Stratabound and vein-type Pb-Zn mineralization at Las Canas, Chanarcillo Group, northern Chile; fluid inclusion microthermometry, and sulfur and lead isotope constraints

LIEBEN, François Claude Serge, et al.

Abstract
The Las Canas stratabound Pb-Zn deposit, in northern Chile, is hosted by the Lower Cretaceous back-arc marine carbonate and subordinate andesitic volcanic and volcaniclastic rocks of the Chanarcillo Group, one hundred meters above a thick pile of magmatic arc-related basaltic to andesitic lavas of the Bandurrias Formation. The deposit is not obviously related to local intrusive rocks, which include an Upper Cretaceous granodiorite batholith and dacite dikes emplaced along normal faults. Stratabound Pb-Zn-Ba mineralization is constrained within several porous stratigraphic units, including a 50 cm thick lapilli-tuff and less well mineralized algal-laminated limestone. Veins that locally carry some Pb-Zn occur along normal faults that displace the stratabound orebodies, and this study shows that they represent a different type of mineralization. Fluid inclusion microthermometric data for ore-stage quartz and barite indicate saline fluids (6 to 30 wt% NaCl eq) and a formation temperature in the range of 80 degrees C to 160 degrees C for the stratabound mineralization. Two types of fluid inclusions occur in the veins. The [...]
Abstract — The Las Cañas stratabound Pb-Zn deposit, in northern Chile, is hosted by the Lower Cretaceous back-arc marine carbonate and subordinate andesitic volcanic and volcanioclastic rocks of the Chañarcillo Group, one hundred meters above a thick pile of magmatic arc-related basaltic to andesitic lavas of the Bandurrias Formation. The deposit is not obviously related to local intrusive rocks, which include an Upper Cretaceous granodiorite batholith and dacite dikes emplaced along normal faults. Stratabound Pb-Zn mineralization is constrained within several porous stratigraphic units, including a 50 cm thick lapilli-tuff and less well mineralized algal-laminated limestone. Veins that locally carry some Pb-Zn occur along normal faults that displace the stratabound orebodies, and this study shows that they represent a different type of mineralization.

Fluid inclusion microthermometric data for ore-stage quartz and barite indicate saline fluids (6 to 30 wt% NaCl eq) and a formation temperature in the range of 80°C to 160°C for the stratabound mineralization. Two types of fluid inclusions occur in the veins. The type I vein fluid inclusions indicate less saline (average 7 wt% NaCl eq) and slightly higher temperature fluids, in the range of 110°C to 220°C. The type II vein fluid inclusions indicate highly saline fluids (25 to 40 wt% NaCl eq) which might be related to minor copper mineralization.

$^{206}\text{Pb}/^{204}\text{Pb}, ^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for galenas from the stratabound mineralization, with mean values of 18.42, 15.59, and 38.25, respectively, fall within the range of stratabound polymetallic deposits of northern and central Chile, and indicate a Lower Cretaceous magmatic rock source. Galenas from veins have slightly more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}, ^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, with mean values of 18.47, 15.61, and 38.34, suggesting two distinct episodes of mineralization.

$\delta^{34}\text{S}$ values for galena and barite range from negative values (-31.2‰ to -12.5‰ and -7.7‰ to +12‰, respectively) in the mineralized tuff to higher values in the algal-laminated limestone (-2.5‰ to +1.2‰ and +12.3‰ to +17.4‰, respectively), close to Lower Cretaceous marine sulfate values for barite, and homogeneous values for the galena from veins (-12.0‰ ± 1‰). Changing redox conditions can partly account for $\delta^{34}\text{S}$ variations in the tuff. Sulfur sources include magmatic rock sulfurs (-1.5‰ to +9.7‰) as well as sedimentary sulfides and marine sulfate. © 2000 Canadian Institute of Mining, Metallurgy and Petroleum. All rights reserved.

Introduction

Stratabound base metal deposits hosted by Mesozoic magmatic arc-related volcano-sedimentary rocks of northern and central Chile are an important economic resource, of mainly copper. The ore deposits have been classified in terms of their paleotectonic setting in the ensialic arc-backarc pair (Fontboté, 1990), and in terms of their dominant volcanic or volcano-sedimentary host rocks (Camus, 1986, 1990), that are characterized by distinct sulfur isotopic compositions (Munizaga and Zentilli, 1994). The Las Cañas stratabound deposit, located 30 km SSE of Vallenar in northern Chile (Fig. 1), is one of the few deposits in northern Chile ever mined for Pb and Zn (Neuenschwander and Taverner, 1942; Ruiz and Peebles, 1988). It occurs near the base of Lower Cretaceous back-arc carbonate rocks of the Chañarcillo Group which overlie volcanic arc rocks of the Bandurrias Formation of similar age (Díaz, 1986; Lieben et al., 1996). The Las Cañas deposit, within a 5 km² area, includes various types of ore that display a wide range of sulfur isotopic compositions (Lieben et al., 1996). A few 100 000 t of high-grade lead ore were mined in the 1930s to 1940s principally from a stratiform orebody hosted by a volcaniclastic layer (Flores, 1942; Neuenschwander and Taverner, 1942). Sulfide veins in faults that crosscut the volcaniclastic layer were exploited locally for copper (Neuenschwander and Taverner, 1942). It was proposed previously that the latter could be the conduits for the stratabound mineralization (Lieben et al., 1996).
Regional Geologic Setting

The Pb-Zn deposit of Las Cañas is hosted by the Lower Cretaceous Chañarcillo Group, that is exposed in a NNE-trending belt extending from 27°30' to 29°S across the Atacama region (Fig. 1). The Chañarcillo Group consists of up to 2000 m of shallow water marine carbonate rocks with volcanic and volcanioclastic intercalations, and is composed of the Nantoco, Totoralillo, and Pabellón formations (Segerstrom, 1967; Abad, 1977; Jurgan, 1977; Cisternas and Díaz, 1990). It overlies, and is laterally equivalent to the west with a volcanic arc sequence composed of calc-alkaline basaltic andesite to dacitic lavas, breccias, volcanioclastic sandstones and tuffs of the Lower Cretaceous Bandurrias Formation (Segerstrom, 1967; Zentilli, 1974; Pincheira, 1991). Stratabound ore deposits in the Chañarcillo Group tend to occur as stratiform orebodies within coarse-grained lithologies near the base of the group above volcanic rocks, and within dark gray algal-laminated limestones and a stratiform breccia in the upper member of the Nantoco Formation (Díaz, 1986; Lieben et al., 1996).

The Lower Cretaceous rocks rest unconformably upon a folded Paleozoic and Triassic-Liassic basement (Moscoso et al., 1982). They are overlain, in small angular discordance, by the elastic continental and andesitic volcanic rocks of the Mid-Upper Cretaceous Cerrillos Formation (Fig. 1). They have been affected by various stages of extensional and contractional tectonics (Moscoso and Mpodozis, 1988, Mpodozis and Ramos, 1990; Mpodozis and Allmendinger, 1993; Ardévalo and Grocott, 1997). According to Moscoso et al. (1982), a main structural feature that affected the Lower Cretaceous rocks in the vicinity of the Las Cañas mine, the Agua de los Burros Fault System, consists of N-S to NNE-SSW folds and thrusts with a dominant western vergence (Fig. 1).

Low-grade metamorphism affected parts of the Cretaceous volcano-sedimentary sequence (Levi et al., 1982, 1988), while higher-grade metamorphic rocks are restricted to the vicinity of large intrusions. An Upper Cretaceous granodiorite batholith, dated at 87 Ma (Farrar et al., 1970), occurs 5 km NW of the mine area (Fig. 1). To the east, a NNE-trending magmatic belt consists of Paleocene and Eocene granodiorite and granite (Farrar et al., 1970; Moscoso et al., 1982; Fig. 1).

Sampling and Analytical Methods

The geological and geochemical characterization of the Las Cañas mine host rock sequence involved bulk rock analyses of selected volcanic and sedimentary rocks and dike samples by XRF at the universities of Geneva and Lausanne. The trace element contents of mineralized samples from the three different ore types at Las Cañas were obtained by ICP and INAA analyses performed by Actlabs, Canada. Microprobe analyses of chlorite were made at the University of Lausanne on a Cameca Camabax SX 50, using an acceleration voltage of 15 kV and a beam current of 30 nA.

Fluid inclusions have been studied in ore-stage quartz and barite from the different ore types at Las Cañas. Where possible, quartz has been preferred to barite, which is considered a less reliable host mineral (Ulrich and Bodnar, 1989).
Microthermometric measurements were made on 100 µ-thick doubly polished sections using a Fluid Inc. adapted U.S.G.S. heating and cooling stage (Roedder, 1984) calibrated with synthetic fluid inclusions (Sterner and Bodnar, 1984) at -56.6°C, 0.0°C and 374.1°C. The precision is 0.1°C for the measurements below 0°C, and 1°C for the high-temperature measurements.

Lead isotopes were measured for eleven galena samples from different ore types and locations within the Las Cañas deposit, and for five galena and one cerussite samples from other stratabound Pb-Zn-Ba deposits and occurrences within the Chañarcillo Group. Three whole rock igneous samples of the Las Cañas mine sequence were also analyzed, including two lavas from the volcanic sequence underlying the deposit and one dacitic dike at the level of the main stratabound deposit. About 1 mg of galena was dissolved in ultra-pure HNO₃ and separated by electrodeposition. For the whole rocks, about 250 mg of sample was leached in HCl and HNO₃ for 24 hours. The residue was completely digested in HF and HNO₃. Lead of the leach and residue was separated in HBr anion exchange columns. The lead was analyzed on a Finnigan MAT 262 mass spectrometer at the University of Geneva using the conventional silica gel technique. The data were corrected for mass isotopic fractionation using a correction factor of +0.08% a.m.u. based on repeated analyses of the NBS981 international standard. Precision estimates are depicted as 2σ error bars in the conventional isotope plots.

The sulfur isotope analyses were carried out on eleven galena and eight barite samples from the different ore types at Las Cañas (some data are reported in Lieben et al., 1996). About 20 mg of sample were hand-picked and purified under the binocular microscope. The sulfur isotope analyses were performed on SO₂ produced by the combustion with copper oxide and tungsten oxide, respectively, on a triple collector VG SIRA 12 mass spectrometer at the Ottawa Carleton Geoscience Centre, Ontario, Canada, and on a Finnigan MAT 251 mass spectrometer at the University of Lausanne. The data are reported as ‰ CDT, with a precision of 0.2‰. The sulfur isotopic compositions of six igneous rock samples from the Las Cañas mine area were obtained by using the KIBA extraction method at the Ottawa Carleton Geoscience Centre.

Geology of the Mine Area

Mine Stratigraphy

The stratigraphic sequence of the Las Cañas mine area has been described by Jurgan (1977), Cisternas (1986), and Cisternas and Díaz (1990). A recent description is given by Nova (1997). It consists of an up to 500 m thick pile of basaltic to andesitic lavas of the Bandurrias Formation that is overlain by 250 m of bioclastic limestones, micritic limestones and subordinate andesite and volcanioclastic rocks of the Chañarcillo Group, gently dipping to the east (Fig. 2).

The limestones have been assigned an Hauertivian age on the basis of their faunal content (Neuenschwander and Tavera, 1942), and they correlate lithologically with the Nantoco Formation (Cisternas, 1986; Nova, 1997).

The sequence from the Quebrada Las Cañas to the Cerro Cañas Norte (Figs. 2 and 3) begins with lavas of dominantly basaltic to basaltic andesitic composition (Fig. 4; Table 1). The basaltic lavas present transitional to slightly tholeitic affinities (Nova, 1997). They present similarities with the Laves Superiores from the Punta del Cobre Formation in the Copiapó area (Nova and Cisternas, 1997), which may have formed during the opening of the back-arc basin (Marschik, 1996). Thin NW-SE and WSW-ENE-trending basic dikes in the Quebrada Las Cañas with a similar com-
position to adjacent lavas probably represent their feeders (Nova, 1997). The lavas are commonly amygdaloidal (top of flow), with a seriate or porphyritic texture and moderately altered plagioclase and pyroxene phenocrysts in an intergranular or pilotaxitic matrix. Calcite, chlorite, quartz, epidote, muscovite, clay minerals, zeolites, prehnite, pumppellyte, alkali feldspar, hematite and barite occur in the lavas as fillings of vacuoles and fractures, and form decimetric epidote and calcite lenses and veins. This regional alteration of the lavas is accompanied in places by albitionization of plagioclase (Table 1). It is not clear whether this regional low-grade alteration of the lavas is related to low-grade burial metamorphism of the prehnite-pumppellyte facies as proposed by Levi et al. (1988), or to an intrusive event.

The lowermost part of the Chiarcy Group (unit I) consists of 100 m of bioclastic limestone, volcaniclastic sandstone, and lavas. Important and rapid facies changes between volcanic-dominant and carbonate-dominant facies, possibly associated with synsedimentary faults, characterize this unit (Jurgan, 1977). The lavas consist of porphyritic and amygdaloidal andesites and basaltic andesites (Fig. 4; Table 1), commonly with a reddish tint, with dominant plagioclase phenocrysts in an intergranular to interseptal matrix with dendritic oxide. Thirty meters of thick-beded bioclastic limestone forms the top of the unit (Fig. 3).

These rocks are overlain by about 60 m of thin-beded micritic limestone and dark gray algal-laminated limestones in the upper part, that are lithologically correlated with the upper member of the Nantoco Formation (Cisternas and Diaz, 1990; Nova, 1997). Numerous centimeter-thick volcaniclastic layers occur within the micritic limestones, including the main ore-bearing interval, that constitutes the base of the unit. The volcaniclastic layers are mainly composed of pyroclastic fragments. Their lateral continuity, good sorting and internal
grading suggest that they were emplaced as waterlain air-fall tuffs (see below). Welded crystal tuff and/or lava also occur (Cisternas, 1986). Near the top of the sequence in Cerro Cañas Norte (Fig. 2), a stratiform breccia occurs within the dark gray laminated limestone, and corresponds to the regionally extensive breccia of the upper member of the Nantoco Formation (Segerstrom, 1967; Cisternas and Díaz, 1990; Lieben, 2000). This unit is host of a second stratiform ore occurrence consisting of a silica-barite lens. This sequence is overlain by volcaniclastic sandstone, bioclastic limestone and cherty limestone of the Totoralillo Formation.

**Petrography of the Volcaniclastic Host Rock**

The volcaniclastic layer hosting the main stratiform orebody is a reversely graded vitric and lithic green tuff with a micritic matrix, bounded on both sides by finer grained strata (Figs. 3 and 5a). The base of the layer, in sharp contact with underlying greenish calcareous mudstone, is composed of a 10 cm thick well-sorted, clast-supported coarse tuff of 1 mm to 3 mm grain size, with less than 10% lapilli. The fragments consist of about 70% greenish shards and pumice fragments, 20% andesitic lithic clasts, and 10% crystals. It is overlain by a 20 cm thick well-sorted, clast- to matrix-supported lapilli-tuff of 3 mm to 10 mm grain size, composed essentially of greenish pumice, with minor lithic clasts and crystals in the matrix. The tuff has an andesitic composition, with a relatively high Cr content of approximately 350 ppm (Table 1). The layer extends regionally for 30 km to 40 km (Jurgen, 1977) and maintains a constant thickness and composition in the mine area. Locally, pumice fragments with strongly flattened vacuoles indicate some degree of welding, compaction or deformation.

<table>
<thead>
<tr>
<th>Lms Unit II</th>
<th>Tuffs Unit II</th>
<th>Dacite Dikes</th>
<th>Lava E</th>
</tr>
</thead>
<tbody>
<tr>
<td>FX-370-5</td>
<td>FX-408-1A tuff (min. layer)</td>
<td>FX-361-1 dacite dyke</td>
<td>FX-358A-2 dacite</td>
</tr>
<tr>
<td>FX-410-4</td>
<td>FX-410-4 tuff (min. layer)</td>
<td>FX-366-3 dacite dyke</td>
<td>FX-358B-2 dacite</td>
</tr>
<tr>
<td>FX-370-6</td>
<td>FX-408-2 tuff</td>
<td>FX-408-4 dacite dyke (border)</td>
<td>FX-358C-2 dacite</td>
</tr>
<tr>
<td>FX-350-2</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358D-2 dacite</td>
</tr>
<tr>
<td>FX-350-3</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358E-2 dacite</td>
</tr>
<tr>
<td>FX-350-4</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358F-2 dacite</td>
</tr>
<tr>
<td>FX-350-5</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358G-2 dacite</td>
</tr>
<tr>
<td>FX-350-6</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358H-2 dacite</td>
</tr>
<tr>
<td>FX-350-7</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358I-2 dacite</td>
</tr>
<tr>
<td>FX-350-8</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358J-2 dacite</td>
</tr>
<tr>
<td>FX-350-9</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358K-2 dacite</td>
</tr>
<tr>
<td>FX-350-10</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358L-2 dacite</td>
</tr>
<tr>
<td>FX-350-11</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358M-2 dacite</td>
</tr>
<tr>
<td>FX-350-12</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358N-2 dacite</td>
</tr>
<tr>
<td>FX-350-13</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358O-2 dacite</td>
</tr>
<tr>
<td>FX-350-14</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358P-2 dacite</td>
</tr>
<tr>
<td>FX-350-15</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358Q-2 dacite</td>
</tr>
<tr>
<td>FX-350-16</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358R-2 dacite</td>
</tr>
<tr>
<td>FX-350-17</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358S-2 dacite</td>
</tr>
<tr>
<td>FX-350-18</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358T-2 dacite</td>
</tr>
<tr>
<td>FX-350-19</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358U-2 dacite</td>
</tr>
<tr>
<td>FX-350-20</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358V-2 dacite</td>
</tr>
<tr>
<td>FX-350-21</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358W-2 dacite</td>
</tr>
<tr>
<td>FX-350-22</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358X-2 dacite</td>
</tr>
<tr>
<td>FX-350-23</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358Y-2 dacite</td>
</tr>
<tr>
<td>FX-350-24</td>
<td>FX-370-6</td>
<td>FX-408-4 dacite dyke</td>
<td>FX-358Z-2 dacite</td>
</tr>
</tbody>
</table>
The distinct pigmentation of the greenish pumices and shards is due to the high abundance of chlorite and the presence of a greenish K-bearing clay mineral (celadonite?) that probably replaces the originally glassy groundmass and fills the abundant sub-millimetric vacuoles. Alteration of the glass produced 50 µ-sized quartz and alkali feldspar crystals, including mainly albite microlites that confer a pilotaxitic to trachytic texture to the clasts. In places, these minerals form an isopachous 30 µ-thick bladed rim cement around the clasts (Fig. 5). Calcite, and lesser amounts of chalcedony, sericite, hematite, and barite also occur as secondary minerals in the tuff mainly within vacuoles of the clasts. Zeolites have been described by Neuenschwander and Tavera (1942) as cements in the tuff, but these have not been identified in this study.

**Structural Setting**

The dominant structural features in the mine area are sub-vertical N-S to NE-SW-trending normal, west-side down faults with a vertical displacement of up to 80 m. The main sub-vertical faults are a NE-SW fault passing through the Cañas Norte mine, a NNE-SSW fault and a N-
S fault in the eastern part of the mine area (Fig. 2). Amphiboile-bearing porphyritic dacite dikes (Fig. 4; Table 1) are emplaced along the NE-SW fault, and parallel to the N-S fault. A N-S-oriented dacitic dike cuts the main tuff-hosted orebody without displacing it (Neuenschwander and Tavera, 1942). East of the mine workings, a NNE-SSW-trending thrust fault brings volcanic and volcaniclastic rocks of the Bandurrias Formation above those of the Chañarcillo Group (Figs. 1 and 2). The rocks of the Chañarcillo Group are locally folded near this fault. The thrust coincides in part with the stratiform breccia of the upper member of the Nantoco Formation, supporting the interpretation that the brecciation is probably in part of tectonic origin (Arévalo and Mpodozis, 1991; Lieben, 2000).

**Ore Occurrences**

Three types of ore occurrences have been observed in the Chañarcillo Group sedimentary rock sequence exposed at Las Cañas: (1) the main stratiform Pb-Zn-Ba orebody disseminated within the tuff layer, (2) a silica-barite lens hosted by dark gray laminated limestone, and (3) Pb-Zn-(Cu)-bearing quartz veins which occur along the normal faults (Fig. 2). The tuff-hosted mineralization and the silica-barite lens
Fig. 5. Stratiform and vein-type mineralization. 

c) Coarse tuff with barite (bar) cement. Alkali feldspar, clay and chlorite occur within vacuoles and as a rim cement (r) around the clasts (cl). Barite (poikilitic) has partly replaced these cements. Fortuna mine, base of volcaniclastic layer, transmitted light, scale bar: 1 mm.
d) Lapilli-tuff with chloritized, devitrified, pumice (cl) cemented by quartz (qz), galena (gn) and barite (bar). Cañas Norte mine, transmitted light, scale bar: 1 mm.
e) Mineralized lapilli-tuff with sphalerite (sp), potassic feldspar (ksp), sericite (ser) and galena (gn) cements. Small albite grains are also present around the chloritized pumices. Fortuna mine, top of volcaniclastic layer, reflected light, scale bar: 250 μ.
f) Detail of mineralized chloritized pumice, showing open space filling and selective replacement of parts of the clasts by the ore minerals, in which early rim cements (r) and chlorite-filled vacuoles have been preserved. Reflected light, scale bar: 250 μ.
g) Galena (gn) rimmed by small sphalerite (sp) and hematite (hm) crystals. Fortuna mine, reflected light, scale bar: 100 μ.
h) Quartz vein with interstitial galena (black), and cross-cutting quartz veinlets with chloritic selvages. NE-SW vein, transmitted light, scale bar: 1 mm.
are at a lower and an upper stratigraphic level, respectively, separated by about 50 m within the upper member of the Nantoco Formation (Fig. 3). In addition, small sulfide disseminations within chalcedony vugs occur throughout the mine sequence (Cisternas, 1986).

**Tuff-hosted Mineralization**

The main orebody is hosted by tuff layers and extends discontinuously for at least 1.5 km, representing a few 100 000 t of ore with a grade of about 3 wt% Pb, 3.5 wt% Zn and 35 ppm Ag (Table 2). It has been exploited along strike notably in the Fortuna mine, at Cañas Norte and other small mines in the eastern part of the mine area where the orebody is repeated by the normal faults (Neuenschwander and Taiera, 1942; Fig. 2). High ore grades are controlled by the high porosity of the tuff relative to the immediately adjacent calcareous mudstone (Fig. 3). The fine-grained volcaniclastic layers are only locally mineralized and to a minor extent. Galena, subordinate sphalerite, and minor pyrite, hematite and chalcopyrite occur together with barite, quartz and potassic feldspar as intergranular cements (Figs. 5c, 5d and 5e), within interconnected vacuoles of the clasts, and as fillings of sub-millimetric fractures. Locally, the clasts are partly replaced and rimmed by these minerals (Fig. 5f). Sphalerite preferentially surrounds clasts and galena occurs as 3 mm large interstitial crystals filling the remaining space, which is commonly rimmed by hematite or pyrite (Fig. 5g). Quartz occurs in small amounts and forms a meniscus cement at the border of the clasts (Fig. 5d), while potassic feldspar and sericite occur locally in a strongly mineralized area of the Fortuna mine. The potassic feldspar contains abundant sericite inclusions, and sericite occurs as radiating aggregates within the main stage galena (Fig. 5e). Barite is a common cement, which fills the remaining intergranular space left by the sulfides where it is associated with them. The quartz contains small sphalerite, galena and barite inclusions, while barite is commonly devoid of sulfide inclusions.

**Silica-barite Lens**

A lens about 10 m long and 2 m thick that consists of mostly silica and barite with up to 3 wt% Pb and lesser Zn is hosted by the dark laminated limestone in the southern part of the mine area (Fig. 2). This lens displays features that are similar to other ore occurrences hosted by the upper member of the Nantoco Formation such as in the Mamilta barite belt (Díaz, 1986; Lieben, 2000). The lens immediately overlies the stratiform breccia, which contains sporadic sulfide cement. The laminated crystalline limestone host rock, consisting of xenomorphic equigranular calcite, is in turn overlain by micritic limestone, which is in part brecciated and cemented by sulfides. In the lens, silica (length-slow chalcedony and quartz), barite, galena and small amounts of sphalerite and pyrite occur as replacements and cavity-fillings, locally arranged as parallel millimeter-thick sheet cavities with bipolar grown crystals (zebra texture, Fig. 5b). Galena is generally associated with small amounts of silica, commonly expressed as chalcedony. Quartz-carbonate veinlets with large ferroan carbonate crystals cut the quartz-sulfide veinlets and vugs in some places.

**Vein-type Mineralization**

This ore-type consists of a sulfide-bearing quartz and quartz-carbonate breccia vein and a stockwork up to 10 m wide along some of the sub-vertical faults, including the NE-SW fault passing through the Cañas Norte mine, and smaller N-S and NW-SE faults and fractures observed at the level of the main tuff-hosted orebody in the eastern part of the mine area (Fig. 2). A notable thickening of the quartz stockwork is observed along the NE-SW vein within a bioclastic limestone at the base of the Nantoco Formation. A centimetric to metric halo of dark brown silicified and chloritized wallrock and breccia fragments occurs around the quartz stockwork. Three analyses of vein samples yielded approximately 4.2 wt% Pb, 0.6 wt% Zn and 0.1 wt% Cu with slightly higher contents of...
Co, As, Sb, Au, Bi, and Se relative to the stratabound ore (Table 2). Evidence of repeated fracturing is common, with quartz-carbonate veinlets cross-cutting or filling open space within quartz veinlets and vugs. The millimetric quartz veinlets contain galena, with lesser chalcopyrite, sphalerite and pyrite which occupy the center of the fine-grained drusy, locally chalcedonic quartz (Fig. 5h). Chalcopyrite, altered to Cu-oxides, is more abundant within veinlets with large brown carbonate. Chlorite forms abundant millimetric patches within the microcrystalline quartz in altered wallrock and breccia fragments, and occurs as linings of the drusy quartz. The bluish-green chlorite is a high Fe/(Fe+Mg) and low Si type, distinct from the chlorites present in the mineralized tuff and in the vacuoles of a lava sample (Fig. 6). Alteration of the limestone and volcaniclastic rocks bordering the vein has produced an enrichment in Si, Fe, Mn, Cu, and Co, and a depletion in Mg, Na, and K (Tables 1 and 2).

**Paragenesis**

A paragenetic sequence for the Las Cañas district is given in Figure 7. The stratabound tuff-hosted mineralization and silica-barite lens are interpreted to have formed during a single metallogenic event, distinct from the vein-type

<table>
<thead>
<tr>
<th>Paragenetic Sequence</th>
<th>Pre Ore</th>
<th>Main Ore Stage</th>
<th>Vein</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>quartz</td>
<td>calcite</td>
<td>chlorite (1)</td>
</tr>
</tbody>
</table>

(1) includes celadonite
(2) includes Zn-bearing smectite
tr.: traces
mineralization. This interpretation is based on the distinctive composition, including the absence of barite, and higher Co, As, Sb, Au, Bi, and Se contents, and distinct alteration with the presence of chlorite and Na and K leaching, of the latter ore type. No thickening of the vein system was observed at the level of the main tuff-hosted orebody. Different fluid inclusion populations, and a homogeneous and different lead and sulfur isotopic signature of vein galena further support this interpretation (see below).

Textural observations in the main orebody suggest that the precipitation of ore cements and associated gangue minerals postdates, at least in part, the pervasive replacement of the clasts and cementation by celadonite and chlorite (Fig. 7). The following cementation sequence is proposed for the tuff (Fig. 8): 1) micritic calcite occupies intergranular spaces, early cements are alkali feldspar, quartz, and clay minerals as rims of clasts, coatings of large vacuoles and fillings of small vacuoles; 2) with increasing temperature, e.g., in response to burial, chlorite forms in the center of the vacuoles; 3) fracturing causes interconnection of the vacuoles, early cements are in part replaced by, and vacuoles and intergranular spaces are filled with, sulfides or barite. Quartz and locally potassic feldspar were more abundantly precipitated during the main stage of sphalerite precipitation, followed by hematite, pyrite, chalcopyrite, and locally sericite during the main stage of galena precipitation (Fig. 7). The transition from potassic feldspar to sericite stability may indicate a change to slightly more acidic conditions. Barite is more abundant at the end of the main ore stage, but also occurs in the pre-ore stage.

Two ore-forming substages are distinguished during the formation of the veins (Fig. 7). An early stage consists of quartz veining with lead and zinc, and is accompanied by most of the silicification and chlorite alteration. A later stage of quartz-calcite veining carries minor copper mineralization.

The rocks in the mine area are pervasively oxidized to a depth of about 25 m (Flores, 1942). Two supergene mineral assemblages have been observed within the main orebody (Fig. 7). The first one is dominated by cerussite which commonly replaces galena pseudomorphically, and coexists with chlorite and/or smectite. The second assemblage with a whitish tint is dominated by anglesite, with kaolinite and gypsum, and contains relict galena. The two mineral assemblages probably formed under alkaline and acidic conditions, respectively. In the first lateral drift of an adit in the Cañas Norte mine, a profile in the cerussite zone shows an enrichment in zinc relative to lead at the base of the tuff (Table 2). The secondary enriched zinc is probably contained within a smectite group clay mineral, which is common in several oxidized zinc ores within the Chañarcillo Group (Lieben, 1999). Other secondary minerals are hemimorphite, covellite, Cu-oxides, aragonite, and limonite.

**Fluid Inclusion Microthermometry**

**Fluid Inclusion Petrography**

Ore-stage quartz cementing the tuff contains few measurable fluid inclusions. The inclusions in barite from the tuff-hosted mineralization include liquid, two-phase liquid-rich and gas-rich inclusions of indeterminate or secondary origin. Most are two-phase inclusions with a high and relatively constant liquid-to-vapor ratio at room temperature.
Large euhtedral quartz crystals from the silica-barite lens contain primary inclusion trails composed of closely spaced, up to 15 μ-sized, tubular inclusions parallel and perpendicular to the growth zonation. The inclusions are mainly two-phase aqueous inclusions with a relatively consistent high liquid to vapor ratio at room temperature, though affected locally by necking-down. The barite intergrown with this quartz contains numerous inclusions of indeterminate origin and shape, including inclusions with a large vapor bubble that likely originated through stretching and decrepitation of the latter inclusions. A few microthermometric measurements of two-phase aqueous inclusions in barite yielded similar results as in quartz. Hydrocarbon inclusions, some with a dark organic daughter mineral, have been observed in a quartz sample from the silica-barite lens. These are secondary with respect to the quartz, and linked to a vug filled with galena.

Only a few, very small 1 to 2 μ-sized, inclusions could be measured in quartz from the veins, except in one sample. The inclusions are generally up to 10 μ primary and (pseudo) secondary two-phase aqueous inclusions with a high liquid-to-vapor ratio at room temperature (type I vein inclusions), and subordinate >10 μ secondary three-phase aqueous inclusions with a halite daughter crystal (type II vein inclusions).

Microthermometric Results

Fluid inclusions in quartz and barite cements from the tuff-hosted mineralization and silica-barite lens yield similar homogenization temperatures, in the range of 70°C to 150°C (Fig. 9). The salinities in the tuff-hosted mineralization are between 6 and 25 wt% NaCl eq, with an average value of 15 wt% NaCl eq. The widest range in salinities, from 3 to 30 wt% NaCl eq occurs in the silica-barite lens, with an average value of 21 wt% NaCl eq (Fig. 9). Initial ice melting temperatures below ~42°C indicate the presence of other dissolved cations such as Ca²⁺. No systematic variation in temperature and salinity was observed in a profile perpendicular to the growth zonation of quartz from the silica-barite lens, but salinity varied abruptly within groups of inclusions. Three hydrocarbon-type inclusions homogenized in the liquid phase at 28.3°C, 29.5°C, and 45.0°C, respectively.

Type I fluid inclusions in the veins are typically H₂O-NaCl fluids, as indicated by high initial ice melting temperature. The homogenization temperature varies between 100°C and 160°C. The salinities average 7 wt% NaCl eq. Type II vein fluid inclusions have homogenization temperatures of around 110°C and salinities of 26 to 40 wt% NaCl eq (Fig. 9).

Lead Isotope Data

The ²⁰⁶Pb/²³⁵Pb, ²⁰⁷Pb/²³⁵Pb and ²⁰⁸Pb/²³⁵Pb ratios of the galenas from Las Cañas vary from 18.40 to 18.48, 15.57 to 15.62, and 38.17 to 38.37, respectively (Fig. 10; Table 3). Along with data from other stratabound Pb-Zn-Ba deposits from the Chañarcillo Group, the data most plot, in ²⁰⁶Pb/²³⁵Pb vs ²⁰⁸Pb/²³⁵Pb and ²⁰⁶Pb/²³⁵Pb vs ²⁰⁸Pb/²³⁵Pb diagrams, within the field of stratabound and vein deposits hosted by the Lower Cretaceous arc and back-arc of northern and central Chile (Puig, 1988; Fontboté et al., 1990; Fig. 10). The galena samples from vein ores at Las Cañas are characterized by a slightly more radiogenic lead isotopic signature (mass center value of 18.46, 15.61, 38.29) than galena from the tuff-hosted and silica-barite ores (mass center value of 18.42, 15.60, 38.27; Fig. 10).

Local potential source rocks for the lead in the Las Cañas mine area include the Lower Cretaceous magmatic rocks, which comprise the dominantly basaltic and basaltic andesite lavas of the upper part of the Bandurrias Formation, andesitic and basaltic andesitic lavas intercalated within the Nantoco Formation, volcanic rocks of the Bandurrias Formation thrust upon the Chañarcillo Group, and volcanic component within sedimentary rocks of the Chañarcillo Group, which forms essentially from the volcanic arc (Cisternas and Díaz, 1990). Other potential local sources include the Upper Cretaceous granodioritic batholith and the dacitic dikes. The lead isotope ratios for the three analyzed samples (Table 3) and the initial lead isotope ratio for a sample of the granodiorite batholith (McNutt et al., 1979) are shown in Figure 10. The basalt sample of the Bandurrias Formation plots close to the field of the analyzed galenas (Fig. 10). Correction for in situ U and Th decay, assuming an age of 130 Ma, corresponding to the Hettneverian age of the host rock sequence, does not significantly alter the lead isotope ratio of this sample. The andesite sample of the Nantoco Formation displays a similar ²⁰⁶Pb/²³⁵Pb ratio, and may lie on an isochron starting from the basalt sample. The ratios could not, however, be corrected because of U and Pb contents below the detection level. The leach and residue aliquots of the dacite dike sample gave different results. The residue sample presents a higher ²⁰⁶Pb/²³⁵Pb ratio and similar ²⁰⁶Pb/²³⁵Pb ratio to the lavas. The lead iso-
Fig. 10. Lead isotopic composition of galena from Las Cañas and other stratabound Pb-Zn-Ba deposits of this study. Field of stratabound deposits hosted by Lower Cretaceous magmatic arc and back-arc basin (Puig, 1988; Fontboté et al., 1990). Whole rock lead isotope data of potential source rocks, including magmatic rocks of the Las Cañas area (this study), and the Cretaceous batholith (McNutt et al., 1979) are also plotted. Model curves are after Zartman and Doe (1981).
Table 3. Isotopic data for the ore types and igneous samples at Las Cañas

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Mineral</th>
<th>$^{206}Pb/^{204}Pb$</th>
<th>$^{207}Pb/^{204}Pb$</th>
<th>$^{208}Pb/^{204}Pb$</th>
<th>$^{87}Sr/^{86}Sr$</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>FX-67</td>
<td>tuff-hosted</td>
<td>galena</td>
<td>18.400</td>
<td>15.573</td>
<td>38.166</td>
<td>(-26)</td>
<td>Fortuna</td>
</tr>
<tr>
<td>FX-70</td>
<td>tuff-hosted</td>
<td>galena</td>
<td>18.843</td>
<td>15.615</td>
<td>38.333</td>
<td>(-12.5)</td>
<td>Cañas Norte</td>
</tr>
<tr>
<td>FX-70</td>
<td>tuff-hosted</td>
<td>barite</td>
<td>18.412</td>
<td>15.587</td>
<td>38.208</td>
<td>-30.2*</td>
<td>San Bartolo</td>
</tr>
<tr>
<td>FX-409-6</td>
<td>tuff-hosted</td>
<td>barite</td>
<td>18.435</td>
<td>15.618</td>
<td>38.316</td>
<td></td>
<td>Fortuna</td>
</tr>
<tr>
<td>FX-408-1b</td>
<td>tuff-hosted</td>
<td>barite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cañas Norte</td>
</tr>
<tr>
<td>FX-308-1</td>
<td>tuff-hosted</td>
<td>barite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Quebrada Larga</td>
</tr>
<tr>
<td>FX-409-1</td>
<td>tuff-hosted</td>
<td>barite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cañas Norte</td>
</tr>
<tr>
<td>FX-370-7</td>
<td>tuff-hosted</td>
<td>barite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>FX-66</td>
<td>silica-barite lens</td>
<td>galena</td>
<td>18.421</td>
<td>15.590</td>
<td>38.221</td>
<td>(-2.5)</td>
<td>barite lens</td>
</tr>
<tr>
<td>FX-66</td>
<td>silica-barite lens</td>
<td>barite</td>
<td>18.441</td>
<td>15.622</td>
<td>38.330</td>
<td></td>
<td>barite lens</td>
</tr>
<tr>
<td>FX-406-4</td>
<td>silica-barite lens</td>
<td>barite</td>
<td>18.436</td>
<td>15.616</td>
<td>38.307</td>
<td>-1.4*</td>
<td>barite lens</td>
</tr>
<tr>
<td>FX-406-6</td>
<td>silica-barite lens</td>
<td>barite</td>
<td>18.459</td>
<td>15.588</td>
<td>38.254</td>
<td>-12.4*</td>
<td>barite lens</td>
</tr>
<tr>
<td>FX-378-2</td>
<td>silica-barite lens</td>
<td>barite</td>
<td>18.465</td>
<td>15.606</td>
<td>38.332</td>
<td></td>
<td>N-S fault (Andacolla)</td>
</tr>
<tr>
<td>FX-356</td>
<td>feede rs</td>
<td>whole rock</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Q. Las Cañas</td>
</tr>
<tr>
<td>FX-357</td>
<td>basalt unit 0</td>
<td>whole rock</td>
<td>18.426</td>
<td>15.573</td>
<td>38.207</td>
<td></td>
<td>Q. Las Cañas</td>
</tr>
<tr>
<td>FX-357-2</td>
<td>basalt unit 0</td>
<td>whole rock</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Q. Las Cañas</td>
</tr>
<tr>
<td>FX-357-2L</td>
<td>leach sample</td>
<td>whole rock</td>
<td>18.158</td>
<td>15.594</td>
<td>38.353</td>
<td></td>
<td>Q. Las Cañas</td>
</tr>
<tr>
<td>FX-412</td>
<td>andesite unit I</td>
<td>whole rock</td>
<td>18.650</td>
<td>15.595</td>
<td>38.689</td>
<td>7.7</td>
<td>Q. Las Cañas</td>
</tr>
<tr>
<td>FX-361</td>
<td>dacite dike</td>
<td>whole rock</td>
<td>18.661</td>
<td>15.610</td>
<td>38.391</td>
<td></td>
<td>NE-SW fault (Cañas Norte)</td>
</tr>
<tr>
<td>FX-408-4</td>
<td>dacite dike</td>
<td>whole rock</td>
<td>18.887</td>
<td>15.566</td>
<td>38.820</td>
<td>2.2</td>
<td>N-S fault (Q. Larga)</td>
</tr>
<tr>
<td>FX-408-4L</td>
<td>leach sample</td>
<td>whole rock</td>
<td>18.437</td>
<td>15.545</td>
<td>38.104</td>
<td></td>
<td>6.3</td>
</tr>
<tr>
<td>FX-363</td>
<td>granodiorite</td>
<td>whole rock</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sulfur isotopes analyses were carried out by the Ottawa Carleton Isotope Centre, except the values marked with an asterisk which were carried out at the University of Lausanne. Values in brackets are from Lieben et al. (1996). The strontium isotopic compositions of barites are also from Lieben et al. (1996).

tope ratios for the leach sample are less radiogenic and plot close to the field of the analyzed galenas (Fig. 10).

Sulfur Isotope Data

The barite and galena samples from Las Cañas display a large range of sulfur isotopic compositions, from -31.2‰ to +1.2‰ for galena and -7.7‰ to +17.4‰ for barites (Fig. 11; Table 3). There is a correlation between the isotopic composition of galena and barite and the ore type (Fig. 11). Galena and barite from the silica-barite lens have the highest $\delta^{34}S$ values of -2.5‰ to +1.2‰ and +13.2‰ to +17.4‰, respectively. The $\delta^{34}S$ values of barites are within the $\delta^{34}S$ range of barites from Ba and Pb-Zn occurrences hosted by the Chañarcillo Group, and span the Lower Cretaceous seawater $\delta^{34}S$ values (Claypool et al., 1980; Fig. 11). The $\delta^{34}S$ values of two barite-galena pairs yield temperatures above 400°C based on the equation of Ohmoto and Rye (1979). Galena and barite from the tuff-hosted mineralization have lower $\delta^{34}S$ values, between -31.2‰ and -12.5‰ and -7.7‰ and +12.0‰, respectively, and display the largest range of sulfur isotopic compositions. Galena from veins has a homogeneous $\delta^{34}S$ value of -12.0 ± 1‰. The four samples come from the same vein at different stratigraphic levels. No sulfate minerals are associated with galena in veins.

Several magmatic rocks present in the Las Cañas mine area could have contributed sulfur to the hydrothermal fluids. Samples of the following groups have been analyzed: (1) basaltic lavas and feeder dikes of the Bandurrias Formation; (2) andesite of the Nantoco Formation; (3) dacite dikes, and (4) granodioritic batholith. $\delta^{34}S$ values are -1.5‰ and +0.1‰ for the more basic lavas and dikes of the Bandurrias Formation, and range up to +9.7‰ for the more evolved magmatic rocks (Fig. 11; Table 3).

Discussion

Geological Context of Mineralization

Current models for stratabound copper deposits in northern and central Chile favor an epigenetic mode of formation (Sato, 1984; Boric, 1985; Camus, 1990; Elgueta et al., 1990; Zentilli et al., 1997). There is no clear evidence for a direct association with magmatic rocks in many deposits. Geological observations at Las Cañas are in agreement with an epigenetic model in which moderate temperature and saline ore-forming fluids are channeled along faults and porous sedimentary rocks. The occurrence of hydrocarbon fluid inclusions might suggest an association with organic matter, which has been proposed by Zentilli et al. (1997) for several stratabound copper deposits of central and northern Chile.
The fluids, circulating in different aquifers, silicified the carbonate host rock, but except for potassic feldspar and sericite locally intergrown with ore minerals, they did not generate a hydrothermal alteration assemblage in volcanioclastic host rocks distinct from the more regional low-grade metamorphic assemblage. Textural observations suggest, however, that the ore minerals post-date the metamorphism (Figs. 5f and 8; see also Boric, 1985). Brine migration could be related to Mid-Cretaceous extension, burial metamorphism and magmatism (Camus, 1990), or Upper Cretaceous compression and uplift (Lieben, 2000).

Salinity and P-T Range of the Mineralizing Fluids

An estimate of temperatures of the ore-forming fluids is given by the fluid inclusion microthermometric data, and chloride and sulfur isotope geothermometry. Temperature estimates from the empirical chlorite geothermometer (Cathelineau and Nieva, 1985; Kranidiotis and MacLean, 1987) are shown in Table 4. These results are subject to caution because (1) paragenetic relations in the tuff-hosted mineralization do not show that chlorite was precipitated by the mineralizing fluids, and (2) the high Fe/(Fe+Mg) ratio of chlorite associated with the vein-type mineralization, which may significantly affect the temperature estimate, could be related to the composition of the fluid or of the rocks they traversed. In the latter case, a geothermometer that takes into account this ratio (Kranidiotis and MacLean, 1987) is more likely to give a correct estimation of the temperature of the fluids.

The main grouping of fluid inclusions in the tuff-hosted mineralization yields homogenization temperatures in the 80°C to 120°C range, and salinities in the range of 10 to 20 wt% NaCleq. The highest homogenization temperatures in barite are subject to caution, because of their poor reliability as a host mineral (Ulrich and Bodnar, 1988), and because of the possibility of post-trapping modifications. Fluid inclusions in barites with higher homogenization temperature and lower salinity may be due to re-equilibration with later higher temperature fluids associated with the veins. Fluid inclusions in the silica-barite lens cover a wider range in homogenization temperature and salinity. Necking-down may explain the relatively larger range in homogenization temperatures, which therefore cannot be used to constrain the original fluid conditions. The larger range in salinity, however, suggests that more than one fluid was present during mineralization, including possibly a more saline Na-CaCl fluid in an algal-laminated limestone aquifer.

The type I fluid inclusions in veins that have the highest homogenization temperatures and lowest salinities, and indicate either the input of a higher temperature and more dilute fluid, or the input of a dilute fluid during a decrease in pressure (e.g., from lithostatic to hydrostatic), or a combination of these two processes (Fig. 12). The type II fluid inclusions correspond to a slightly cooler highly saline fluid, which might be related to the second paragenetic stage of the veins and to the introduction of copper.

Temperatures obtained from the chlorite geothermometer used in conjunction with the fluid inclusion data allow us to constrain the pressure of formation (Table 4; Fig. 12). Stratigraphic considerations indicate that the thickness of the overlying rock pile probably did not exceed 6 km, i.e., a pressure of 1.6 kilobars under lithostatic conditions with a rock density of 2.7 g/cm³, and 0.6 kilobars under hydrostatic conditions. The pressures indicated by the chlorite geothermometer of Cathelineau and Nieva

(\[ \delta^{34}S \% (CDT) \])

Fig. 11. Sulfur isotopic composition of galena and barite from the three ore-types at Las Cañas, and of magmatic rocks from the Las Cañas area. The sulfur isotope range of barites in the Chañarcillo Group (Spiró and Puig, 1988, Lieben et al., 1996), and Lower Cretaceous seawater \( \delta^{34}S \) range (Claypool et al., 1980) are plotted for comparison.
Table 4. Application of chlorite geothermometers to the chlorite analyses from Las Cañas

| Table 4. Application of chlorite geothermometers to the chlorite analyses from Las Cañas |
| Geothermometry — Cathelineau and Nieva (1985) |
| T (°C) | P (kbars) | Depth, P litho (km) | Depth, P hydro (km) |
| Mean vein (n=11) | 327±16 | 3.2 to 5 (±0.3) | 12.1 to 18.9 | 32.6 to 51.0 |
| Mean tuff (n=11) | 248±32 | 2.8 to 3.8 (±0.7) | 10.6 to 14.3 | 28.5 to 38.7 |

| Geothermometry — Kranidiotis and MacLean (1987) |
| Mean vein (n=11) | 207±6 | 0.9 to 2.3 (±0.1) | 3.4 to 8.7 | 9.2 to 23.4 |
| Mean tuff (n=11) | 153±10 | 0.7 to 1.6 (±0.2) | 2.6 to 6.0 | 7.1 to 16.3 |

To the exception of chlorite analyses with Na₂O+K₂O+CaO > 0.5 wt%.

(1985) would be unrealistically high (Table 4). Those given by the chlorite geothermometer of Kranidiotis and MacLean (1987) may give a more realistic pressure estimate, under conditions close to lithostatic (Table 4). The calculations show that, with the restriction mentioned above, the higher homogenization temperatures of the type I fluid inclusions in veins should reflect an increase in temperature (arrow 1, Fig. 12) of the fluids rather than a pressure decrease (arrow 2, Fig. 12). The highly saline type II vein fluid inclusions suggest that this event was followed by an additional pulse of mineralization.

Source of Metals and Polyphase Emplacement

Galena samples from stratobound base metal deposits within the Lower Cretaceous magmatic arc and back-arc basin of northern and central Chile have a homogeneous lead isotopic composition, with low radiogenic ratios compared to polymetallic deposits of the central Andes that occur in other formations or paleotectonic setting (Puig, 1988; Fontboté et al., 1990). Plotted on a $^{207}$Pb/$^{204}$Pb vs $^{206}$Pb/$^{204}$Pb diagram, galena from this group extends along and partly below the orogenic growth curve within the field of modern primitive arcs (Zartman and Doe, 1981; Fig. 10). Regional lead isotope studies support the concept that lead in these deposits was derived from the Lower Cretaceous magmatic host rock sequence (Puig, 1988; Fontboté et al., 1990), which is characterized by a relatively primitive geochemical signature (McNutt et al., 1975; Berg et al., 1983; Åberg et al., 1984). A few lead isotope data from Mid- to Upper Cretaceous intrusions are generally more radiogenic relative to the field of the Lower Cretaceous stratobound ore deposits (McNutt et al., 1979; Marschik et al., 1997), suggesting that they cannot represent the only source of lead for the ores. Paleozoic and Triassic-Liassic basement rocks are not likely an important lead source, because they would yield more radiogenic lead than that in the galenas from the Las Cañas ores. Similarly, $^{87}$Sr/$^{86}$Sr ratios for barite from Las Cañas (0.7050 to 0.7055), are lower than for the host limestone (>0.7064), and therefore consistent with derivation of ore-associated strontium from the magmatic host rock sequence, with only a limited influence of seawater (Lieben et al., 1996).

The lead isotopic ratios for magmatic rocks support the hypothesis that ore lead was leached from the underlying volcanic pile, and from volcaniclastic sandstones and lavas intercalated within the Chañarcillo Group, rather than from the granodiorite or dacite dikes (Fig. 10). A lead isotope composition for one leachate of the dacite that is similar to galena compositions suggests that this sample was contaminated by the mineralizing fluids. Similarly, the high anomalous lead and zinc contents found in certain sedimentary and volcanic rocks of the Las Cañas sequence, particularly in the upper member of the Nantoco Formation (Cisternas, 1986), suggests that these elements were added to these rocks by the hydrothermal ore-forming fluids. The high mobility of lead and zinc is in contrast to copper which is characterized by the absence of anomalous values outside the orebodies. The absence of copper could be due to a relatively high pH of the fluid controlled by the abundant carbonate rocks in the leached sequence, and the low solubility of copper under these conditions (Reed, 1997).

Fig. 12. Isochores for fluid inclusions in the main tuff-hosted mineralization, and for type I and type II vein fluid inclusions, calculated according to the equation of Zhang and Frantz (1987), using the program MacFlinCor (Brown and Hagemann, 1995). Possible P-T path (1) T increase, (2) P decrease, and (3) a combination of these two mechanisms.
The distinct paragenesis and alteration assemblage of Pb-Zn veins at Las Cañas suggests that they represent a different metallogenic event with respect to the stratabound Pb-Zn-Ba ores. Therefore, it is unlikely that the veins could have been the feeders for the stratabound orebodies, as suggested previously (Lieben et al., 1996). The slight difference in lead isotope data of galena from the two ore types is consistent with such an interpretation. Two scenarios can be envisaged. In the case of contemporaneity between the two ore types, the different isotopic compositions may indicate that lead is derived from two different reservoirs, with lead in the veins coming from a more radiogenic source, such as magmatic rocks with an upper crustal affinity. However, such a scenario would imply that there is little to no interaction between both hydrothermal systems, which would be unlikely considering the tight spatial association of both ore types. An alternate and more likely scenario is that the veins are younger than the stratabound ore with lead possibly derived from the same reservoir. In the latter case, the difference in lead isotopic composition would correspond to an age difference of 25 Ma between the two mineralizing events, using a mean $\mu$ value of 10. Such an age difference is compatible with the regional geological setting of the ore occurrences. Some lead may have been remobilized from the older stratabound mineralization during the second veiningiferous hydrothermal event. Admittedly, the data set is small and the difference in lead isotopic compositions may be interpreted solely in terms of analytical dispersion if considered on their own. However, combined with the distinct mineralogical assemblages and the fluid inclusion data of the two ore types, we consider that the difference in lead isotope compositions likely reflects a time gap between two distinct and unrelated mineralization events.

### Source of Sulfur and fO$_2$-pH Conditions

In contrast to the homogeneous lead isotopic composition, the sulfur isotopic composition of stratabound base metal deposits in the Lower Cretaceous magmatic arc and back-arc basin of northern and central Chile shows a wide range, apparently related to the nature of the host rocks (Sprio and Puig, 1988; Munizaga and Zentilli, 1994; Lieben et al., 1996).

At Las Cañas, the stratabound tuff-hosted orebody and silica-barite lens, which belong probably to the same hydrothermal event as suggested by their similar lead isotope signature, display different $\delta^{34}$S values. For both ore types, the temperatures given by the $\delta^{34}$S values of barite-galena pairs are clearly higher than those given by fluid inclusion data and chlorite geothermometry, and indicate that the minerals were not in isotopic equilibrium during precipitation. Therefore, an estimate of sulfur source is based on the derivation of reduced and oxidized sulfur species from different reservoirs, or, alternatively, on the assumption that only a partial isotopic equilibrium has been reached between the sulfur species (Zheng, 1991; Ohmoto and Goldhaber, 1997).

Different sulfur isotopic compositions of the tuff-hosted mineralization and silica-barite lens may reflect stratigraphically distinct aquifers in which the hydrothermal fluids circulated. In the higher stratigraphic level, sulfur in the silica-barite lens probably originated from a Lower Cretaceous marine sulfur reservoir with $\delta^{34}$S value near 16‰ (Fig. 11), represented by evaporites, or an $\text{SO}_4$-bearing fluid trapped in the algal-laminated limestones of the upper member of the Nantoco Formation (Cisternas and Díaz, 1990; Lieben et al., 1996). The $\delta^{34}$S values of galenas may be explained by the thermochemical reduction of this sulfate, or by a small amount of organically bound sulfur, which could provide sulfur about 15% lighter than the associated sulfate (Thode and Monster, 1965; Kesler et al., 1994). In addition, sulfur in galena may also have been derived from the basic magmatic rocks.

In the case of negative $\delta^{34}$S values for barites in the tuff-hosted mineralization, a contamination of barite sulfur by sulfide sulfur during the analysis can be reasonably excluded, because there are no optically detectable sulfide inclusions in the barite. The wide range of $\delta^{34}$S values for galena and barite in this ore-type may indicate an involvement of bacteriogenic sulfur, together with sulfur derived from magmatic rocks and from the marine sulfate reservoir (Sprio and Puig, 1988; Munizaga and Zentilli, 1994). Alter-

---

**Fig. 13.** pH-fO$_2$ diagram showing the probable depositional environments of the tuff-hosted and vein-type mineralization at Las Cañas as deduced from the mineral associations and from the sulfur isotopic composition of galena and barite, assuming a partial equilibrium fractionation factor between the two minerals (after Ohmoto, 1972). Boundaries between sulfur species and Fe-minerals at 150°C and 0.01 m S (equilibrium constants calculated with SUPCRT95).
natively, such a wide range might be accounted for by a single sulfur source, assuming a partial isotopic equilibrium between the sulfur species and a variation in the oxidation state of the fluid (Ohmoto, 1972). The $\delta^{34}S$ values of galena around -30‰ and of barite between -8‰ and 0‰ could be associated with a fluid with a high dissolved sulfate/sulfide ratio, and higher values (-12‰ gn, +12‰ bar) with a fluid with a lower sulfate/sulfide ratio (Fig. 13). A high oxidation state of the fluid that precipitated some of the galena is indicated by hematite rims around galena crystals (Fig. 5g). A strong effect of the redox conditions on the sulfur isotope composition of the fluid might have been facilitated by a relatively low sulfur content of the fluid for this ore-type.

In the case of the tuff-hosted mineralization and different sulfur sources, it is not possible to define these sources precisely. In the hypothesis of a single source of sulfur, the $\delta^{34}S$ value of the fluid cannot be accounted for solely by the analyzed magmatic rocks from the Las Cañas area (Fig. 11). Degassing of SO$_2$ under oxidizing conditions might have produced magmatic rocks enriched in $^{34}$S and a fluid depleted in $^{33}$S (Sakai et al., 1982). Alternatively, the leaching may have involved sedimentary sulfides with lower $\delta^{34}S$ values.

The homogeneous $\delta^{34}S$ value around -12‰ of the vein galenas (Fig. 11) sampled in different parts of the vein system, suggests the absence of significant temperature, redox and pH variations in the ore-forming fluids during the vein stage mineralization. The sulfur for this ore-type may have come from a similar mixed magmatic and sedimentary source, or from recycling of sulfur from the stratabound ore.

Implications for Ore-forming Mechanisms

The fluid inclusion and isotopic data allow us to place constraints on possible ore-forming mechanisms at the Las Cañas ore occurrences. The tuff-hosted Pb-Zn-Ba mineralization and silica-barite lens were likely formed by saline, near neutral fluids which have leached lead and zinc from the volcanic and volcanioclastic rocks. Different characteristics of these two types of stratabound occurrences suggest different ore-forming processes in relation to the different aquifers which carry the mineralization. At the higher stratigraphic level, mixing of the metal-bearing fluid with a fluid of different salinity carrying marine sulfur is the most likely ore-forming mechanism, and accounts for the precipitation of significant amounts of barite and for the large spread in salinity recorded by the fluid inclusions. However, the data cannot exclude a minor contribution of sulfur from the magmatic rocks.

Isotopically light sulfur isotope values for galena and barite in the tuff-hosted mineralization can be explained by sulfur contributed from different sources including bacteriogenic sulfur, or by redox processes affecting a small amount of sulfur in the fluid from a single sulfur source. Precipitation of this ore-type was therefore possibly controlled by a reduction process, such as that proposed for several Andean copper deposits (Flint, 1986; Lortie and Clark, 1987; Munizaga et al., 1994), and/or, considering the metal solubility constraints in the temperature and pH range of the ore-bearing fluid (Anderson and Macqueen, 1982), by mixing with a second sulfur-bearing fluid. Local acidification, indicated by sericitization of K-feldspar cement and sericite cements intergrown with galena, can be accounted for by the acid produced during intense sulfide precipitation (Anderson and Macqueen, 1982).

The geochemical data support the interpretation that the Pb-Zn veins represent a different metallogenetic event. This event may be broadly contemporaneous with the stratabound ore-forming event, but with a distinct input of metals by a hotter, more acid and dilute fluid, or by formation several million years later from fluids with a similar lead and sulfur source, and possibly of a small fraction remobilized from the stratabound mineralization. A second hydrothermal pulse in veins, which carry minor copper mineralization, may be associated with significantly more saline fluids.

Conclusions

Among the northern Chile base metal deposits, largely dominated by Cu, Las Cañas is unusual because it contains low-temperature lead-zinc ores with only subordinate copper content. Various Pb-Zn ore-types exposed in the Las Cañas mine, which in part are recognized elsewhere in the carbonate rocks of the Lower Cretaceous Chañarcillo Group (Lieben et al., 1996), belong to at least two mineralizing events, as indicated by the distinct paragenesis, fluid inclinations, and lead and sulfur isotopic composition of galena from stratabound Pb-Zn-Ba mineralization and Pb-Zn veins. Though it cannot be totally excluded that these events were contemporaneous, a likely scenario involves the circulation of near neutral to slightly acid, saline fluids that formed the stratabound mineralization, followed by pulses of hotter, more acid and dilute fluids (type I) and highly saline fluids (type II) that circulated in post-mineralization faults. The lead and strontium isotope data support the hypothesis that the metals were derived from the volcano-sedimentary host rock sequence. The sulfur isotope systematics indicate differences in genetic processes and sources for the ore-types, which might be related to the different nature of their ultimate aquifers. Redox processes were likely involved in the formation of the main tuff-hosted orebody. Mixing of a metal-bearing fluid with sulfur derived from a Lower Cretaceous marine sulfate source is the most likely mechanism to form the silica-barite lens, and may have operated regionally.

Acknowledgments

The authors acknowledge W. Goodfellow and D.F. Sangster for their critical review of the manuscript. Support for this research was provided by a Swiss National Foundation grant 20-47.260.96. The three sulfur isotope analyses at the University of Lausanne were made by L. Linares (lab. J. Explor. Mining Geol., Vol. 8, Nos. 1 and 2, 1999.
Hunzicker, J. Spangenberg). XRF analyses were made by F. Capponi at the University of Lausanne (lab. H.-R. Pfeiffer).

References


LEVI, B., AGUIRRE, L. and NYSTRÖM, J.O., 1982. Metamorphic gradients in burial metamorphosed vesicular lavas: Comparison of basalt and splelite in Cretaceous basic flows from central Chile. Contributions to Mineralogy and Petrology, 80, p. 49-58.


NOVA, A., 1997. Estudio petroquímico de las volcanitas neocomianas en el sector Quebrada Las Cañas, Región de Atacama, Chile. Memoria de título, Universidad de Concepción, Chile.


