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Mineralogical evolution of the Las Cruces gossan cap (Iberian Pyrite Belt): From subaerial to underground conditions

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ABSTRACT

The Las Cruces VMS deposit is located at the eastern corner of the Iberian Pyrite Belt (SW Spain) and is overlain by the Neogene–Quaternary sediments of the Guadalquivir foreland Basin. The deposit is currently exploited from an open pit by Cobre Las Cruces S.A., being the supergene Cu-enriched zone the present mined resource. The Las Cruces orebody is composed of a polymetallic massive sulfide orebody, a Cu-rich stockwork and an overlying supergene profile that includes a Cu-rich secondary ore (initial reserves of 17.6 Mt @ 6.2% Cu) and a gossan cap (initial reserves of 3.6 Mt @ 3.3% Pb, 2.5 g/t Au, and 56.3 g/t Ag).

The mineralogy of the Las Cruces weathering profile has been studied in this work. Textural relationships, mineral chemistry, deposition order of the minerals and genesis of the Las Cruces gossan are described and discussed in detail. A complex mineral assemblage composed by the following minerals has been determined: carbonates such as siderite, calcite and cerussite; Fe-sulfides including pyrite, marcasite, greigite and pyrrhotite; Pb–Sb sulfides and sulfosalts like galena, stibnite, fulöppite, plagionite, boulangerite, plumosite, and the jordanite–geocronite series, Ag–Hg–Sb sulfides and sulfosalts including miargyrite, pyrargyrite, sternbergite, acanthite, freibergite, cinnabar, Ag–Au–Hg amalgams; and Bi–Pb–Bi sulfides and sulfosalts such as bismuthinite, galenobismutite, others unidentified Bi–Pb-sulfosalts, native Bi and unidentified Fe–Pb–Sb-sulfosalts. Remains of the former oxidized assemblage appear as relicts comprised of hematite and goethite.

Combining paragenetic information, textures and mineral chemistry it has been possible to derive a sequence of events for the Las Cruces gossan generation and subsequent evolution. In that sense, the small amount of Fe-oxyhydroxides and their relict textures replaced by carbonates and sulfides suggest that the gossan was generated under changing physico-chemical conditions. It is proposed that the Las Cruces current gossan represents the modified residue of a former gossan mineralization where prolonged weathering led to dissolution and leaching out of highly mobile elements and oxidation of the primary sulfides. Later, the gossan was subject to seawater-gossan interaction and then buried beneath a carbonated-rich cover. The basinal fluids-gossan interaction and the equilibration of fluids with the carbonated sediments brought to the carbonatization and sulfidation of the gossan, and thus to the generation of Fe-carbonates and Pb–Sb-sulfides.

The Las Cruces mineral system likely represents a new category within the weathering class of ore deposits.

1. Introduction

Gossan deposits derived from the supergene alteration of massive sulfide deposits have been documented from many different metallogenetic provinces (e.g., Lachlan Fold Belt, Australia (Scott et al., 2001); Bathurst Mining Camp, Canada (Boyle, 1994); Golden Grove District, Australia (Mann, 1984; Smith and Sing, 2007); Khomas Schist Belt, Namibia (Andrew, 1984); Iberian Pyrite Belt (Capitán, 2006; Velasco et al., 2013). Commonly, the surface exposition of sulfide-rich deposits involves mineralogical and chemical alteration of the protores, remobilization of metals and their reprecipitation in secondary Fe-oxyhydroxides-sulfate-rich bearing mineralizations (Mann, 1984; Boyle, 1994). As a general rule, these deposits depict a well-defined internal zonation resulted from the geochemical and mineralogical transformations during leaching (Scott et al., 2001; Taylor, 2011). The mobility of metals and mineralogical changes of sulfide deposits during weathering have been widely investigated (Andrew, 1980; Taylor et al.,

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1984; Thornber, 1985; Scott et al., 2001). Properties controlling the mobility and aqueous geochemistry of Fe, Cu, Zn, Pb, Au and Ag have been described by Mann and Deutscher (1980), Mann (1984) and Thornber (1985). In addition, weathering profiles are also well known due to their high concentration in precious metals, which may concentrate to form economic ores (Boyle, 1979; Webster and Mann, 1984; Groen et al., 1990; Benedetti and Bouleguè, 1991; Gray, 2001; Hough et al., 2009; Fairbrother et al., 2012; Reith et al., 2012).

Numerous studies have shown that major mineralogical features in gossan caps concerns with precipitation of newly-formed oxyhydroxides, oxides, sulfates, oxy-sulfates, sulfo-arsenates, arsenates, halides, native metals and phyllosilicates after leaching its protores, under acidic and oxidizing conditions. Common minerals in supergene profiles include: goethite, hematite, pyrolusite, rutile, cassiterite, cuprite, tenorite, barite, anglesite, alunite, chalcanthite, jarosite, argentojarosite, plumbojarosite, beudantite, scorodite, chlorargyrite, iodargyrite, bromargyrite, native gold, native silver, halloysite, chrysocolla and delafossite (Scott et al., 2001; Freyssinet et al., 2005; Capitán, 2006; Koski, 2012; Velasco et al., 2013).

Many efforts have been put on the generation mechanisms of oxides and sulfates in weathering profiles in order to elucidate how metals are redistributed within the supergene deposits (Taylor et al., 1984; Thornber, 1985; Bigham et al., 1996; Dutrizac and Jambor, 2000; Capitán et al., 2000). Many other investigations have been devoted to the study of Au and Ag mineralogy, in order to understand their mobilization and fixation during the weathering of primary deposits (Webster and Mann, 1984; Stroffregen, 1986; Groen et al., 1990; Benedetti and Bouleguè, 1991; Gray, 2001; Freyssinet et al., 2005; Fairbrother et al., 2012; Reith et al., 2012).

The generation of volcanic-hosted massive sulfides (VHMS) in the Iberian Pyrite Belt (IPB) has been related to the palaeogeographic evolution of the IPB Basin at the uppermost Devonian, and more specifically to the breakup of the basin in response to the onset of the Variscan orogeny (Moreno et al., 1996). The subsequent uplift of the Variscan chain drove to the erosion and exhumation of part of the IPB during the upper Oligocene-lower Miocene (Essalhi et al., 2011; Velasco et al., 2013). The aerial exposition of large amounts of massive sulfide deposits resulted in the generation of supergene profiles, including gossan caps and cementation zones. These have been targeted for Cu and precious metals in the IPB for more than five millennia (Nocete et al., 2005).

Due to the long history of base and precious metal production in the IPB, only few gossan caps have remained well preserved. This explains the scarcity of publications on the genesis of IPB supergene profiles. Of these, most are focused on the reserves, metallurgy and mining features of economic gossans (García Palomero et al., 1986; Viñals et al., 1995; Sanchez et al., 1996; Roca et al., 1999).

The available data indicate that, as a whole, the IPB gossans show general features comparable to weathering profiles of other massive sulfides (Andrew, 1980; Taylor, 1984; Scott et al., 2001). Some examples of well-studied gossans in the IPB are: San Miguel (Álvaro and Velasco, 2002); Riotinto (Williams, 1950; Amorós et al., 1981; Arribas, 1998); and Tharsis (Capitán et al., 2003; Capitán, 2006). General reviews on the IPB gossans are published by Kosakevitch et al. (1993, 1994), Viallefond (1994) and Velasco et al. (2013). According with all these authors the main features of the IPB gossan are: (i) major mineralogy consisting of oxidized facies including goethite, hematite, minerals of the jarosite group, and quartz; (ii) main textures including massive, boxwork, colloform and open space fillings; and (iii) common development of vertical zonation with three clearly discernible horizons: a lower zone composed by goethite and quartz with jarosite, an intermediate zone comprised of goethite, quartz and hematite, and an upper zone dominated by hematite and quartz (Velasco et al., 2013). In contrast, the features exhibited by Las Cruces weathering profile do not match any of these general patterns (Yesares et al., 2015a).

Las Cruces is a currently exploited volcanic-hosted massive sulfide deposit at the eastern end of the IPB, about 24 km NW of Seville (SW region of the Iberian Peninsula), that is covered by a detrital and carbonate sequence, 150 m thick, consisting of sediments of the Guadalquivir foreland Basin. The deposit includes a polymetallic massive sulfide orebody, a Cu-rich stockwork (initial reserves of 4.5 Mt of Cu-rich ore @ 3.3% Cu and 20.7 Mt of polymetallic-rich ore @ 4.2% Zn and 2% Pb; Doyle et al., 2003) and an overlying supergene profile, which includes the Cu-rich secondary ore (initial reserves of 17.6 Mt @ 6.2% Cu) and the gossan cap (initial reserves of 3.6 Mt @ 3.3% Pb, 2.5 g/t Au, and 56.3 g/t Ag) (Cobre Las Cruces S.A. data updated on May 11, 2015).

The Las Cruces deposit was recently subject to several research papers mainly focused on the supergene profile (Knigth, 2000; Capitán, 2006; Blake, 2008; Tornos et al., 2014; Yesares et al., 2014, 2015a,b). These include the description of its geological, structural, mineralogical and geochemical features, as well as the discussion on different hypotheses regarding its genetic conditions. The most noticeable gossan features are the absence of internal structure, and the unusual mineralogy, which includes newly formed siderite, calcite, Fe-sulfides and galena, with goethite and hematite as minor components. According to these attributes, Knigth (2000) proposed a genetic model for the Las Cruces Cu-rich secondary mineralization involving: 1) the oxidation of primary sulfides during the last stages of the hydrothermal ore-forming system and; 2) a later fluctuation of the geothermal gradient in relation to the tectonic burial and uplifting events affecting the deposit after its genesis. Capitán (2006) suggested that the evolution of the Las Cruces gossan was controlled by the Miocene transgressive–regressive episodes in the area. Yesares et al. (2014, 2015b) reported several supergene precious metals mineralizations within the supergene profile and proposed two different mechanisms for Au and Ag mobilization and concentration. Blake (2008) and Tornos et al. (2014) proposed that the unusual features of the Las Cruces gossan were related to bacteriogenesis processes. Finally, Yesares et al. (2015a) reported mineralogical and geochemical data on the whole deposit and proposed a genetic model for the supergene profile linking its evolution to the interaction between the gossan and the sedimentary cover.

Although the genesis of the Las Cruces gossan has been highly debated in recent times, no detailed mineralogical studies, nor mineral chemistry and mineral association descriptions were present so far. In consequence, the present study aims to fill this knowledge gap and describes comprehensively the unusual mineralogy of the Las Cruces weathering profile.

This work provides the first mention of the occurrence of newly-formed carbonates, sulfides and sulfosalts, previously unreported in gossanous deposits. The geology, mineralogy and mineral chemistry of the Las Cruces gossan has been evaluated, in order to obtain information on the mineral evolution sequence and on the distribution of ore minerals. The mineral chemistry and textural descriptions of these minerals can offer valuable information about their physico-chemical conditions of formation, thus contributing to a better understanding of the Las Cruces metallogenic evolution.

2. Geological background

2.1. Iberian Pyrite Belt

The Iberian Pyrite Belt is recognized as one of the most prolific massive sulfide provinces in the world (Leistel et al., 1998; Sáez et al., 1999). It is located at the southwestern corner of the Iberian Peninsula, forming a band circa 230 km long and 40 km wide, that extends from the surroundings of Seville, in Spain, to southern Lisbon, in Portugal (Fig. 1).

The IPB is the largest of the three domains comprising the South Portuguese Zone, and the southernmost zone in the Iberian Variscan Massif. It has been interpreted as a tectonostratigraphic terrane sutured to the Iberian Massive during Variscan times (Leistel et al., 1998, and references therein).

The stratigraphic succession of the IPB is composed by sedimentary and igneous rocks of Middle Devonian–Pennsylvanian age, arranged in