

Fluid Evolution in the Patricia Zn-Pb-Ag vein deposit (Paguanta, NE Chile): fluid inclusion assemblages and laser ablation ICP-MS evidence.

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Abstract. The Patricia Zn-Pb-Ag ore deposit represents the first known example of economic mineralization in the northern part of the Andean late Eocene – Oligocene metallogenic belt in Chile. The hydrothermal evolution has been deduced based on detailed mineralogy, fluid inclusion petrography, microthermometry and laser ablation ICP-MS analysis. We present microthermometric data for fluid inclusion assemblages (FIAs) in co-genetic ore and gangue minerals through the different mineralization stages. In the pre-ore stage, early quartz-hosted FIAs indicate high salinity values (22 to 6 wt.% NaCl) with homogenization temperatures from 270 to 205°C. During the base metal and silver stage, a drop in temperature from 250 to 140 °C and salinity less than 10 wt.% NaCl is related to the main ore precipitation. Primary FIAs in the post-ore stage indicate temperature up to 245°C and low salinity (4 to 3 wt.% NaCl). The LA-ICP-MS analyses of fluid inclusions show that the metal content in the base metal stage is significantly higher than in the pre-ore and post-ore stages. This study documents the existence of different fluid pulses characterized by cooling and low salinity conditions favourable for the main ore deposition during the base metal and silver stage. The ore mineralogy and the associated hydrothermal alteration define the Patricia ore as an intermediate-sulfidation epithermal deposit with low-sulfidation events.

Keywords. microthermometry, paragenesis, intermediate sulfidation, epithermal.

1 Introduction

The Patricia ore deposit represents the only known example of an economic Zn-Pb-Ag mineralization in northern Chile. It is located in the Late Eocene to Oligocene metallogenic belt in the Tarapacá Province, 1st Region, Chile, at latitude 19°81'S and longitude 69°06'W, 150 km northeast of Iquique and 30 km from the international border with Bolivia. The host rocks consist mainly of a succession of subaerial, andesitic volcanic rocks, including breccias, pyroclasts, agglomerates, tuffs, lapilli and lavas. These rocks are gently folded and commonly affected by pervasive propylitic alteration.

The Patricia ore deposit consists of a well-developed mineralized stockwork along subvertical dipping and E-W to ENE-WSW oriented mineralized veins that range from centimetres to few metres thick.

Three stages of mineralization are defined: (1) pre-ore stage, (2) base-metal and silver stage and (3) post-ore stage. The pre-ore stage is characterized by quartz, pyrite and arsenopyrite. The base-metal and silver stage is characterized by sphalerite (6 to 15 mol.% FeS), galena and Ag-bearing minerals (Chinchilla et al. 2013), chalcopyrite and pyrrhotite. The post-ore stage is defined by late quartz, Mn-carbonates and minor sulfides (arsenopyrite, sphalerite, pyrite and galena).

Two main types of hydrothermal alteration are observed associated with the mineralized veins within the host rock: chloritic (chlorite ± pyrite and arsenopyrite ± apatite ± titanium oxides) and sericitic/phyllitic (quartz + sericite/illite ± pyrite ± Mn-carbonates) alteration. Besides that, chlorite and illite also occurs in association with the base-metal ores within mineralized veins. Chlorite is the most common phase and illite occurs as small crystals intergrown with chlorite.

In this contribution we present new microthermometric and LA-ICP-MS fluid inclusion data of the three stages of mineralization in the Patricia ore deposit. These results allow characterizing the evolution of the hydrothermal fluids involved in the formation of the Zn-Pb-Ag mineralization.

2 Fluid inclusion study

2.1 Microthermometric analysis

Fluid Inclusion Assemblages (FIAs) (i.e a group of inclusions trapped at the same time (Diamond, 1990; Bodnar, 2003) were identified based on petrographic relations observed in polished thick sections. Microthermometric measurements of FIAs of the three stages of mineralization were obtained using a Linkam heating-freezing stage (THMS600) mounted on an Olympus microscope. The studied fluid inclusions are hosted by quartz (Qz₁ and Qz₂ in stages 1 and 3) and by sphalerite (in stage 2), both within mineralized veins. Fluid inclusions were identified in stage 2A in sphalerite, which is commonly characterized by zoned sphalerite without any sulfide inclusion, and in stage 2B, characterized by zoned sphalerite containing trace amounts of chalcopyrite, pyrrhotite or Ag-bearing minerals. All fluid inclusions in the Patricia deposit are

liquid-rich at room temperature and do not contain recognizable CO₂.

1. Pre-ore stage. Fluid inclusions occur in comb-type quartz grains located on the outer bands of symmetric mineralized veins with base-metal sulfides in the center. Primary FIAs along growth zones in quartz are scarce whereas secondary trails of FIAs are common and inclusions are smaller than those in the primary FIAs. Primary FIAs have salinities ranging from 22 to 6 wt.% NaCl and homogenization temperatures (Th) ranging from 240 to 205°C. The salinity of the secondary FIAs range from 10 to 1 wt.% NaCl and Th from 270 to 212°C (Fig. 1). Both primary and secondary FIAs contain trapped crystals of illite (Fig. 2A) identified by Raman spectroscopy (e.g. Moncada and Bodnar, 2012).

2. Base-metal and silver stage. FIAs were studied in sphalerite (Sp1 and Sp2) within the two substages 2A and 2B, respectively. FIAs are common in Sp₁, typically showing elongated fluid inclusions along growth bands of zoned sphalerite (Fig. 2B). Primary fluid inclusions are usually larger than secondary inclusions which commonly form trails cross-cutting growth bands within the sphalerite (Sp₁). Primary FIAs have salinities of 9 to 1 wt.% NaCl and Th ranging from 251 to 172°C. Secondary inclusions have salinities ranging from 4 to 3 wt.% NaCl and Th ranging from 247 to 195°C (Fig. 1). FIAs in Sp₂ were more difficult to study than those in Sp₁ because Sp₂ is more Fe-rich and is dark making it difficult to identify fluid inclusions. Fluid inclusions observed are commonly associated with solid inclusions of minor sulfides such as chalcopyrite, pyrrotite and Ag-bearing

minerals (Fig. 2C). In the stage 2B, salinity ranges from 10 to 2 wt.% NaCl and Th from 182 to 138°C (Fig. 1).

3. Post-ore stage. FIAs were studied in prismatic grains of quartz (Qz₂). Primary fluid inclusions are larger but less common than secondary inclusions. The salinities of primary fluid inclusions are ~ 3 wt.% NaCl and Th ranges from 245 to 175°C. Secondary fluid inclusions show slightly lower salinity values, ~ 2.4 wt.% NaCl and Th ranging from 242 to 227°C (Fig. 1). As in Qz₁, these FIAs also have trapped illite crystals (Fig. 2D).

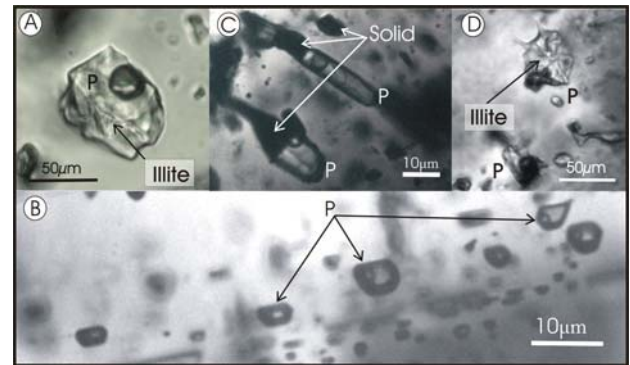


Figure 2. Photomicrographs of FIAs observed in the three main stages of mineralization. Primary fluid inclusion in (A) quartz in pre-ore stage, (B) in sphalerite (Sp₁) distributed in parallel growth bands, (C) in sphalerite (Sp₂) with the presence of solids associated to the fluid inclusions, (D) in post-ore stage. Note the presence of a fibrous hydrous phyllosilicate, interpreted as illite, trapped in the fluid inclusion (A–D).

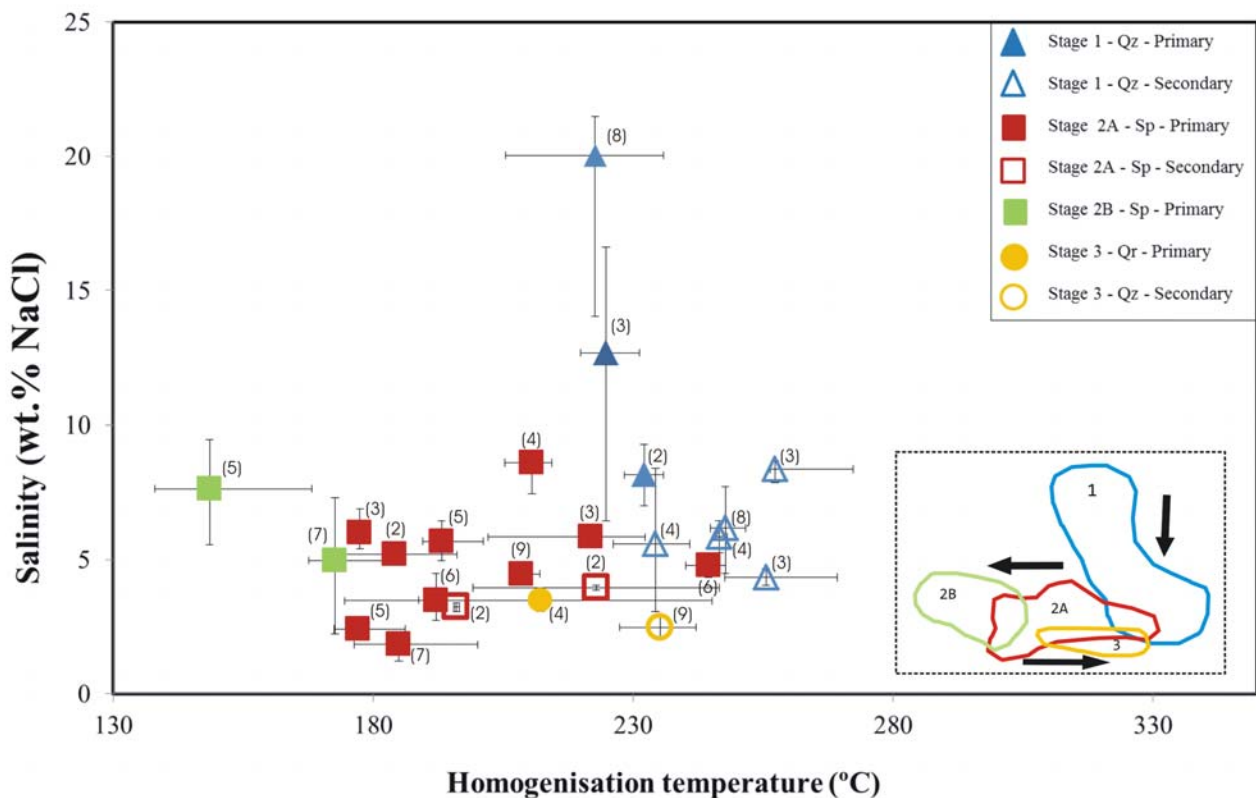


Figure 1. Evolution of individual fluid inclusion assemblages (FIAs) observed in the Patricia ore deposit. Each data point corresponds to the average homogenization temperature and salinity for the fluid inclusion assemblage and the error bars represent the minimum and the maximum of values for each FIA. A possible evolution path of the mineralizing fluids in the deposit is shown in the lower right corner. (n) Number of fluid inclusions in each FIAs.

4 Laser Ablation-ICP-MS analysis

Major and trace element concentrations of the mineralizing fluids responsible for mineral deposition in the three stages were determined by quantitative microanalysis of individual fluid inclusions in quartz and sphalerite using a 193 nm GeoLasPro Excimer Laser Ablation system coupled to an Agilent 7500ce inductively coupled plasma mass spectrometer. Fluid inclusions were ablated with a laser beam diameter (from 10 μ m to 60 μ m) selected such that the inclusion was wholly encompassed within the ablation pit. A NIST610 glass standard was analyzed before and after each sample for calibration. Data processing was carried out using the AMS software (Mutchler et al, 2008).

For pre-ore stage and post-ore stage, quartz was a good mineral host for the study because quartz typically contains very low concentrations of elements other than Si and O, so the detection of Fe, Zn, Sb or Pb is interpreted to represent metals in the fluid and not the host. In the base-metal and silver stage, sphalerite was the host mineral and it does not contain significant concentrations of Ag, Sb or Pb so the obtained values for these elements within the FI are interpreted to represent the fluid whereas the contents of Zn, Fe, Cu and Cd likely include contributions from the host.

Fluid inclusions in Qz₁ show the following metal concentration range (values in ppm): 0.7 – 6 Fe, 0.5 – 3 Zn, 0.7 - 6 Pb and 1 – 5 Sb. Fluid inclusions of Sp₁ and Sp₂ are compositionally similar and have higher metal contents than Qz₁: 0.5 - 20 Ag, 0.5 - 9 Sb and 0.6 - 35 Pb. In the post-ore stage, FI in Qz₂ have 0.8- 4 Fe, 0.6 – 2 Zn and 0.6 – 0.9 Pb. Arsenic is below detection in all the stages.

5 Discussion and conclusions

The evolution of the hydrothermal fluids at Patricia ore deposit is shown in figure 1. The pre-ore stage is characterized by saline fluids, close to saturation in NaCl, with a minimum circulation temperature of 205°C. In contrast, the fluids related to stages 2 and 3 show lower salinities, from 10 to 1 wt.% NaCl. This may suggest a possible fluid dilution, due to mixing with meteoric waters (e.g. Einaudi et al, 2003; Sillitoe and Hedenquist, 2003; Simmons et al, 2005). The stage 2 gave rise to the main base metal sulfide and Ag mineralization. This stage is characterized by a gradual cooling from 250 to 140°C at constant low salinity. Ag-bearing minerals mainly occur at the end of this stage at temperatures ranging from 180 to 140°C (Fig. 1). LA-ICP-MS analysis of the fluid inclusions show that Pb, Ag and Sb contents increase from stage 1 to 2, suggesting that these elements are associated with the low salinity fluid. During stage 2, Ag, Sb and Pb contents increase from the sub-stage 2A to 2B, thus favouring the precipitation of Ag-bearing minerals during the sub-stage 2B. The post-ore stage has minor amounts of sulfides and the fluid inclusions have homogenization temperatures ranging from 245 to 175°C, higher than those observed for the sub-stage 2B. This implies the existence of different fracturing and circulation fluid pulses as evidenced by textures in the

mineralized veins.

The presence of illite in the mineralized veins and within fluid inclusions of stages 1 and 3 indicates that the hydrothermal processes developed under slightly acidic to neutral conditions, as illite forms at pH from 5.8 to 6.3 (Romberger, 1991) and temperatures from 220 to 300 °C (Henley and Ellis, 1983; Reyes, 1990).

Mineralogical and geochemical evidence indicate variations in the sulfidation state of the deposit. During the early stage 1, the common occurrence of arsenopyrite in the quartz-pyrite assemblage suggests likely conditions of low-sulfidation (LS) (e.g. Baumgartner et al. 2008) as in intermediate- sulfidation conditions (IS) arsenopyrite is uncommon (e.g. Einaudi et al. 2003; Hedenquist et al. 2000; Sillitoe and Hedenquist 2003). During the base-metal and silver stage 2, the mineralogy and geochemistry of the sulfide assemblages are more similar to an IS event and similar to other base-metal deposits elsewhere (e.g. Bendezu and Fonboté 2009; Camprubí and Albinson 2006; Carillo-Rosúa et al. 2008; Einaudi et al. 2003; Hedenquist et al. 2000; Sillitoe and Hedenquist 2003; Simmons et al. 2005). The sphalerite composition ranges from 6 to 15 mol.% FeS which is typical for IS systems where the molar proportion of FeS ranges from <1 to 10 %, locally up to 20 % (Einaudi et al. 2003; Hedenquist et al 2000; Simmons et al 2005). Furthermore, the hydrothermal alteration assemblage illite \pm chlorite \pm quartz present in Patricia is typical of IS deposits (Einaudi et al. 2003; Simmons et al. 2005). Finally, in the post-ore stage, the presence of mineralogy similar to the pre-ore stage (quartz and sulfide as pyrite and arsenopyrite) suggests a return to LS conditions.

The fluid inclusion observations in the Patricia ore deposit are also consistent with the existence of different sulfidation states for each mineralization stage. The base-metal stage is characterized by moderate salinity values up to 10 wt.% and a gradual cooling from 250 to less than 140°C whereas the fluids in pre-ore and post- ore stage are characterized by temperature from 200 to 250°C and salinity ranging from 22 wt.% NaCl to less than 4 wt.% NaCl, respectively.

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