km thick sequence extending for about 1000 km along the Coastal Range of central-northern Chile. Most of the basic lavas belong to the high-K calc-alkaline and shoshonite series (Levi et al. 1987), although a transition to the calc-alkaline series has been observed to the north. At a more local scale (Quebrada Marquesa Quadrangle) these Formations are intruded by a Lower to Middle Cretaceous (108–89 Ma, K/Ar; Boric 1985) batholith varying in composition from diorite to granite. Other plutonic rocks include stocks of intermediate to acid composition of Upper Cretaceous–Lower Tertiary age (Aguirre and Egert 1965). Important hydrothermal alteration zones developed during the late episodes of intrusive activity (Fig. 1).

The stratigraphic units are gently folded and strongly disrupted by block tilting, which in some places increases the dip of individual structural units up to 35° due to west-directed clockwise, and east-directed counterclockwise block rotation. Field relationships and structural correlations with other zones in the region (Oyarzun et al. 1996), allow definition of three episodes of faulting (Figs. 1 and 2): (1) N to NNW normal faulting, of probable Lower Cretaceous age; (2) minor E-W reverse faulting cross-cutting the earlier normal faults; and (3) NW to NNE listric normal faulting and block tilting of Tertiary age, involving major vertical displacements of up to 2 km (Aguirre and Egert 1965). The latter episode ultimately led to the unroofing of the oldest stratigraphic unit, i.e., Arqueros, which accounts for most of the plateau observed northward of Quebrada Marquesa (Arqueros Block, Fig. 1). Another consequence of this episode was the reactivation of the early N to NNW set of normal faults.

The Talcuna district

Most of the Talcuna district is located within a small area of ~3 × 2 km in which the following informal units have been defined for the Quebrada Marquesa Formation (Boric 1985) (Fig. 2): **Unit 1**, breccias, lapilli tuffs, andesites. **Unit 2**, which can be subdivided into: (a) the Manto Talcuna (bottom); and (b) the amigdaloidal andesites (top); both of them hosting the manto-type copper mineralization. The Manto Talcuna is a 2 to 15 m thick unit comprising well-stratified andesitic pyroclastic fall deposits. These consist of rhythmic, alternating graded beds (5–50 cm thick) of fine ash (grain size: 0.2–0.4 mm) and lapilli (grain size: up to 15 mm). **Unit 3**, manto-type manganese mineralizations (Mn_2), volcanic sandstones, shales and gypsum beds (Aguirre and Egert 1965). **Unit 4**, ash fall deposits, sandstones and shales. **Unit 5**, breccias and andesites. **Unit 6**, slightly mineralized shales and sandstones, ash and lapilli fall deposits and andesites; **Unit 7**, andesites. These rocks display variable intensity of propylitic alteration with albite, calcite, chlorite, epidote, prehnite and zeolite.

The Talcuna units gently dip either to the W or E, and are affected by N to NNW normal faults. An east-west trending reverse fault dipping 70° to the south cross-cuts the earlier normal faults, and is believed to have caused an uplift by 200 m of the southern block (Fig. 2). The main normal faults have induced vertical throws of up to 100 m. Of major importance is the NNW trend as it hosts the most important veins (e.g., Mercedes) and lodes in the deposits. The only intrusive rocks cropping out within the district are a set of late, ENE to NE trending post-mineral andesitic dykes which cross-cut the units, faults and veins.

The Arqueros district

The Arqueros Formation (Fig. 1) consists of a 1020 m thick sequence of volcanic and marine sedimentary rocks. Aguirre and Egert (1970) subdivided this unit into five members which from the base to top are the following: **Ka1**, porphyritic andesites; **Ka2**, chert, sandstones and limestones; **Ka3**, porphyritic andesites; **Ka4**, limestones, sandstones and andesites; and **Ka5**, Andesites, intercalations of volcanic sandstones and manganese manto-type deposits (Mn_1). The Arqueros sector corresponds to an uplifted structural block, bound by two major NW and NE trending normal faults. Within this major block both the Arqueros and Quebrada Marquesa Formations crop out as a series of individual blocks, bound by minor associated normal faults. This chaotic disposition of units is well exemplified by the Cerro Blanco allochtonous block, consisting of hydrothermally altered ignimbrites and dacitic rocks (Los Elquinos Formation), which tectonically rest on top of andesites and sandstones belonging to the Quebrada Marquesa Formation.

The area as a whole has been the site of hydrothermal activity as shown by widespread, low-relief altered (argillic and propylitic) zones. Evidence of mineralization is observed at the Arqueros vein silver deposits, from which 555 metric tons of silver were extracted during the period 1825–1881 (Cucurella et al. 1991). The deposits were later mined until not many years ago for barite. Host rocks of the mineralizations are breccias and lapilli tuffs belonging to the lowest unit of the Quebrada Marquesa Formation and porphyritic andesites and limestones belonging to the uppermost unit of the Arqueros Formation (**Ka5**). Some of these rocks exhibit a strong chloritization. Similar to the Talcuna district, the uplifted Arqueros block hosts stratiform manganese deposits included within the uppermost unit of the Arqueros Formation (**Ka5**).

Mineralization-alteration processes

The Talcuna–Arqueros zone displays the effects of a complex geologic and mineralizing history spanning from the Lower Cretaceous to Tertiary time, involving mineralizing-alteration processes that led to formation of manganese, copper and silver deposits. The stratigraphic-structural relationships allow definition of at least three episodes of stratiform Mn deposition, associated stratiform (manto-type) copper deposition (e.g., Mn_2-Manto Talcuna; Lower Cretaceous), and a major final episode of vein and stratiform copper and silver vein deposition (Tertiary).

Manganese deposits

Manganese hydrothermal deposition developed along three well-defined stratigraphic horizons ($Mn_{1\text{-}3}$) within the Arqueros (Mn_1) and Quebrada Marquesa ($Mn_{2\text{-}3}$) (Aguirre and Egert 1965, 1970). These manganese episodes are not only restricted to the study area but can be traced as scattered stratiform mineralizations along a 70×25 km N-S belt (Aguirre and Egert 1965, 1970; Peebles and Ruiz-Fuller 1990). The Arqueros manganese deposits (Mn_1) are stratigraphically related to bedded copper deposits (oxides-sulfides), which occur as intercalations between the Mn beds (Aguirre and Egert 1970; Peebles and Ruiz-Fuller 1990). The manganese mineralogy consists of braunite, pyrolusite, hausmannite and psilomelane.

The Quebrada Marquesa manganese deposits ($Mn_{2\text{-}3}$) occur associated with iron jasperoids and carbonates. The beds (Mn_2) are 0.2 to 0.6 m thick and hosted by volcanic sandstones altered to epidote (piedmontite) and calcite (Aguirre and Egert 1965). Lensoid gypsum beds of up to 5 m thick are also recognized within the volcanic sandstone sequence. The manganese ore mineralogy consists of braunite, pyrolusite, psilomelane and manganite (Boric 1985). Of major economic importance are the stratiform copper mineralizations underlying the manganese beds, along the Manto Talcuna (Unit 2). Mn_2-equivalent manganase deposits can be observed at Corral Quemado ($\sim$60 km to the south of Talcuna) (Peebles and Klohn 1970; Peebles and Ruiz-Fuller 1990) where the manganese beds occur associated with carbonate sinters, red-iron jasperoids and calcite-chlorite altered sandstones. The origin of these manganese mineralizations has been related to hot-spring sources which deposited the mineralization as travertines (Peebles and Ruiz-Fuller 1990). Abundant colloform textural features and the presence of carbonate sinters support this interpretation.

Copper mineralization: the Talcuna manto and vein deposits

Although the term manto (stratiform mineralization) identified for decades the Talcuna district, the mining maps of the underground works reveal that the miners worked the N to NNW trending mineralized structures and that only small lateral works were done, i.e., towards the manto-type mineralization. Furthermore, the most comprehensive work on the mining geology of the district (Kamono and Boric 1982) shows that copper grades in the Talcuna Manto fall rapidly (e.g., from $\sim$2.5% to 0.5% Cu; 21 de Mayo-Socorro sector) over a few meters, or tens of meters at the most, from the vein mineralization. However, recent exploration works and mine development at Coca-Cola show that major manto-type mineralization, with little or no associated veining account for most of the new mine reserves (L. Martínez personal communication). This situation deserves special attention because it indicates that the copper mineralization was not produced during a single episode but during at least two events, i.e., the one related to manganese deposition (Mn_2-Manto Talcuna) and a later one involving vein formation. Vein formation is clearly a late phenomenon, of Tertiary age, as it vertically cross-cuts the units of Quebrada Marquesa (Fig. 2). On the other hand, the structural characteristics of the recently found, major stratiform copper ore-body of Coca-Cola, rule out veining as the only mineralizing mechanism. Furthermore, the stratigraphic relationships between the Manto Talcuna (Unit 2) and the manganese deposits of Unit 3, strongly suggest that both units were mineralized within the same early episode (Mn_2; Lower Cretaceous). The manto-type mineralization (Fig. 3A) is restricted to the lower half of Unit 2 (Manto Talcuna), where at least three mineralized horizons (up to 8 m thick) can be recognized. Grades and alteration intensity are higher in the pyroclastics with coarser grain size. Ore minerals include chalcopyrite and bornite, with minor chalcocite, galena, sphalerite and pyrite. These minerals infill the rock matrix surrounding the barren clasts. Average grades are around 1.5% Cu.

The veins are subvertical and strike N-S to NNW. The most important one is Mercedes, which strikes for a length of 1.5 km, with an average thickness of 2 m. The other veins do not exceed a few hundred meters along strike and have thicknesses of less than 1 m. Smaller, irregular veins (lodes) are also a typical feature of the district. The internal morphology of the veins vary from banded to breccia-type (hydraulic and collapse). No timing relationships can be established between brecciation and banded infilling of the fractures as both processes alternate and overlap during the development of the veins in a regime of tectonic instability. Grades of up to 5% Cu have been mined from the larger veins. Other textural features of the veins include crustifications and comb arrangements, indicative of open space filling.

Most veins develop a thin layering which involves mineralogical, color and grain-size changes, with fine-grained minerals on the walls of the veins and coarser grain size towards the centre. This mineralizing style has been named the banded ore (Figs. 3B and 4A) here. The outermost bands of the veins are sometimes disrupted by minor later fractures. Perfect symmetrical banding is locally observed (e.g., 21 de Mayo barite-rich veins), although this is not a widespread feature in the district. Hydraulic brecciation is found in both Coca-Cola and 21 de Mayo and is restricted to the smaller veins. The hydraulic breccias are characterized by the presence of up to 0.8 m long angular clasts contained in a matrix of calcite (Fig. 3C). Collapse breccias are broader and contain up to 0.3–0.4 m long, randomly oriented, mineralized rectangular clasts contained in a matrix of banded mineralization (e.g., Mercedes vein, Coca-Cola mine, Fig. 3D). The matrix consists of successive microscopic layers of calcite, fine-grained in the inner bands around the clasts and of coarser grain moving outwards. The degree of mineralization of the matrix is less intense than the one observed in the banded ore and includes disseminations and irregular bands of chalcopyrite, chalcopyrite-galena, chalcopyrite-tetrahedrite and chalcopyrite-tetrahedrite-galena-bornite outlining the fragment contours.

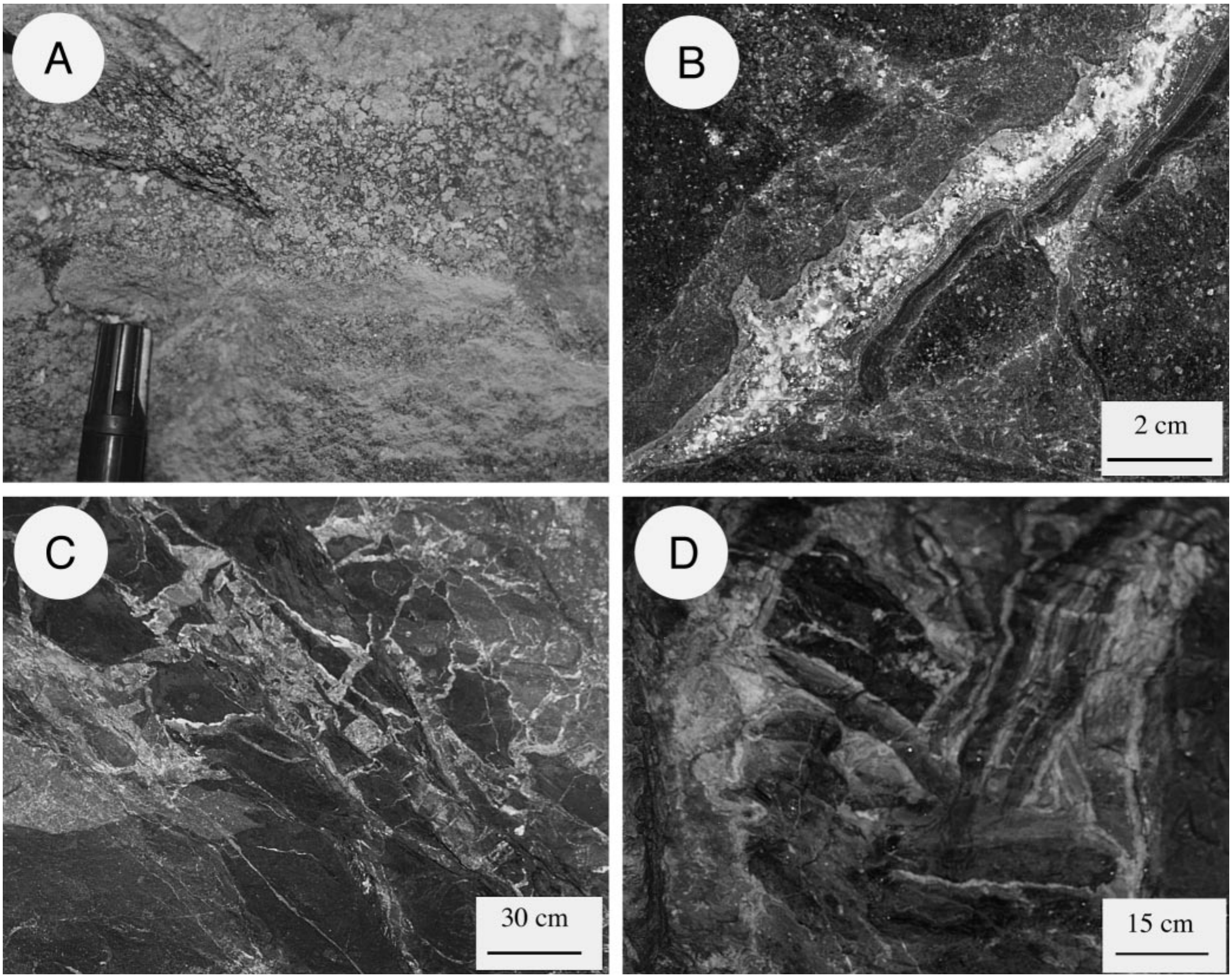

Fig. 3A–D Talcuna district mineralization styles. **A** Local aspect of the Manto Talcuna (21 de Mayo mine) showing mineralized lapilli tuffs (*upper half*). **B** Banded vein showing external bands of very fine grained calcite and sulfides, layers of chalcopyrite and coarse-grained calcite in the *center* (Coca-Cola mine). **C** Hydraulic breccia (21 de Mayo mine), note the *angular clasts* defining the typical 'puzzle'-type morphology (*sensu* Jébrak 1992). **D** Collapse breccia (Coca-Cola mine), note the *abundant matrix*, and the previous (pre-collapse) *banded mineralization* displayed by some clasts (*center*)

The ore mineralogy is similar in both styles of mineralization (banded and breccia) and consists of chalcopyrite and bornite, with variable amounts of galena, tetrahedrite, chalcocite, sphalerite, pyrite, hematite, digenite and covellite. The banded ore is mainly defined by mm to cm thick alternating layers of chalcopyrite and/or bornite (Fig. 4A), or different mineral associations including chalcopyrite-galena, bornite-primary chalcocite, bornite-chalcocite-galena, chalcopyrite-galena-tetrahedrite, chalcopyrite-bornite-tetrahedrite (Fig. 4B) and chalcopyrite-galena-bornite-tetrahedrite. These layers of massive mineralization, which include minor very fine-grained calcite, sometimes cryptocrystalline, alternate with almost barren bands of coarser-grained calcite. Sulfides in the massive layers occur as anhedral crystals generally showing mutual grain boundaries, although myrmekitic intergrowths between bornite and galena have been observed in the 21 de Mayo veins (Fig. 4C). Chalcopyrite and bornite mostly occur as cogenetic phases all over the deposits, however evidence of some hypogene replacement of bornite by chalcopyrite along crystallographic directions has been locally observed, sometimes accompanied by the formation of acicular aggregates of hematite (Fig. 4D). Tetrahedrite can be locally abundant at the microscopic scale, notably in the Coca-Cola sector (Fig. 4B). Minute grains of native silver were identified in samples from 21 de Mayo by SEM microscopy.

Calcite is the main gangue mineral and occurs along with barite. Based upon the grain size three main types of calcite are recognized: (a) cryptocrystalline calcite, of grey color in hand specimen, occurring close to the vein walls, accompanying the banded ore and surrounding the breccia fragments along with sulfides; (b) medium-grained calcite, occurring towards the center of the veins, interlayered with the massive bands of sulfides; (c) coarse-grained calcite, which generally occupies the

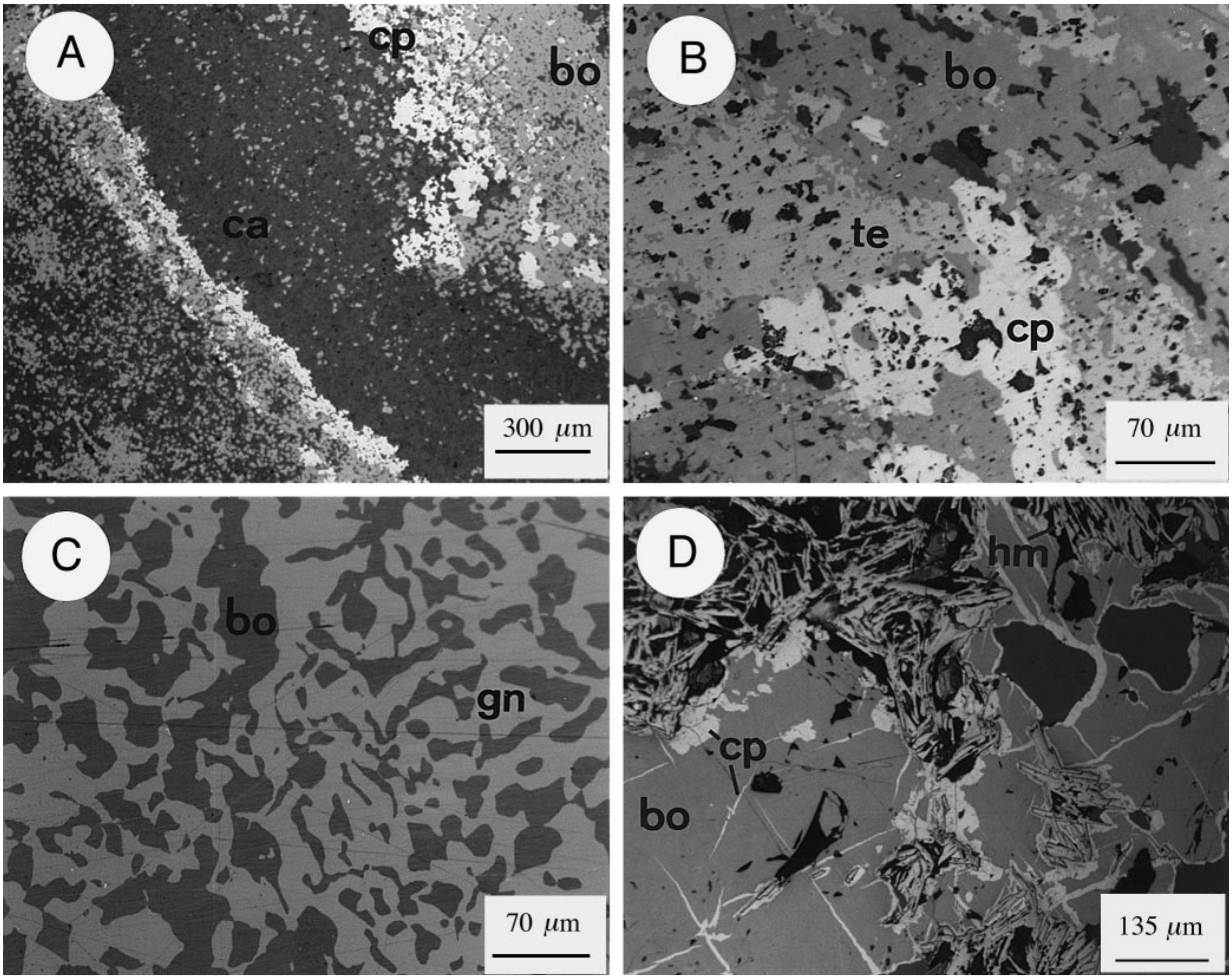

Fig. 4A–D Mineralogy and textures of the Talcuna vein-type mineralizations (reflected light microscopy, parallel polars). **A** Microscopic banding defined by bornite (*bo*), chalcopyrite (*cp*) and calcite (*ca*), 21 de Mayo. **B** Chalcopyrite (*cp*) – bornite (*bo*) – tetrahedrite (*te*) assemblage, Coca-cola. **C** Myrmekitic intergrowth between bornite (*bo*) and galena (*gn*), 21 de Mayo. **D** Bornite (*bo*) being replaced by chalcopyrite (*cp*) along crystallographic planes and surrounded by acicular crystals of hematite (*hm*), 21 de Mayo

central part of the veins, sometimes showing comb textures, but also occurring in vugs and filling microscopic fractures in the external bands. In the breccias this coarse calcite occurs either in microscopic fractures cross-cutting the fragments or surrounding them as a second layer after the cryptocrystalline calcite. Barite, much more abundant in the 21 de Mayo–Socorro sector, occurs as subhedral tabular medium to coarse-grained crystals and may be locally replaced, and even pseudomorphized by calcite.

The mineralogical and textural features of ore and gangue minerals described here initially suggested the existence of separate events of mineral precipitation. However, some evidence goes against this idea. The distribution of the different ore assemblages across the veins does not show any zonation and suggests that the vein fillings represent an overlapping sequence of precipitation of sulfides in which no paragenetic chronology can be established. Furthermore, the study of calcite by cathodoluminiscence and fluid inclusion data did not show differences between fine and coarse-grained calcite. By contrast, the increasing size of calcite grains towards the center of the veins can be explained by the theory of crystal nucleation (Chernov 1984). This indicates an evolution in the supersaturation of the fluids at the time of precipitation from very high supersaturation, yielding cryptocrystalline calcite and massive sulfides at the beginning of mineral precipitation, to almost barren coarse-grained calcite toward the end of the vein filling.

Alteration processes can be divided into two categories, those of widespread lateral extension, controlled by stratigraphic-lithologic features (*LK alteration* → chlorite-epidote-calcite-albite, prehnite, zeolite), and those associated to the local mineralized structures (*Tt alteration* → chlorite-calcite, sericite). The *LK alteration* is more intense in the lapilli rocks (Manto Talcuna; Unit 2) which may have allowed better conditions for fluid circulation. The *Tt alteration* is spatially restricted to the immediate vicinity of veins and consists of sericite, chlorite and calcite. This local alteration can be distinguished in volcanic rock fragments in mineralized breccias, in which calcite replaces younger zeolites within vugs.

The Arqueros veins

Mining of the Arqueros deposits (Fig. 1) during the nineteenth century left the *Colección Ignacio Domeyko* (a major collection belonging to the Mineralogical Museum of University of La Serena, Chile) as the only main mineralogical record of the deposits. Based on these samples and early descriptions the following reconstruction of the mineralogy has been made (Cucurella et al. 1991). Arquerite, argentite, native silver, polybasite, cerargyrite and pyrargyrite-proustite are the main ore minerals and occur in a gangue of barite and calcite. Arquerite is the most abundant silver phase and occurs associated with argentite, polybasite and pyrargyrite and locally replacing pyrargyrite and polybasite. Argentite shows two textural features: euhedral crystals, in association with polybasite, chalcocite, covellite, galena and sphalerite, and corroded grains, partially replaced by native silver and arquerite and closely associated with silver halides such as cerargyrite, yodirite and bromirite. Native silver is relatively abundant and exhibits various textures, including dendritic and skeletal crystals, rhythmic layering with argentite and exsolutions in polybasite. These mineral assemblages and textures are typical of the secondary enrichment and oxidation zones of the deposit, the ones which were mined in the past. It is worthy to note that native gold has been observed in the samples, although no information on gold production in the district is available.

Gangue minerals have been studied from the old mine dumps. Barite and calcite are distributed in layers of different grain size and shapes, with banded textures. Barite occurs as layers of tabular large crystals, in intergrowths with equidimensional coarse-grained calcite, alternating with microscopic layers of very fine-grained calcite and bands of centimeter-long prismatic crystals of calcite developing scalenohedron faces in one end and growing perpendicular to the banding. These textures are indicative of open space deposition.

Fluid inclusion data

As stated earlier, the copper deposits of the Talcuna district are the result of two different major episodes of mineralization, one related to the manganese deposition (Mn_2, Manto Talcuna) and a later one related to the development of veins. In order to characterize hydrothermal fluids during these periods, fluid inclusions studies were performed with two sets of samples. One set, named Las Cañas samples from now on, corresponds to calcite-chlorite filled cavities in andesites (top of Unit 2) related to red-iron jasperoids (Mn_2-Manto Talcuna). The second group of samples belong to veins from Coca-Cola and 21 de Mayo mines (Talcuna district). Fluid inclusions in banded calcite-barite samples from the Arqueros silver deposits were also studied.

Calcite was found to be the most suitable material for microthermometry of fluid inclusions, since barite often showed inclusions with metastable behavior. Two fluid inclusion populations, with uneven distribution, have been recognized. The largest population is made up by two-phase (L + V) aqueous liquid-rich inclusions. They have been observed in all the samples, either in groups or distributed in planes, which do not cross the calcite crystal edges and may have primary character. A second, well-contrasted population consists of vapor monophase inclusions, scarce compared to the aqueous inclusions. Their origin from necking down of liquid-rich inclusions has been discarded since they occur in linear arrays of exclusively monophase inclusions, thus confirming (e.g., Bodnar et al. 1985) that a vapor phase was present in the hydrothermal system.

Inclusions from the Talcuna and Arqueros vein deposits provide unequivocal evidence of fluid immiscibility. Alignments of aqueous inclusions with consistent liquid to vapor ratios also contain true monophase vapor inclusions. This coexistence of liquid-rich and vapor inclusions suggests that the two fluid populations are contemporaneous and were trapped from a boiling fluid. Such petrographical evidence is not available for Las Cañas samples, where vapor-rich inclusions have not been found.

Microthermometry was performed in a Chaixmeca cooling and heating stage on a Nikon Labophot microscope and the results for the different deposits are summarized in Table 1 and in Figs. 5, 6 and 7. Since monophase vapor inclusions did not show any phase change on cooling to −170 °C, all the microthermometric data refer to aqueous liquid-rich inclusions. Based on the *Th*/salinity plots (Figs. 5 and 7) two separate groups of inclusions with distinct salinities and homogenization temperatures can be distinguished, one corresponding to the manto-type (Las Cañas gulch) and the other to the vein-type deposits from Talcuna (Coca-cola and 21 de Mayo) and Arqueros districts.

Aqueous inclusions related to the Mn_2-Manto Talcuna episode show a degree of filling (V_L/V_T) of 0.7–0.8 and sizes up to 20 μm. First melting of ice occurs around −50 °C, thus indicating that the trapped fluids are complex $CaCl_2$- and NaCl-bearing polysaline brines, according to Crawford et al. (1979). Salinity values range from 11 to 19 wt.% NaCl equivalent and total homogenization takes place between 120 and 205 °C into liquid. Inclusions in calcite from Talcuna and Arqueros mineralized veins show a degree of filling of 0.8–0.95 and smaller size than the previous inclusions, always below 10 μm. Microthermometric data indicate a widespread salinity range, from 3 to 27 wt.% NaCl equivalent, with slight variations from one deposit to

Table 1 General characteristics of the Talcuna and Arqueros mantos- and vein-type deposits. Mineralogy and fluid inclusion data from Coca-Cola and 21 de Mayo refer only to the vein-type deposits, although most of the ore mineralogy is also common to the copper mantos. V_L/V_T: degree of filling, volume of liquid to the total volume. *Th*: homogenization temperature

Locality	Rock unit	Mineralization	Mineralogy	Fluid inclusion data
Las Cañas	Fm. Quebrada Marquesa, Unit 2	Iron jasperoids (Mn_2)	Goethite Calcite, epidote, chlorite.	H_2O-NaCl-$CaCl_2$ V_L/V_T: 0.7–0.8 Salinity: 11–19 wt.% NaCl eq. *Th*: 120–205 °C
Coca-Cola	Fm. Quebrada Marquesa, Unit 2	Copper manto-, and vein-type deposits	Bornite, chalcopyrite, galena, chalcocite, tetrahedrite, sphalerite, pyrite, barite. Calcite, chlorite, sericite.	H_2O-NaCl-$CaCl_2$ V_L/V_T: 0.8–0.9 Salinity: 5–26 wt.% NaCl eq. *Th*: 70–170 °C
21 de Mayo	Fm. Quebrada Marquesa, Unit 2	Copper manto-, and vein-type deposits	Bornite, chalcopyrite, galena, chalcocite, tetrahedrite, sphalerite, calcite, barite. Calcite, chlorite, sericite.	H_2O-NaCl-$CaCl_2$ V_L/V_T: 0.85–0.95 Salinity: 5–27 wt.% NaCl eq. *Th*: 70–150 °C
Arqueros	Fm. Arqueros	Silver vein-type deposits	Arquerite, argentite, polybasite, native silver, pyrargirite-proustite, silver halides, barite. Calcite, chlorite.	H_2O-NaCl-$CaCl_2$ V_L/V_T: 0.85–0.95 Salinity: 3–27 wt.% NaCl eq. *Th*: 70–155 °C

another in the lower limit of this range. First ice melting temperature is close to –50 °C, indicative of salts (e.g., $CaCl_2$) other than NaCl. Total homogenization values are within the intervals 70–170 °C, 70–150 °C and 70–155 °C (into L) for Coca-cola, 21 de Mayo and Arqueros samples, respectively. It is worth noting that similar microthermometric results have been obtained, no matter what the grain size of the host calcite was or the location of the sample across the vein. In barite, this fluid population often shows metastable behavior, as the inclusions mostly occur as monophase liquid inclusions at room temperature, becoming two-phase (L + V) during the microthermometric runs. Ice melting temperatures are within the same range than those from aqueous liquid-rich inclusions in calcite, thus confirming that inclusions observed in barite belong to the same fluid batch than those in calcite.

Fluid circulation during the manto-, and vein-type mineralizing episodes

Fluid inclusions from the manto-, and vein-type hydrothermal episodes (Talcuna and Arqueros) show that fluids involved in both mineralizing episodes were aqueous NaCl- and $CaCl_2$-bearing fluids (Fig. 7). Fluid circulation during the Lower Cretaceous manto-type mineralization stage took place between 120 and 205 °C, while the Tertiary vein-type deposits formed from fluids circulating at lower temperatures in the range 70–170 °C (Coca-Cola) and 70–150 °C (21 de Mayo and Arqueros). Since mineralization processes were shallow-seated (e.g., Peebles and Ruiz-Fuller 1990; Cucurella et al. 1991), i.e., a low-pressure environment, these homogenization temperatures require little or no pressure correction, and represent trapping temperatures (e.g., Bodnar et al. 1985). Regarding salinity, the manto-type ore forming fluids show a relatively narrow range of values that contrasts with the wide distribution of salinities observed in the vein-type deposits (Fig. 7).

The two mineralizing episodes also differ in the mechanisms involved in mineral precipitation. The *Th*/salinity trends for the manto-type deposits (Figs. 5 and 7) suggest that fluids followed a simple cooling path during this mineralizing event. In the vein-type deposits boiling is considered to be the main hydrothermal process, responsible for most of the mineralogical, textural and fluid inclusion characteristics. Major evidence of boiling is provided by the occurrence of hydraulic breccias, the contemporaneous trapping of both liquid-rich and vapor inclusions and the abundance of high salinity inclusions. The presence of calcite (displaying comb texture) as the main gangue mineral is also indicative of boiling as precipitation of such calcite in open spaces is favored in near-vertical structures where rising fluids boil (Simmons and Christenson 1994). However, this process alone cannot fully explain the most important feature of fluid inclusion data from Talcuna and Arqueros vein-type

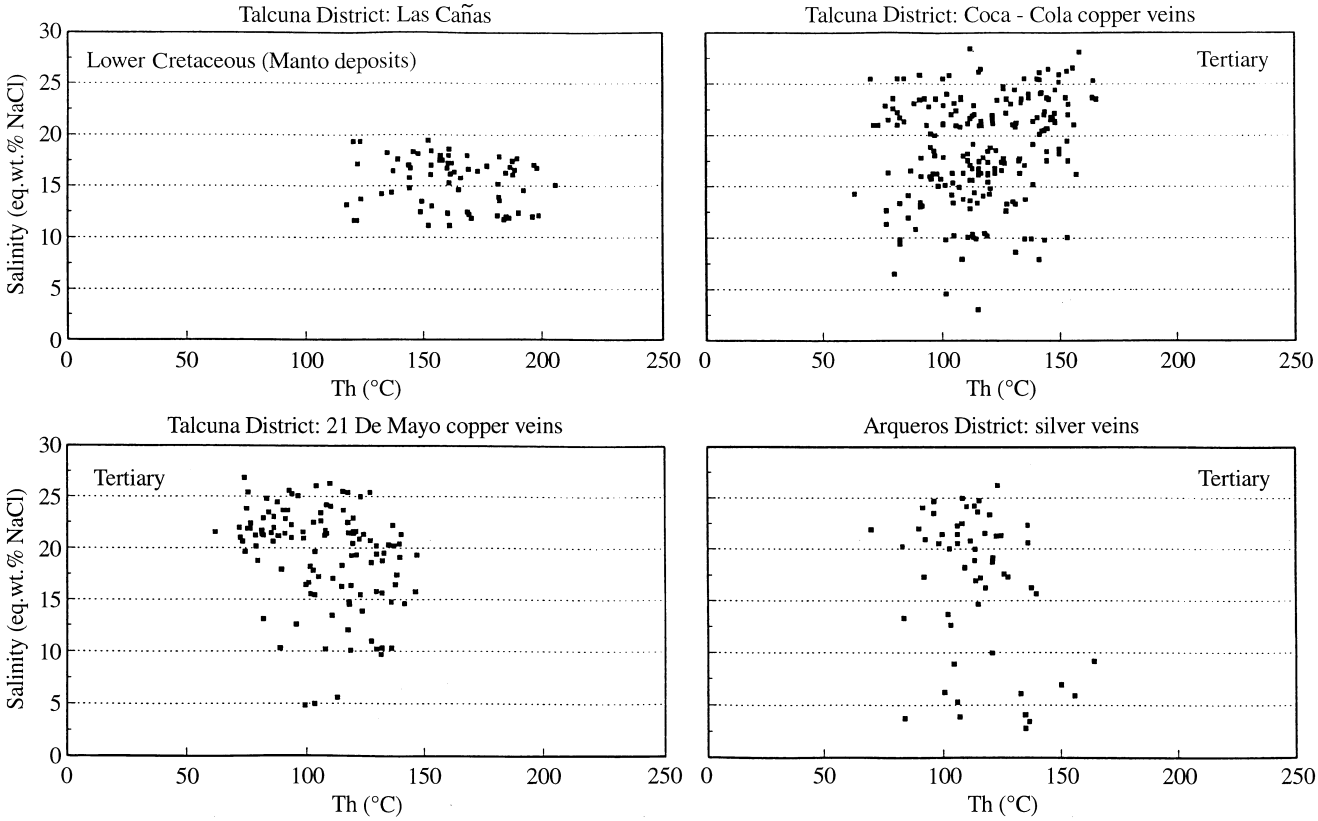

Fig. 5 Homogenization temperature (*Th*) versus salinity plots from the Mn_2-Manto Talcuna mineralizing episode (Las Cañas) and the vein-type deposits (Coca-Cola, 21 de Mayo and Arqueros)

deposits, i.e., widespread salinity values within the whole *Th* interval. It is well known that one of the potential effects of boiling in the fluid composition is a notable increase of salinity. Hence, higher salinity inclusions (Figs. 5 and 7) may represent the brines exsolved during boiling. However, the presence of inclusions of low salinity, although much less common than the high salinity ones, may indicate the presence of a different, more diluted fluid. This hypothesis is supported by the presence of barite which strongly suggests the interaction between fluids of different sources, as barite is not a common depositional product of boiling (Drummond and Ohomoto 1985) but of fluid mixing (e.g., Hayba et al. 1985; Concha et al. 1992; Canals et al. 1992; Plumlee 1994). Therefore, the widespread salinities observed in these vein deposits could be explained by the combination of the two mentioned processes (boiling and fluid mixing): the higher salinity fluids together with the vapor trapped in the monophase inclusions may represent the products of boiling and the lower salinity set would correspond to an external diluted fluid. The intermediate field would comprise inclusions from moderate to high salinity resulting from different situations, which may possibly include trapping of the parent fluid before boiling, mixing of the exsolved brine with the parent fluid and/or mixing of both (or any of them) with the external low-salinity fluid. According to Cathelineau and Marignac (1994) these complex associations of elementary processes are probably more frequent than it is usually suspected (e.g. Broadlands and Wairakei New Zealand; Henley 1985; Hedenquist et al. 1992).

Discussion

The geologic record of the Talcuna-Arqueros realm indicates a complex geologic evolution with two main events of copper deposition, one during the Lower Cretaceous (manto-type) and one during the Tertiary (vein-type). The first event was accompanied by the *LK alteration*. Equivalent alteration phenomena to those of the *LK alteration* can be traced in other Jurassic and Cretaceous volcanic units of northern and central Chile (e.g., Levi 1970; Aguirre et al. 1989; Vergara et al. 1994). Wherever these facies are spatially associated with ore deposits they are generically described as *regional alteration* (e.g., Oyarzun et al. 1996). This alteration includes facies ranging from greenschist, through prehnite-pumpellyite to zeolite. These facies have been traditionally regarded in Chile as the consequence of burial metamorphism of the thick volcanic sequences (e.g., Levi 1970; Aguirre et al. 1989; Vergara et al. 1994). However, although this may be valid at a very general scale, a more local approach suggests that at least part of these mineral assemblages developed in response to more localized hydrothermal alteration processes (e.g., Camus, 1986). The coexistence of greenschist, prehnite-pumpellyite and zeolite facies within short vertical sequences (a few hundred of meters) indicates conditions

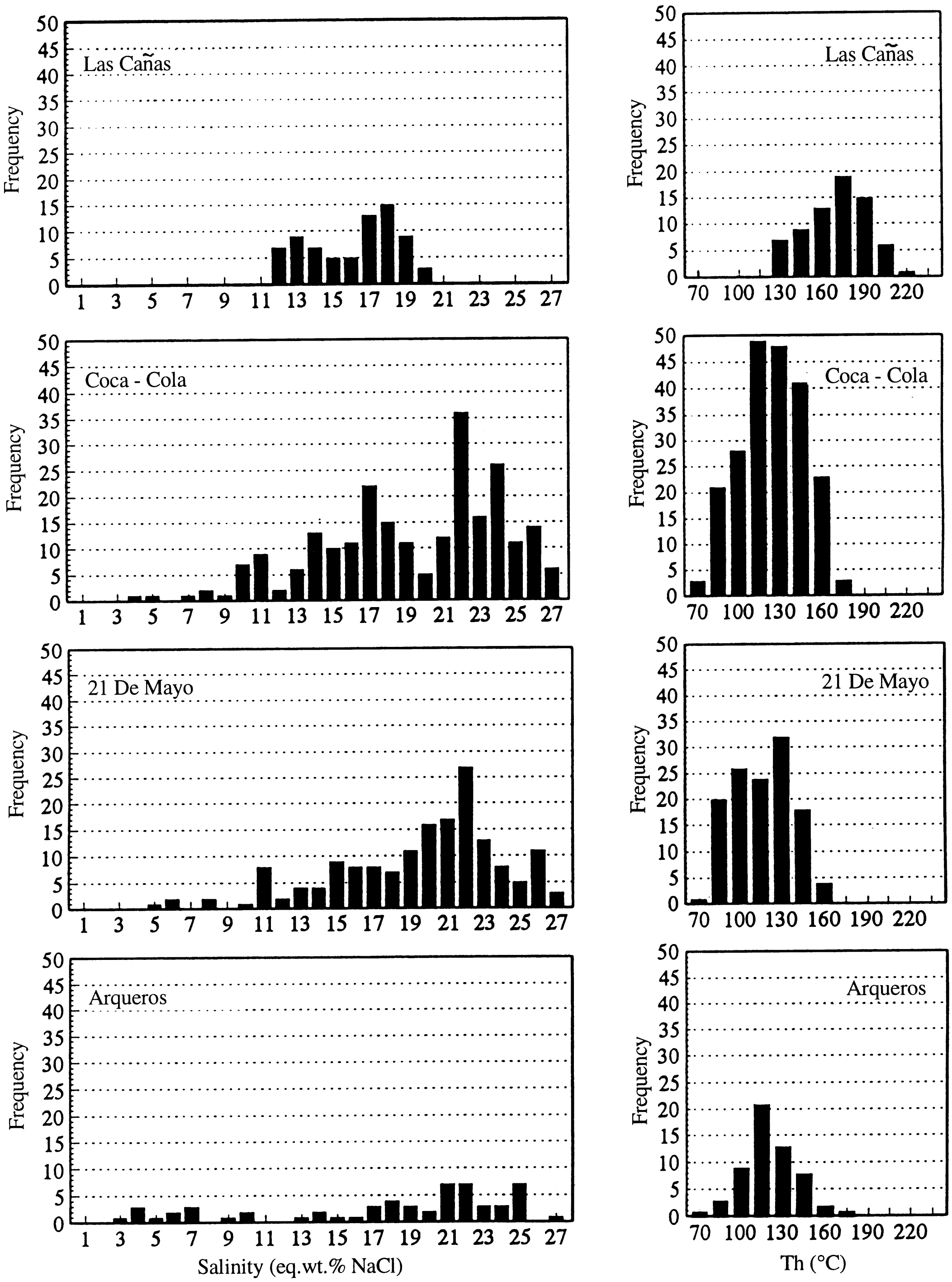

Fig. 6 Histograms of salinity and homogenization temperatures for the Mn_2-Manto Talcuna mineralizing episode (Las Cañas) and the vein-type deposits (Coca-Cola, 21 de Mayo and Arqueros)

approaching those of the geothermal fields, i.e., to the hydrothermal or low-grade metamorphism of geothermal fields (e.g., Liou et al. 1987; Yardley 1989). These alteration processes occur in response to steep geothermal gradients provided by volcanic activity, and the interaction between rocks and fluids (e.g., Yardley 1989). Evidence supporting Lower Cretaceous geothermal activity in the Quebrada Marquesa Formation is provided by: (1) hot-springs type manganese deposition (Peebles and Ruiz-Fuller 1990), typical of the geothermal environment (e.g., Roy 1992; Crespo et al. 1995); and (2) the irregular vertical distribution of the low-grade alteration minerals. For instance, epidote and chlorite may be found at higher stratigraphic positions than zeolite. This is opposed to what is observed in the classic vertical zoning developed in areas that have been subjected to burial metamorphism (e.g., Liou et al. 1987). There, a well-defined transition from greenschist

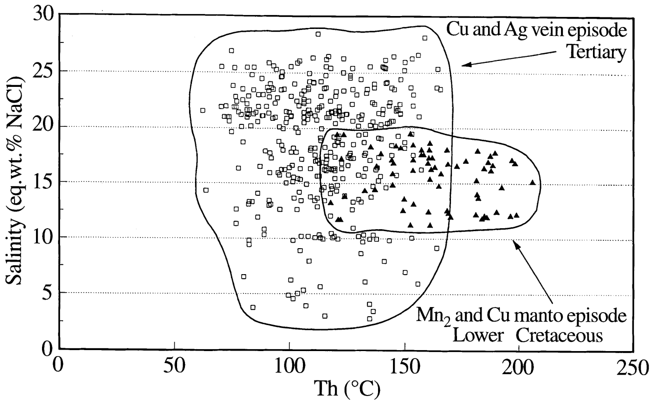

Fig. 7 Distribution of fluid inclusion data (homogenization temperature versus salinity) corresponding to the two main mineralizing episodes in Talcuna and Arqueros districts: (1) manganese (Mn_2) and copper mantos and (2) copper and silver veins. This diagram comprises all the data plotted separately in Fig. 5

(bottom), through prehnite-pumpellyte to zeolite facies (top) occurs along kilometers of stratified volcanics/sediments (e.g., Taringatura Hills, New Zealand, 8 km; Yardley 1989). The combined thickness of the Arqueros and Quebrada Marquesa Formations is about 2.5 km, far too thin to allow a full-scale development of the vertical mineral zoning observed in the classic occurrences of burial metamorphism (*sensu* Coombs et al. 1959). Moreover, at the time of Mn_1 deposition, the thickness of Arqueros was only about ~850 m (Ka5; Aguirre and Egert 1965). An interesting analogue may be provided by the Reykjanes geothermal field in Iceland (Yardley 1989). There, within a short vertical sequence of volcanics (~2 km), and under a steep geothermal gradient a chlorite, zeolite, epidote, prehnite, pumpellyite, calcite assemblage developed.

In contrast to the typical geothermal environment, characterized mostly by low-salinity, meteoric waters (e.g., Henley 1985), the fluids that gave rise to manto-type mineralization were moderate to high-salinty (11 and 19 wt.% NaCl equivalent) solutions, similar to those commonly known as basinal brines (e.g., Kyser and Kerrich 1990). The stratigraphy of the Quebrada Marquesa Formation (Aguirre and Egert 1965) offers a plausible explanation for this fact. As described, the volcanic sandstone sequence hosting the manganese deposits of Talcuna also contains gypsum beds (Aguirre and Egert 1965). These evaporites must have formed within a shallow basin, under a hot, arid setting leading to rapid evaporation, and hence to supersaturation of salts and precipitation (e.g., Collinson and Thompson 1989). Under these conditions hydrothermal circulation within a geothermal system would have been dominated by high-salinity, basinal brines.

Major block faulting during Tertiary time led to the unroofing of the older unit (Arqueros Formation) in given sectors (Arqueros Block, Fig. 1). Normal faulting during this episode was accompanied by intrusive activity (granitic to dioritic porphyries). Although there is no unequivocal evidence linking this intrusive episode to the vein-type mineralization processes in the Talcuna and Arqueros districts, two pieces of evidence make it very likely: first, this episode did trigger hydrothermal activity within the Quebrada Marquesa Quadrangle and beyond (alteration zones in Fig. 1), and second, the major Talcuna and Arqueros veins are clearly a late feature as they entirely cross-cut the Arqueros and Quebrada Marquesa units (Fig. 2).

Conclusive petrographical evidence linking ore mineral deposition to only one specific process in the Arqueros and Talcuna districts is difficult to find. However, boiling is considered to be the main responsible process of ore precipitation, at least in the vein deposits. In the vein case boiling must have been enhanced by the drastic vertical changes in rock permeability (e.g., Phillips 1972; Jébrak 1992). The local stratigraphic columns for the Talcuna district (Kamono and Boric 1982) show that massive andesites occur toward the higher sectors of Unit 1, i.e., immediately below the Manto Talcuna. These andesites must be regarded as an impermeable barrier which contributed to the build up of the hydrothermal solution pressure along the fractures (e.g., Phillips 1972). Subsequent rupture along the impermeable barrier would have resulted in a sudden drop in pressure, boiling and mineral precipitation. This idea is well supported by the existence of widespread hydraulic brecciation in the Manto Talcuna (Fig. 3C), a clear indicator of boiling and associated fracturing (e.g., Phillips 1972; Jébrak 1992). The vein-channeled ascending ore fluids extended laterally when crossing the volcaniclastic units of high permeability (e.g., Manto Talcuna), mineralizing and locally enriching the already mineralized horizons (manto-type episode). This would explain why some mantos show higher copper grades in the vicinities of veins.

Conclusions

The Quebrada Marquesa Quadrangle has been the site of recurrent mineralizing processes (Fig. 8). Hydrothermal activity during the Lower Cretaceous occurred in response to highly favorable geologic conditions including persistent magmatic activity. Of major economic relevance was the Mn_2-Manto Talcuna event which led to manto-type copper and manganese deposition in the Talcuna district. As discussed already, this event may have involved widespread hydrothermal activity of the geothermal type, within an environment characterized by restricted shallow basins in which evaporite facies (e.g., gypsum) were deposited. The moderate to high-salinity fluids associated to the manto-type event would have been derived from basinal brines ponded in these basins. Manganese and copper deposits such as Balcanes and Coca-Cola respectively, formed during this event. Major block faulting and magmatism in Tertiary time triggered hydrothermal activity along faults, ultimately leading to vein forma-

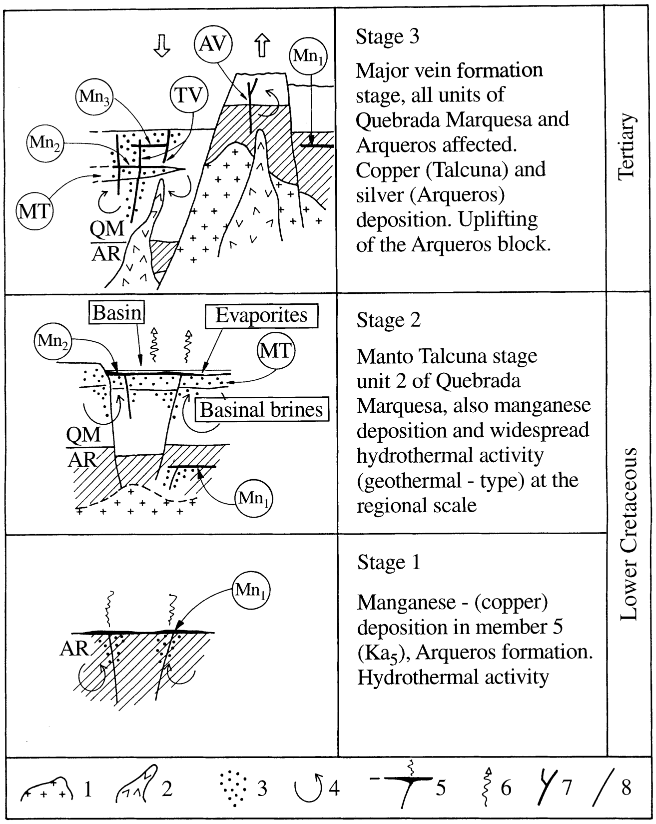

Fig. 8 Schematic model (not to scale) for the evolution of the Talcuna and Arqueros districts. *1*, granitoids; *2,* porphyries; *3*, hydrothermal alteration; *4*, convection cells; *5*, manganese deposits; *6*, strong evaporation; *7*, veins; *8*, faults. *AR*: Arqueros Formation; *AV*: Arqueros veins; $Mn_{1\text{-}3}$ manganese episodes 1, 2 and 3; *MT*: Manto Talcuna; *QM*: Quebrada Marquesa Formation; *TV*: Talcuna veins

tion in the Arqueros and Talcuna districts (Fig. 8). The Manto Talcuna became locally enriched in copper during this episode. An example of these veins in the Talcuna district is Mercedes. This process is well defined by the ore grades spatial distribution, showing a general decrease from the vein contacts outward. The manto-type deposits formed from fluids of salinity between 11 and 19 wt.% NaCl equivalent and temperatures between 120 and 205 °C. Those belonging to the vein stage circulated at lower temperatures, between 70 and 170 °C, with salinity values in a wide range from 3 to 27 wt.% NaCl equivalent Although there is evidence for both fluid mixing and boiling, the latter is considered to be the main forming process of the vein deposits, as shown by the mineralogical, textural and fluid inclusion features.

Acknowledgements We thank Cobrex and the Rendic family for continuing cooperation in providing access to their properties. Special thanks go to L. Martínez (Chief Geologist of Coca-Cola) for the many and long helpful discussions on the geology of the Talcuna district. The manuscript benefited from the comments of two reviewers: B. Lehmann and B.K. Townley.

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