

A mineralogical and fluid inclusion study of the Patricia Zn-Pb-Ag Deposit (Paguanta, NE Chile)

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Abstract. The Patricia Zn-Pb-Ag ore deposit is located within the Paguanta mining project, situated at the northern end of the Andean Oligocene Porphyry Copper Belt of Chile. The sulfide mineralization occurs as W-E oriented veins hosted in volcanic rocks, mainly andesite (pyroclastic, ash and lavas), of Upper Cretaceous to Middle Tertiary age. The ore mineralogy comprises pyrite, sphalerite (5.5 -10.89 wt % Fe), arsenopyrite, galena, chalcopyrite and Ag-bearing sulfosalts. These Ag-bearing sulfosalts are typically phases of the series freibergite - argentotennantite, polybasite and stephanite and minor argentite, pyrrargirite and diaphorite. All these phases are commonly associated with chalcopyrite, galena, sphalerite and pyrite and, to a lesser extent, quartz. Alteration minerals are dominated by chlorite, illite and kaolinite. The primary fluid inclusions indicate fluids with moderate salinity (11 - 17.8 wt % eq. NaCl) and temperatures between 180 °C and 200 °C. This study suggests that the Patricia deposit represents an example of epithermal mineralization of intermediate sulfidation state.

Keywords Ag-bearing sulfosalts, Zn-Pb-Ag epithermal deposit, fluid inclusions, Patricia, Paguanta

1 Introduction

The Patricia Zn-Pb-Ag ore deposit represents economic mineralization (4.53 Mt with average grades of 3.7 % Zn, 1.3 % Pb, 83 g/t Ag and 0.2 g/t Au, www.herenciaresources.com) discovered by Herencia Resources Plc in 2006 during exploration over mine workings dating back to the nineteenth century. The ore mineralization forms part of the Paguanta mining project that also includes other two prospects called, La Rosa and Doris. The Paguanta project is located in the Tarapacá region ~ 150 km NE from Iquique and ~ 30 km from Colchane on the border with Bolivia (Fig. 1). It is located at the boundary between the Precordillera and Western Cordillera of the Andes (UTM coordinates - (WGS84): 19K 494 300 E - 7809300 S). Geologically, the project is at the northern end of the Andean Oligocene Porphyry Belt of Chile that hosts 9 of the 16 largest porphyry Cu-Mo deposits associated with the Circum-Pacific Belt (Teniente, La Escondida, Chuquicamata, El Salvador) (Camus and Dilles, 2001; Behn et al., 2001). The porphyry belt is structurally controlled by the N-S-oriented Domeyko fault system characterized by sinistral transpressive kinematics and



Figure 1. Schematic map showing the position of Paguanta in the Oligocene Porphyry Copper belt of Chile. Modified from Camus (2003).

important extensional areas (pull-apart basins) (Maksaev et al., 2007). The Paguanta project consists of three main prospects:

- Patricia: located at the south part of the project and constitutes the most explored and economically interesting resource. It is a hydrothermal Zn-Pb-Ag sulfide mineralization infilling veins with E-W orientation.
- La Rosa: comprises a 3 km² area located to NNW of Patricia with intense argillic alteration in a pull apart basin. It hosts disseminations and veinlets of Cu-oxides, pyrite and Fe oxy-hydroxides.
- Doris: this prospect located NNE of Patricia is characterized by the presence of fractures filled with secondary copper minerals (*i.e.*, chrysocolla and atacamite).

In this contribution, we present a preliminary mineralogical study of the Patricia Zn-Pb-Ag ore

deposit, including the first fluid inclusion data.

2 The Patricia Zn–Pb–Ag ore deposit

The lithologies forming the surroundings in Patricia area comprise sequences of intermediate and acidic volcanic rocks, mainly andesites (pyroclastics, ash and lavas) of Upper Cretaceous to Middle Tertiary age (Sillitoe, 1991). These rocks are unconformably overlain by ignimbrites of Miocene to Quaternary age (Bouzari and Clark, 2002). Regionally, the bedrock is formed by volcanic and sedimentary rocks of Paleozoic to Mesozoic age with strong folding and fracturing (Camus and Dilles, 2001).

The ore deposit comprises four main vein systems, generally oriented E-W to ENE-WSW, and called from N to S: Campamento, Central, Carlos and Catedral. The term vein refers to an area with intense mineralization, in the form of well-developed stockwork structures (Fig. 2). These veins range in thickness between 1 and 100m at Catedral and between 1 and 15 m at Campamento, Central and Carlos. They typically thin out towards both east and west from a thicker central zone where the old workings are located. Ongoing exploration has recently identified other new veins to the south of the above, which may eventually lead to enlarge the Patricia total resources.



Figure 2. Typical well-developed stockwork (Catedral vein system at Patricia area).

The veins are hosted by volcanic and volcanoclastic andesitic breccias with variable-sized clasts. These rocks show regional propylitic (chlorite) alteration superimposed by illite and kaolinite alteration in the mineralized area making difficult recognizing the original rock texture. Silicification and disseminations of arsenopyrite and pyrite in the host rocks are locally present. The ore minerals in the veins comprise in order of abundance, pyrite, sphalerite (5.5 - 10.89 wt % Fe, 9.8-19 % mol FeS and 0.52 wt % Cd), galena, arsenopyrite, chalcopyrite and Ag-bearing sulfosalts. The veins show a zoned and banded internal structure with pyrite at the edges and sphalerite in the center (Fig. 3). The Ag occurs mostly as Ag-Cu-Sb sulfosalts, in order of abundance: series freibergite - argentotennantite ((Ag, Cu)₁₀(Fe, Zn)₂Sb₄S₁₃) – ((Ag, Cu)₁₀(Fe, Zn)₂As₄S₁₃), polybasite ((Ag, Cu)₁₆(Sb, As)₂S₁₁) and stephanite (Ag₅SbS₄) (Fig. 4). Other minor Ag phases such as

argentite (Ag₂S), pyrargirite (Ag₃SbS₃), and diaphorite (Pb₂Ag₃Sb₃S₈) were also identified. These Ag phases are typically associated with the base-metal sulfides. Freibergite occurs filling voids within sphalerite, chalcopyrite and at the contact between sphalerite and galena (Fig. 4 and 5).



Figure 3. Photograph of drillcore showing a zoned mineralized veinlet cross-cutting the andesitic host rock.

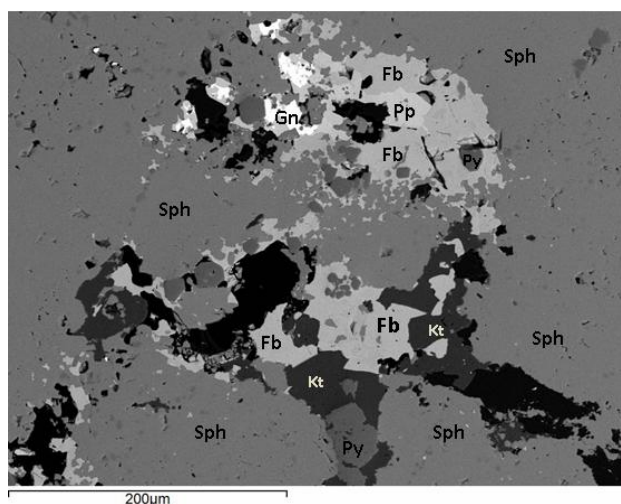


Figure 4. Representative back-scattered electron microprobe image of Ag-bearing sulfosalts. Freibergite (Fb), polybasite (Pp), galena (Gn) and pyrite (Py) filling voids between crystals of sphalerite (Sph). Kutnohorite (Kt) also occurs.

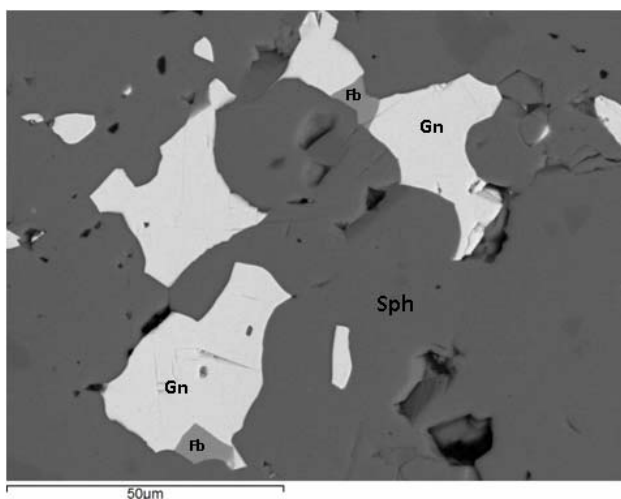


Figure 5. Representative back-scattered electron microprobe image of Ag-bearing sulfosalts. Freibergite (Fb), galena (Gn) and sphalerite (Sph).

Polybasite, stephanite, pyrargirite and argentite are mostly in close association with freibergite. In the case of diaphorite, it commonly occurs filling voids between galena crystals or as inclusions within galena. Some minor Ag-bearing sulfosalts are also identified between

pyrite crystals. The gangue minerals consist of quartz and carbonates identified by XRD as kutnahorite (Ca (Mn, Mg, Fe) (CO₃)₂).

4 Fluid Inclusions

The fluid inclusions study was carried out on samples from a mineralized vein formed by microcrystalline quartz which surrounds a nodule of sulfides grading to zoned prismatic quartz crystals with sizes ranging from 200 µm to 2 mm. The studied primary inclusions are two phase and are distributed from the center to the edges in the growth faces of prismatic quartz. The selected inclusions represent the fluid circulating through fractures when the mineralization precipitated.

During the cooling process, ice + hydrohalite nucleation is observed between -40 °C to -46 °C. Hydrohalite phase was confirmed by performing four cooling-heating cycles between -25 °C and -20 °C. The melting temperature obtained for the hydrohalite was -21.3 °C, which corresponds approximately to the eutectic temperature of NaCl-H₂O system. The ice melting temperature is between -3.4 °C and -14 °C, with a modal value of -13 °C, indicating salinity values between 11% and 17.8% eq. by weight of NaCl. The homogenization temperature ranges between 140 °C and 240 °C. However, 44% of fluid inclusions became homogenized between 180 °C and 200 °C.

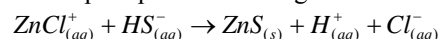
5 Concluding remarks

The alteration halo around mineralized veins is characterized by illite and kaolinite, minerals typically formed by fluids with a pH below 6 (very slightly acidic to slightly acidic). This halo is superimposed upon the regional propylitic alteration whose pH is almost neutral. The presence of carbonates in veins that cut the previous alterations indicates that conditions varied at the end of the process towards neutral-alkaline pH.

The ore paragenesis has a polymetallic character, with pyrite, sphalerite and galena as major sulfides. Silver occurs forming own minerals (freibergite, argentotennantite, polybasite, stephanite), not having identified argentiferous galena. The phases of ~ 25% Ag, corresponding to the series freibergite – argentotennantite, are the most common in the deposit while the Ag-rich phases (~ 70%), corresponding to polybasite, stephanite and pyrargyrite, are less abundant, appearing only in areas with high percentage of argentiferous minerals.

The fluid inclusion data indicate that the mineralizing fluid had salinity between 11% and 17.8% eq. by weight of NaCl and a minimum temperature of circulation between 180 °C and 200 °C. Regarding the composition of the fluid, the average salinity for mineralizing fluids of Au-Ag and Pb-Zn-Ag ore deposits is commonly lower than 5 % eq. NaCl and from 10 to 20 % eq. NaCl, respectively (Simmons et al., 2005; Hedenquist and Lowenstern, 1994). Accordingly, the results obtained in this study are typical of Ag polymetallic deposits. Higher salinity of fluids in Pb-Zn-Ag deposits favors metals to be transported as chlorine complexes while in the Au-Ag deposits these precious metals are transported as sulfide

complexes (Hedenquist and Lowenstern, 1994). The sphalerite would precipitate following the reaction:



According to Barton et al. (1977), the substitution of Fe by Zn in the sphalerite is common, resulting in extensive solid solutions whose composition is indicative of the sulfur fugacity of the system. Sphalerite ores commonly contain up to 24% moles of Fe, although there have been reports of up to 56% molar of FeS replacing ZnS (Patrick et al. 1998). The sphalerite crystals analyzed in Patricia exhibit FeS molar contents between 9.8% and 19%, so that the composition would be in the normal range of Fe-Zn replacement. According to the log aS₂ vs. log aO₂ plot (Barton et al., 1977), the sphalerite would precipitate from a fluid with values of log aS₂ ranging from -12 to -12.8 and values of log aO₂ lower than -36.

All these results suggest that the Patricia Pb-Zn-Ag ore deposit probably represents an example of epithermal mineralization of intermediate sulfidation state, with periods of lower sulfidation state during sphalerite deposition (Simmons et al., 2005; Hedenquist and Lowenstern, 1994).

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