Supergene ore modifications of epithermal silver mineralization at Martha Mine, Deseado Massif, Argentina

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Abstract. The Martha underground silver mine is located in the southwestern portion of the Deseado Massif, Santa Cruz province, Argentina. Martha is an intermediate sulphidation epithermal deposit with a complex mineralogy dominated by Ag-As-Sb sulphosalts and Cu-Pb-Zn sulphides. The deposit is characterized by a structurally controlled vein system characterized by a complex history of fracturing and cementation, arranged in nine paragenetic stages that can be grouped into four episodes. Metal ratio vs. depth profile show a shallow 20 m thick oxidation zone dominated by mean Ag/Au ratio of about 800:1. This upper zone is composed an association of kaolinite, plumbogummite, limonites, jarosite, cerussite, chlorargyrite/embolite, native silver, malachite and azurite. Below the oxidized zone, a 30 m thick enrichment zone can be recognized by a sharp increase in the Ag/Au ratio (up to 20,000:1). This zone is composed by a mineral assemblage dominated mainly by argentite/acanthite, pyrargirite, native silver, chalcocite, digenite, covelite, and minor bornite and spionkopite. Below the enrichment zone, the primary hypogene zone is characterized by a progressive reduction in the Ag/Au ratio to values of about 1000:1. These changes are the first mention of a supergene enrichment blanket in the Deseado Massif; this possibility must be considered during exploration, as high grade ore-shoots may be concealed below a lower grade oxidized horizon at surface.

Keywords. Silver enrichment, Epithermal deposit, Jurassic, Deseado Massif, Patagonia.

1. Introduction

Supergene ore modifications, such as oxidation and secondary enrichment, can be a main factor in building up an economic-grade mineral deposit. This is especially true in terms of porphyry systems (e.g. Sillitoe and McKee, 1996; Hartley and Rice, 2005), but can also be an important ore forming process contributing to high grade ore shoots in epithermal deposits (e.g. Gröpper et al., 1991; Milési et al., 1999, Greffié et al., 2002; Chauvet et al., 2006).

The Deseado Massif (Fig. 1) is a 60 000 km^2 geological region located in the southern part of Extra-Andean Patagonia in the central portion of Santa Cruz province. For the past 15 years, this region has produced more than 3 million oz of gold and over 40 million oz of silver from four operational mines (Cerro Vanguardia, Martha, Manantial Espejo and San José; Fig. 1). This gold and silver producing district also has a great potential for expanding its known resources, as there are currently more than 50 prospects undergoing different stages of exploration.

In this work we address the role of supergene ore mobilization in an epithermal environment from the Deseado Massif, analysing the consequences on mineralogy and grade distribution in one of richest silver deposits in Patagonia, with significant implications for future exploration activities in the Deseado Massif and other epithermal districts.

2. Geologial setting

During the Middle to Upper Jurassic (177.8 to 150.6 Ma; Pankhurst et al. 2000), a volcanic mega-event occurred in Patagonia giving rise to the Chon Aike Large Igneous Province (Pankhurst et al., 1998; Pankhurst et al., 2000). In the Deseado Massif, this event is represented by a volcanic suite that was named the Bahía Laura Volcanic Complex (BLVC; Fig. 1) by Guido (2004). Pyroclastic rocks predominate within the BLVC, with subordinate amounts of intercalated lavas of andesitic to rhyolithic composition, and with a calcalkaline, peraluminous and high potassium signature (Pankhurst et al., 1998; Guido, 2004). Intricate stratigraphic relationships characterise this complex, with multiple intercalations of different rock facies (Echeveste et al., 2001; Lopez, 2006; Ruiz, 2012; Wallier, 2009).

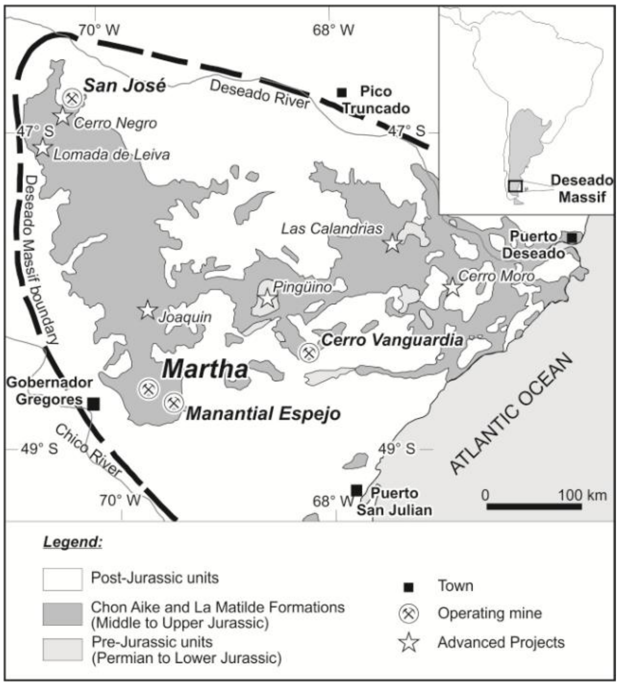

Figure 1. Map of the Deseado Massif showing the location of the study area and other localities mentioned in the text.

The BLVC contains numerous gold and silver epithermal deposits, leading Schalamuk et al. (1999) to define the Deseado Massif as an Au–Ag metallogenic province. The majority of the Au-Ag occurrences are low sulphidation (LS) style (Guido and Schalamuk, 2003; Echavarría et al., 2005; Fernández et al., 2008), but in the past few years intermediate sulphidation and polymetallic deposits also have been reported (Gonzalez Guillot et al., 2004; Guido et al., 2005; Jovic et al., 2010; Páez, 2012). Associated with the epithermal veins, widespread hot spring deposits are present (Guido and Campbell, 2011).

3. Martha Mine epithermal deposit

The Martha underground silver mine is located in the southwestern portion of the Deseado Massif (Fig. 1). The mine is operated by Coeur d'Alene Mines Corporation and has been under production since 2001. It has produced more than 21 million oz of silver (more than 50% of the Deseado Massif's total silver production) and over 28,000 oz of gold, with an average grade of about 3,500 g/t Ag and almost 5 g/t Au (Páez, 2012).

This deposit is characterized by a structurally controlled vein system hosted in Jurassic acid rocks of the BLVC that are locally represented by thick ash flow tuffs with thin intercalations of epiclastic sediments derived from a pyroclastic source (Páez et al. 2010). Mineralized veins can be subdivided into two groups (Páez et al. 2011): master structures that trend N120 (Martha and R4 veins), and tensional structures that trend E-W and coalesce into the master structures (Catalina, Francisca and Belén veins). High grade mineralization (up to 20% Ag eq.) has been encountered in both systems (Páez, 2012).

3.1. Vein paragenesis

Martha is an intermediate sulphidation epithermal deposit with a complex mineralogy dominated by Ag-As-Sb sulphosalts and Cu-Pb-Zn sulphides (Gonzalez Guillot et al., 2004; Gonzalez Guillot et al., 2008; Márquez-Zavalía et al., 2008; Páez, 2012). Veins are characterized by a high Ag/Au ratio of about 800:1 (Páez, 2012).

Mineralized structures at Martha are characterized by a complicated history of fracturing and cementation (Páez et al. 2011), arranged in nine paragenetic stages that can be grouped into four episodes (Páez, 2012). The first episode (E1) is characterized by a barren quartz-adularia vein network with no associated sulphides and is poorly represented within the deposit (Páez, 2012).

The second episode (E2) comprises four stages with a progressively decreasing sulphide content, ranging from a massive sulphide stage to an almost sulphide free stage (Páez, 2012). This episode is responsible for part of the high grade ore and is composed of silver and base metal bearing sulphides and sulphosalts, mostly pyrite, sphalerite, chalcopyrite, galena, silver bearing tetrahedrite (freibergite), native silver, electrum, pyrargirite, miargyrite, polybasite and minor arsenopyrite. Gangue minerals with this episode are adularia and minor quartz with associated illite. This episode has typically a breccia texture; however some crustiform banding may be present locally.

The third episode (E3) is composed of two barren stages characterized by massive adularia and minor quartz (Páez, 2012). This episode is typically massive to brecciated in texture and widespread among all vein structures, in most cases building up to the 95% of the veins.

Finally, the fourth and last episode (E4) is characterized by two late stages that partially remobilized the previously deposited metals, mostly due to re-brecciation followed by partial dissolution and re-precipitation (Páez, 2012). This episode is composed by discontinuous chalcedonic breccias with highly variable sulphide content and a system of thin (1-5 mm) sulphosalt veins that can locally build up a dense network. Ore minerals are composed mostly by pyrargirite, miargirite and native silver with minor chalcopyrite. This episode has a widespread distribution among Martha and R4 veins, but is less important or even absent among the E-W trending veins (Páez, 2012).

4. Supergene ore modifications

The shallowest portions of the Martha Mine vein system was affected by a series of changes that can be related to supergene alteration and secondary enrichment.

4.1. Geochemical changes

To analyze the effects of the supergene alteration on the metal distribution in the mineralized structures, a geochemical database of 3,226 geochemical assays were used in order to analyze the vertical distribution of metal ratios and Au, Ag, Cu, Pb and Zn contents.

The metal ratio (Ag/Au) vs. depth profile shows a shallow 20 m thick oxidation zone (Fig. 2) dominated by a maximum Ag/Au value of about 2,000:1 (with a mean value of 800:1); this shallow portion of the deposit is also characterized by higher Pb contents along with lower Cu and Zn grades, respect to the primary zone.

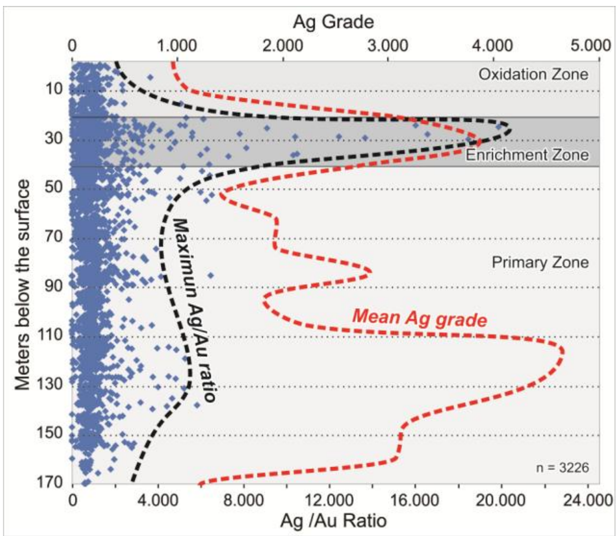

Figure 2. Vertical extent of the oxidation, enrichment and primary zones of Martha Mine as indicated by the changes in the Ag/Au ratio.

Below the oxidized zone, a 20-30 m thick enrichment zone can be recognized by a sharp increase in the maximum value of the Ag/Au ratio (up to 20,000:1, Fig. 2); this change is followed by an increase in Cu and Zn grades, and a progressive reduction in Pb contents.

Downwards, the primary hypogene zone (Fig. 2) is defined by a progressive reduction in the Ag/Au ratio to values as high as 4,500:1 (with a mean of 1,000:1), Cu and Zn values are also lower but they remain higher than in the oxidized zone; finally, Pb values reach the lowest values in the profile.

4.2. Mineralogical changes in the vein paragenesis

Geochemical changes are accompanied by a series of mineralogical modifications in the upper parts of the vein system (Páez, 2012). The newly formed minerals usually overprint the original textures, obscuring the paragenetic scheme discussed earlier.

The ore mineral association of the oxidized zone is characterized by native silver (*Ag*°), limonites ($FeO(OH)\cdot nH_2O$), jarosite ($KFe_3(SO_4)_2(OH)_6$), plumbojarosite ($PbFe_6(SO_4)_4(OH)_{12}$), chlorargyrite-embolite (*Ag(Br,Cl)*), boleite ($KPb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$), cerussite ($PbCO_3$), malachite ($Cu_2(CO_3)(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$). This assemblage is recognized usually as thin veinlets and/or as cavity infill (Fig. 3a).

The enrichment zone is typically composed of argentite/acanthite (Ag_2S), pyrargyrite (Ag_3SbS_3), native silver (*Ag*°), chalcocite (Cu_2S), digenite (Cu_9S_5), covellite (*CuS*), and minor bornite (Cu_5FeS_4) and spionkopite ($Cu_{1,4}S$). These minerals can be identified partially replacing the primary sulphides (Fig. 3b), forming thin veinlets, or also as small cavity infill.

Finally, the enrichment zone grades downward into the primary mineral association, composed of Ag-As-Sb sulphosalts and Cu-Pb-Zn sulphides (Páez, 2012).

4.3. Mineralogical changes in the host rocks.

During hydrothermal circulation, the pyroclastic host rocks were altered to a narrow halo of adularia + illite ± smectite around the veins (Baluz et al., 2010; Páez, 2012).

This assemblage was overprinted by a supergene weathering, which produced an association of low crystallinity kaolinite + jarosite ± plumbogummite ($PbAl_3(PO_4)_2(OH)_5\bullet H_2O$) defining a advanced argillic alteration zone (Cedillo Frey et al., 2009; Páez, 2012) that is related to the descent of post hydrothermal acidic meteoric waters (Scott, 1990; Tzvetanova, 2003; Páez, 2012).

5. Concluding remarks

During extensive weathering of mineralized bodies, significant amounts of silver and copper may be dissolved from oxidizing zones and may be redeposited as supergene sulphides and sulphosalts at deeper levels dominated by reduced conditions (Boyle, 1968; Mann, 1984; Sillitoe and McKee, 1996; Greffié et al., 2002).

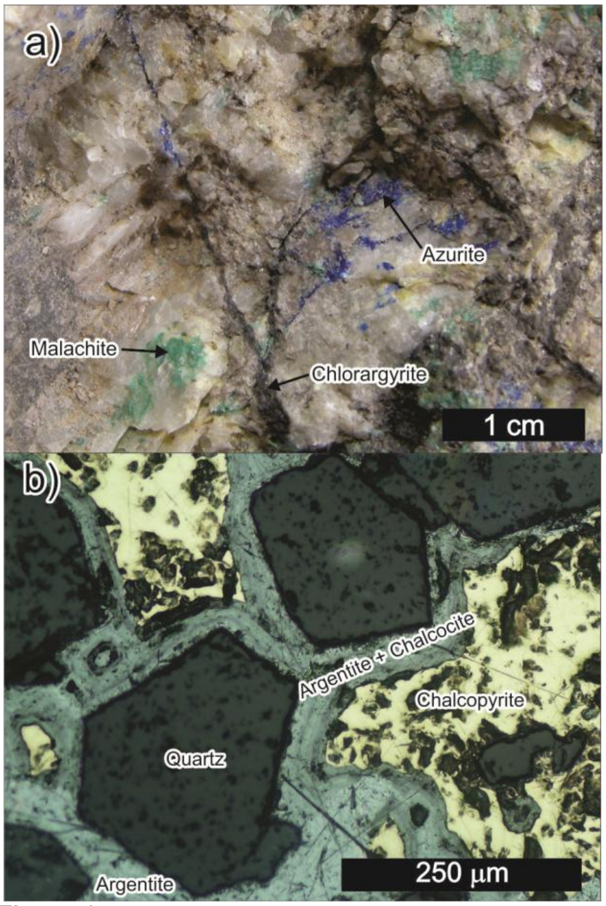

Figure 3. Examples of supergene modifications at Martha Mine. (a) Veinlets in the oxidation zone. (b) Replacement patches in the enrichment zone.

At Martha Mine, the vertical changes in geochemistry and in the mineralogy allow the definition of a 40-50 m thick zone with evidences for dissolution and re-precipitation of silver and copper minerals.

The presence of Fe and Pb sulfates, Cu and Pb carbonates and Ag, Cu and Pb chlorides in the mineralized structures, along with jarosite, kaolinite and alunite group minerals in the host rocks, suggests that acidic and oxidizing conditions prevailed in the upper 20 m of the Martha deposit, leading to the mobilization of certain metals (especially copper and silver) and the consequent destruction of most sulphides (Scott, 1990; Sillitoe and McKee, 1996; Hartley and Rice, 2005).

Below this supergene zone, the presence of Cu and Ag sulphides and sulfosalts with replacement textures over primary ore minerals, indicate a 20-30 m thick zone where reduced conditions prevailed, leading to the re-precipitation of ore metals (mostly copper and silver) from descending waters (Sillitoe and McKee, 1996; Greffié et al., 2002; Hartley and Rice, 2005).

These changes are the first mention of a supergene enrichment blanket in an epithermal vein system from the Deseado Massif; and should be taken into consideration during exploration, as high grade portions of a silver deposit may be concealed below a lower grade oxidized horizon at surface as exemplified in Fig. 2.

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