

# Universidad de Huelva

Departamento de Geología



## El Gossan de Las Cruces : geología, mineralogía y mecanismos de concentración de metales preciosos

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presentada por:

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**Universidad de Huelva**  
**Facultad de Ciencias Experimentales**  
**Departamento de Geología**

**“El Gossan de Las Cruces: Geología,  
Mineralogía y Mecanismos de Concentración  
de Metales Preciosos”**

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**Tesis presentada para optar al grado de Doctor en Ciencias por  
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El doctorando M<sup>a</sup> Dolores Yesares Ortiz y los directores de la tesis Gabriel Ruiz de Almodóvar Sel, José Miguel Nieto Liñán y Reinaldo Sáez Ramos, Garantizamos, al firmar esta tesis doctoral, que el trabajo ha sido realizado por el doctorando bajo la dirección de los directores de la tesis y hasta donde nuestro conocimiento alcanza, en la realización del trabajo, se han respetado los derechos de otros autores a ser citados, cuando se han utilizado sus resultados o publicaciones.

Huelva, 18 de Noviembre de 2015

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## RESUMEN

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**El depósito VMS de Las Cruces** se sitúa en el extremo Este de la Faja Pirítica Ibérica (FPI) (SW de la Península Ibérica), bajo los sedimentos Neógeno-Cuarternarios de las Cuenca de antepaís del Guadalquivir. Estos sedimentos cubrieron y preservaron el perfil supergénico desde su formación hasta su reciente descubrimiento. Por esta razón, el depósito de Las Cruces, junto con Lagoa Salgada en Portugal, son los únicos depósitos conocidos de la FPI que conservan intacto su perfil de meteorización, incluyendo el gossan y la zona de enriquecimiento secundario de Cu.

La mineralización primaria consiste en un cuerpo de sulfuros masivos y semimasivos polimetálicos y un stockwork pirítico-cuprífero suprayacente. La parte superior de los sulfuros masivos está formada por un perfil supergénico que incluye el gossan la zona de cementación rica en Cu.

Actualmente, el depósito está siendo explotado por una corta por Cobre las Cruces S.A., siendo su mayor recurso la zona de enriquecimiento secundario de Cu (reservas iniciales de 17.6 Mt @ 6.2% Cu). Además, el depósito también incluye importantes reservas en el gossan (reservas iniciales de 3.6 Mt @ 3.3% Pb, 2.5 g/t Au, y 56.3 g/t Ag) y metales base en los sulfuros primarios (4.5 Mt de mineralización cuprífera @ 3.3% Cu y 20.7 Mt de mineralización polimetálica @ 4.2% Zn y 2% Pb) (datos de Cobre las Cruces S.A. actualizados en Mayo de 2015).

Este estudio proporciona nuevos datos sobre los yacimientos de la FPI y su posterior evolución post-Paleozoica. En este sentido, los datos mineralógicos y geoquímicos confirman que la mineralización primaria de Las Cruces es semejante a otros depósitos de la FPI respecto a distribución de metales y evolución geológica, sin embargo, el gossan y la zona de cementación presentan una evolución poco común para este tipo de perfiles supergénicos. La mayor particularidad que hace que la mineralización supergénica Las Cruces sea notablemente diferente de los demás yacimientos de la FPI o de otras partes, es su composición mineralógica inusual.

Con el fin de estudiar intensivamente la mineralogía del gossan Las Cruces, las muestras fueron investigadas con microscopio óptico, difracción de rayos X (XRD), microscopía electrónica de barrido con espectroscopía de energía dispersiva (SEM-EDS) y microsonda de electrones (EPMA). Las relaciones texturales, química mineral, orden de deposición y génesis del gossan Las Cruces se describen y analizan en detalle. Se ha determinado una compleja asociación mineral compuesta por los siguientes minerales: carbonatos como siderita, calcita y cerusita; sulfuros de Fe incluyendo pirita, marcasita, greigita y pirrotina; sulfuros y sulfosales de Pb-Sb como galena, estibina, fulloppita, plagionita, boulangerita, plumosita y minerales de la series jordanita-geocronita; sulfuros y sulfosales de Ag-Hg-Sb incluyendo miargirita, pirargirita, esternbergita, acantita, freibergita cinabrio, amalgamas de Ag-Au-Hg; sulfuros y sulfosales de Bi-Pb como bismutinita y galenobismutita; metales nativos como Bi y Au. Además, se han identificado relictos del gossan primario compuestos de hematites y goethita.

En cuanto al contenido de metales preciosos, los análisis de las muestras de testigos de sondeo muestra una distribución heterogénea dentro del perfil supergénico, con valores medios de 5,1 ppm de oro y 155 ppm de plata, siendo las de tenencia general creciente hacia la parte inferior del gossan. El contenido en Au varía entre 0,01 ppm a > 100 ppm, y se encuentra en tres mineralizaciones diferentes: (1) concentración de Au en la parte inferior de la gossan asociado con niveles de pizarras negras lixiviadas, en el contacto entre el gossan y las zona pirítica estéril dentro de la mineralización supergénica de Cu; (2) mineralización de Au en la parte superior de la gossan asociada a las litofacies oxidadas; y (3) mineralización de Au en la zona de la cementación asociada a los fallas subverticales.

Para caracterizar las partículas de Au y Ag, han sido usadas técnicas de hidroseparación para obtener concentrado de minerales pesados de muestras seleccionadas de diferentes mineralizaciones. Las técnicas de análisis para estudiar las partículas de Au empleadas fueron microscopía electrónica de barrido con espectroscopía de energía dispersiva (SEM-EDS) y microsonda de electrones (EPMA). Se identificaron numerosas diferencias entre las diferentes mineralizaciones previamente definidas como las litologías huéspedes de Au, las asociaciones minerales, las texturas, tamaño de grano de las partículas, morfologías y pureza. El conjunto de fases de Au incluye: Au nativo, electrum y amalgamas de Au-Ag-Hg. Estas partículas de Au está asociadas a oxihaluros de Pb, óxidos de Fe, galena, pirita, cinabrio y sulfosales de Ag.

Combinando la información paragenética, texturas, química mineral, equilibrio mineral y la distribución geoquímica de los metales, se ha propuesto un modelo de tres etapas genéticas para el depósito de Las Cruces:

- (1) Génesis y evolución de mineralización primaria similar a otros depósitos la FPI.
- (2) Génesis de la mineralización secundaria de Cu y de la mineralización de gossan rica en oxihidróxidos de Fe por meteorización en condiciones oxidantes y ácidas de la parte superior del depósito de sulfuros masivos, tras la exhumación Miocena.

Durante esta etapa, los mecanismos de enriquecimiento de metales preciosos en el perfil supergénico incluyen la disolución de Au y Ag de los sulfuros primarios como complejos clorurados durante la meteorización del depósito primario en condiciones subaéreas. Los metales preciosos disueltos fueron transportados hacia cotas inferiores del supergénico en condiciones ácidas y oxidantes. La deposición de los metales preciosos se produce por su desestabilización controlada por las reacciones redox. Como consecuencia, precipitaron partículas de Au de grano grueso y de alta finura asociadas a oxihidróxidos de Fe. Esto dió lugar a la concentración secundaria de Au en la parte superior del gossan.

- (3) La evolución tardía del perfil de meteorización de Las Cruces se produce bajo los sedimentos carbonatados de la Cuenca del Guadalquivir, con el consecuente cambio en las condiciones redox debido a la interacción agua-roca entre el perfil supergénico y los fluidos de cuenca. De esta manera, los oxihidróxidos de Fe formados durante la formación del gossan primario fueron reemplazados por carbonatos y sulfuros. Esto indica que el gossan primario se modificó en condiciones físico-químicas variables. Todo esto implica la interacción de los fluidos de cuenca y el gossan, el equilibrio de los fluidos con los sedimentos carbonatados, y la carbonatación y sulfuración del gossan que condujo a la precipitación de carbonatos de Fe, y sulfuros y sulfosales de Pb-Sb.

Durante esta etapa, tuvo lugar una removilización tardía de metales preciosos como haluros, hidróxidos, tiosulfatos, sulfitos hacia la parte inferior del gossan y la zona de cementación. Las

principales vías de migración de los fluidos enriquecidos a la zona de la cementación fueron zonas de permeabilidad secundaria asociadas a la reactivación Alpina de la fallas Variscas. Varios ciclos de disolución-precipitación de Au y Ag se produjeron por cambios en las condiciones de pH-Eh. La deposición de metales preciosos está relacionada con la interacción de los fluidos con litologías reductoras, incluyendo pizarras negras situadas en la base del gossan, y los sulfuros masivos en la zona de la cementación. Como consecuencia, precipitaron partículas de Au de pureza media y baja asociadas a cinabrio, sulfuros y sulfosales de plata en la base del gossan y en la zona de la cementación.

## ABSTRACT

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**The Las Cruces VMS deposit** is located at the eastern corner of the Iberian Pyrite Belt (IPB) (SW Iberian Peninsula), beneath the Neogene-Quaternary sediments of the Guadalquivir foreland Basin. These sediments covered and preserved the supergene profile somewhat after its generation until its recent discovering. For this reason, the Las Cruces ore deposits, together with LagoaSalgada in Portugal, are the only known deposits in the IPB that preserve the entire weathering profile, including both the gossan and the secondary Cu-enrichment zone.

The primary mineralization consists of massive and semi-massive polymetallic sulfides overlaying a Cu-rich stockwork. The upper part of the massive sulfide body consists of a supergene profile including a gossan mineralization above a copper-rich cementation zone

The deposit is currently mined from an open pit by Cobre las Cruces S.A., being the main operation focused on the supergene Cu-enriched zone (initial reserves of 17.6 Mt @ 6.2% Cu). In addition, the deposit also includes important resources in the gossan cap (initial reserves of 3.6 Mt @ 3.3% Pb, 2.5 g/t Au, and 56.3 g/t Ag) and base metals in the massive sulfide orebody (4.5 Mt of Cu-rich ore @ 3.3% Cu and 20.7 Mt of polymetallic-rich ore @ 4.2% Zn and 2% Pb) (after data from Cobre las Cruces S.A. actualized to May 11, 2015).

The present study provides new data on the IPB ore deposits and their post-Palaeozoic evolution. In this sense, mineralogical and geochemical data confirm that the primary mineralization at Las Cruces resembles other IPB deposits in terms of distribution and evolution, however the gossan and cementation zone show an uncommon evolution for this kind of supergene profile. The major singularity that makes the Las Cruces supergene mineralization noticeably different from others in the IPB or elsewhere resides in its unusual mineralogical composition.

In order to study the whole rock mineralogy of the Las Cruces gossan cap, samples were investigated by optical microscope, X-ray diffraction (XRD), scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS) and electron microprobe analyses (EPMA). Textural relationships, mineral chemistry, deposition order 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, fuloppite, plagionite, boulangerite, plumosite, jordanite-geocronite series, Ag-Hg-Sb sulfides and sulfosalts including miargyrite, pyrargyrite, sternbergite, acanthite, freibergite cinnabar, Ag-Au-Hg amalgams; and Bi-Pb 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.

Regarding the precious metals content, drill core analyses show a heterogeneous distribution within the supergene profile, with mean values of 5.1 ppm of gold and 155 ppm of silver, being the absolute tenures increased towards the bottom of the weathered profile. The Au grade ranges from 0.01 ppm to >100 ppm, and occurs as three different Au ore types: (1) Au concentration in the lower part of the gossan associated with leached black shale horizons, where the gossan makes contact with a barren pyrite zone within the supergene Cu-rich mineralization; (2) Au mineralization in the upper part of the gossan linked to Fe-oxihydroxide lithofacies; and (3) Au ore in the cementation zone related to subvertical faults.

In order to characterize the Au-Ag-bearing particles, a hydroseparation technique has been used to obtain heavy mineral concentrates from selected samples of different ore types. Reflected-light microscopy, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and electron probe microanalysis (EPMA) were used to study the separated Au particles. Significant

differences between the defined ore types include the Au-bearing lithologies, mineral associations, textural features, particle sizes, morphologies, and fineness. Au-rich minerals include native Au, Au-Ag electrum, and Au-Ag-Hg amalgams. Gold-bearing mineral associations include Pb-oxihalides, Fe-oxides, galena, pyrite, cinnabar, and Ag-sulfosalts.

Combining paragenetic information, textures, mineral chemistry, mineral equilibrium and geochemical distribution, a three-stage genetic model has been proposed for the Las Cruces deposit:

(1) Ore genesis and evolution of primary mineralization, which seems to be similar to other IPB deposits.

(2) Genesis of Cu-rich secondary mineralization and Fe-oxyhydroxides-bearing gossan by weathering, after Miocene exhumation, of the upper part of the massive sulfide deposit, under oxidizing and acidic conditions.

During this stage, the precious metal enrichment mechanism in the supergene profile involves the dissolution of Au and Ag from the primary sulfides as chloride-rich ionic complexes during the weathering of the primary deposit under subaerial conditions. The dissolved precious metals were transported downward through the supergene profile by acidic and oxidized solutions. Deposition of precious metals occurs by its destabilization which is controlled by redox reactions. As a consequence, coarse-grained, high-fineness Au particles precipitated in association with Fe-oxyhydroxides. This resulted in secondary concentration in the upper gossan.

(3) Late evolution of the Las Cruces weathering profile occurs below the carbonated-rich sediments of the Guadalquivir Basin, with the subsequent change in the redox conditions due to water-rock interaction between the supergene profile and basinal fluids. In this way, the Fe-oxyhydroxides formed during the early gossan stage, were replaced by carbonates and sulfides suggesting that the early gossan was modified under changeable physico-chemical conditions. All these suggest the basinal fluid-gossan interaction, the equilibration of the fluid with the carbonated sediments and the subsequent gossan carbonatization and sulfidation led the Fe-carbonates and Pb-Sb-sulfides and sulfosalts.

During this stage, it took place a later precious metals remobilization as hydroxidehalide, hydroxide, thiosulfate, and bisulfide complexes to the lowermost gossan and cementation zone. The main pathways for migration of enriched fluids to the cementation zone were secondary permeability zones linked to Alpine reactivation of Variscan faults. Several cycles of dissolution-precipitation of Au and Ag occur by changes in the pH-Eh conditions. Deposition of precious metals seems to be related to fluid interaction with reductant lithologies, including black shales located to the lower gossan, and the primary massive sulfides in the cementation zone. As a consequence, medium and low fineness Au particles associated to cinnabar, Ag-sulfides and sulfosalts precipitated in the lower gossan and the cementation zone.



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## CHAPTER 1. INTRODUCTION

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**This PhD thesis** arose from the collaboration between the University of Huelva and the mining company Cobre Las Cruces S.A. (First Quantum Minerals Ltd.). The main interest of this collaboration was focussed on achieving scientific knowledge about the mineral deposits and decoding the intricate nature of the deposit given the interest of the mining company in improving economic benefits. As a consequence of this research, and outside the PhD thesis goal, additional collaboration with the company related to the study of the mineral resources and metallurgy has come up.

The main subject of this PhD thesis is the Las Cruces deposit. In particular, this research is focused on the geological, mineralogical and geochemical features of the gossan cap(\*) as well as the precious metals supergene mineralizations and its genetic model.

The Las Cruces deposit is located at the eastern corner of the Iberian Pyrite Belt (IPB), about 25 km northwest of Seville (SW Spain), and it is covered by a detrital and carbonate sequence, 150-m-thick, of the Guadalquivir foreland Basin. The Las Cruces deposit includes a polymetallic massive sulfide orebody and a Cu-rich stockwork (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). At the upper part, it includes a supergene profile containing a gossan cap (initial reserves of 3.6 Mt @ 3.3% Pb, 2.5 g/t Au, and 56.3 g/t Ag) and a Cu-rich secondary ore (initial reserves of 17.6 Mt @ 6.2 % Cu) which represents the current economic resource (Cobre Las Cruces S.A. data calculated on May 11, 2015).

(\*) Gossan cap is defined as an intensely altered sulfide-rich rock previously subjected to supergene alteration processes under subaerial environments, including: weathering, oxidation, dissolution, lixiviation and precipitation of newly-formed minerals stable with the new thermodynamic system condition.

Although in the case of the Las Cruces deposit, the weathering profile is not a gossan *sensu stricto*, this manuscript refers to “gossan” as the weathering profile developed under subaerial condition and transformed due to subsequent evolution (explained below).

## **1.1. PREVIEW WORKS**

In general terms, exposition to subaerial conditions of sulfide-rich deposits involves weathering of primary mineralizations. This mainly consists on the oxidation of sulfide ores followed by leaching, remobilization of metals and reprecipitation as newly-formed Fe-oxyhydroxides-sulfate-rich secondary ores (Williams, 1950; Andrew, 1980; Mann, 1984; Taylor, 1984; Thornber, 1985; Boyle, 1994; Scott et al., 2001). Microbial activity usually plays a pivotal role catalysing and accelerating these processes (Nordstrom and Alpers, 1999; Bigham and Nordstrom, 2000). The resulting supergene mineralizations normally show well defined internal zonations in response to the geochemical transformations during lixiviation (Scott, 2001; Capitán 2006; Velasco et al., 2013). The metal zonation and the mineralogical changes of sulfide deposits during weathering have been recurrent matter of research (Williams, 1950; Andrew, 1980; Mann, 1984; Taylor, 1984; Thornber, 1985; Boyle, 1994; Scott et al., 2001). The mobilization mechanisms of Fe, Cu, Zn, Pb, Au and Ag and their aqueous geochemistry have been investigated by Mann and Deutscher (1980), Mann (1984), Taylor et al. (1984), Thornber (1985) and Scott et al. (2001).

Gossan caps related to the weathering of massive sulfide deposits are documented from several metallogenetic provinces and mining districts (e.g.: Lachlan Fold Belt, Australia (Scott et al., 2001); Bathurst Mining Camp, Canada (Boyle, 1994); Golden Grove District, Australia (Mann, 1984; Nickel,

1984; Smith and Singh, 2007); Khomas Schist Belt, Namibia (Andrew, 1984); IPB (Capitán 2006; Velasco et al., 2013).

These studies reveal that the main mineralogical features in gossan caps consist on the precipitation of newly-formed oxides, oxysalts, halides and native metals after leaching of its protores under oxidizing and acidic conditions. The common mineralogy of weathering profiles includes: goethite, hematite, pyrolusite, rutile, cassiterite, cuprite, tenorite, barite, anglesite, alunite, chalcantinite, jarosite, argentojarosite, plumbojarosite, beudantite, scorodite, chlorargyrite, iodargyrite, bromargyrite, native gold, native silver, halloysite, chrysocolla and delafossite) (Taylor et al., 1984; Webster and Mann, 1984; Scott et al., 2001; Freyssinet et al., 2005; Capitán 2006; Koiski, 2012; Velasco et al., 2013)

Another recurring subject of research is the generation of oxides and sulfates in weathering profiles as a way to understand metals redistribution along the supergene profile, as well as the depositional mechanisms (Andrew, 1980; Taylor et al., 1984; Thornber, 1985; Bigham et al., 1996; Dutrizac and Jambor, 2000; Scott et al., 2001; Capitán et al., 2003, 2006; Velasco et al., 2013).

Gossan caps have also been subject of research due to its precious metals content, which may concentrate for form economic ores (Boyle, 1979; Webster and Mann, 1984; Stoffregen, 1986; Freyssinet et al., 1989, 2005; Groen et al., 1990; Benedetti and Bouleguè, 1991; Vasconcelos, 1991; Krupp and Weiser, 1992; Bowell, 1993; Gray, 2001; Hough et al., 2008, 2009; Fairbrother et al., 2012; Reith et al., 2012).

Many efforts have been focused on the mineralogy of Au and Ag in order to understand its mobilization and fixation during the weathering of deposits (Webster and Mann, 1984; Stoffregen, 1986; Groen et al., 1990; Benedetti and Bouleguè, 1991; Vasconcelos, 1991; Krupp and Weiser, 1992; Bowell, 1993; Gray, 2001; Freyssinet et al., 2005; Hough et al., 2008, 2009; Fairbrother et al., 2012; Reith et al., 2012).

In that sense, supergene precious metal ores occur fundamentally as result of dissolution and redistribution of Au and Ag during weathering of its protores. In near-surface environments and under extreme conditions, precious metals are released during the oxidative dissolution of primary sulfides and mobilized through the weathering profile via complexation with organic-, halide-, hydroxide-, halide-hydroxide and sulfur ligands. Their relative role mainly depend on the weathering conditions (Boyle et al., 1975; Mann, 1984; Webster, 1986, Groen et al., 1990; Benedetti and Bouleguè, 1991; Freyssinet et al., 2005; Tagirov et al., 2006; Usher et al., 2009; Ta et al., 2014). Au and Ag are mobilized downwards until they reach an environment with physical-chemical conditions favourable for precipitation, although are also concentrated and redistributed through

the gossan cap by residual concentration processes. Biological activity can also contribute to dissolution-precipitation processes of Au during weathering in near-surface environments (Reith et al., 2006, 2007, 2012, 2013; Southam et al., 2005, 2009; Hough et al., 2008; Fairbrother et al., 2012).

In general, these processes result in the generation of relatively low grade Au deposits with concentrations ranging between 1 to 5 ppm (Butt, 1998). Secondary Au occurs as fine-grained particles of variable size, in many cases associated with Fe-oxyhydroxide gossans (Mann, 1984; Butt, 1998; Capitán et al., 2003, 2006; Freyssinet et al., 2005; Andreu et al., 2014). Secondary Ag can occur as native element, halides, such as chlorargyrite [ClAg], iodargyrite [IAg] and bromargyrite [BrAg], or as sulfates of the jarosite group (i.e. argentojarosite [AgFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>]) (Dutrizac and Jambor, 1987).

The IPB is recognized as one of the most prolific massive sulfide provinces on Earth (Leistel et al., 1998; Sáez et al., 1999). It is located at the southwester corner of the Iberian Peninsula, extending about 230 km long and 40 km wide, from Seville in Spain to south of Lisbon in Portugal.

It hosts more than 100 inactive or working mines, totalling the 22% (14) of the world class VMS deposits (Tornos, 2006). Eight of these deposits (Riotinto, Tharsis, La Zarza, Sotiel, Masa Valverde and Aznalcollar in Spain, and Neves Corvo and Aljustrel in Portugal) have been classified as giants (>100Mt). The IPB contains original reserves above 1700 Mt (Leistel et al., 1998; Carvalho et al., 1999), and even after five thousand years of fairly continuous metal extraction (Leblanc et al., 2000; Sáez et al., 2003; Nocete et al., 2005), it still hosts exceptionally large metal reserves.

Many efforts have been focused on the structure, petrology, mineralogy and geochemistry of primary mineralizations in the IPB. See, for example, Strauss et al. (1977), Routhier et al. (1980), Barriga (1990), Sáez et al. (1996, 1999), Leistel et al. (1998), Almodóvar et al. (1998), Carvalho et al. (1999), Tornos et al. (2000; 2006); and Relvas et al. (2001). However, the numbers of publications on the IPB supergene profiles are scarce because the intense mining history, including ore removal, resulted in a bad state of preservation.

In that sense, only few gossan caps remain well preserved in the area, what considerably reduces their possibilities study. While most of the published works to date deal with data about reserves, metallurgy and mining of the economic gossans (García Palomero et al., 1986; Viñals et al., 1995; Sánchez et al., 1996; Roca et al., 1999), only few of them are devoted to the genesis and evolution of supergene profiles such as those of San Miguel (Álvaro et al., 2002), Riotinto (Williams, 1950; Arribas, 1998; Amorós et al., 1981; Capitán, 2006), or Tharsis (Capitán et al., 2003; Capitán, 2006), or at best, provide a general analysis of the IPB gossans (Kosakevitch et al., 1993,1994; Viallefond, 1994; Velasco et al., 2013).

In general terms, the IPB gossan caps match the most common features of massive sulfide weathering profiles (Andrew, 1980; Taylor, 1984; Thornber, 1985; Scott et al., 2001). According to the studies referred above the main highlight features of the IPB gossans are: (i) main mineralogy formed by oxidized facies such as goethite, hematite, minerals of the jarosite group, and quartz; (ii) main textures include: massive, boxwork, colloform and open space fillings; and (iii) vertical zonation. These characteristics were used to define three major 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).

The IPB gossan caps have been targeted for precious metals exploitation for more than five millennia (Sáez et al., 2003; Nocete et al., 2005; Nocete et al., 2014). Examples of gossans mined for Au and Ag since prehistoric times include Riotinto, La Lapilla, and Filón Sur-Tharsis. All these deposits were also mined for precious metals during the past century.

Little attention has been paid to the geologic features of Au-Ag-rich gossans in the IPB. Nevertheless, native Au has been reported in Filón Sur-Tharsis at intermediate levels associated with goethite (Capitán et al., 2003; Capitán 2006), whereas Au-rich ores have been documented in Riotinto near to the boundary between unweathered massive and oxidized sulfides (Williams, 1950; Viñals et al., 1995; Arribas, 1998). Regarding the Ag-bearing phases, halides, acanthite, and argentojarosite have been reported both in Riotinto (Viñals et al., 1995; Capitán, 2006) and Tharsis (Capitán, 2006). In addition, Velasco et al. (2013) have recently proposed that native gold, in gossans of the IPB, is scarce, very fine-grained and of low fineness.

The features and genesis of the Las Cruces ore deposit have been discussed in recent studies (Knigh, 2000; Capitán, 2006; Blake, 2008), with the main interest focused on the cementation zone and gossan mineralizations. These studies include the description of its mineralogical and geochemical features as well as the proposal of different hypotheses about the forming conditions. All of them enhance, as the most noticeable gossan features, the absence of internal structure and the uncommon mineralogy characterized by newly formed siderite, calcite, Fe-sulfides, galena, with minor goethite and hematite. Knigh (2000) suggested the genesis of the Las Cruces Cu-rich secondary ore as linked to: (1) the oxidation of primary sulfides during the last stages of the hydrothermal ore-forming system, and (2) the increasing/decreasing geothermal gradient associated to the deposit burial affecting the supergene profile after its genesis. Capitán (2006) proposed for the Las Cruces gossan an evolution controlled by the Miocene transgressive-regressive episodes affecting the area. Finally, Blake (2008) suggested that the uncommon mineralogy characterizing the Las Cruces gossan was related to anaerobic microbial activity.

Just after the beginning of this PhD thesis, other research team commenced a parallel investigation on the Las Cruces deposit, but taking a different research line. In this way, Tornos et al. (2014) proposed that the unusual features of the Las Cruces gossan were solely caused by bacteriogenic-related processes. According to this idea these authors presented a genetic model based on a "bioreactor" for de Las Cruces gossan.

### **1.3. MOTIVATION AND OBJECTIVES**

One of the main incentives of this PhD thesis was the fact that the Las Cruces deposit has remained buried and preserved below the sediments of the Guadalquivir Basin since its development. The possibility of study this deposit offered an excellent opportunity to improve knowledge on the IPB supergene profiles. In that sense, a further stimulus for a detailed study of the Las Cruces gossan was that this could be done in parallel to the deposit mining, obtaining therefore a 3-D whole knowledge of the mineralizations.

Another powerful reason that encouraged the approach of this PhD thesis was the reported peculiarities of the Las Cruces supergene profile (Knigh, 2000; Capitán, 2006; Blake, 2008). Comparing to others, the Las Cruces weathering profiles exhibits complex mineralogical and geochemical features, jointly with an exceptional amount of precious metals.

The excessive complexity of the Las Cruces geological system precluded detailed studies of the problem. As a result, there were not enough data for a full understanding of the intricate genesis of the Las Cruces gossan. In consequence, the aims of this PhD thesis are to describe comprehensively its unusual mineralogy, mineral chemistry and paragenesis, and to establish a model for the generation of the Las Cruces gossan, including the concentration of precious metals.

In order to achieve these general goals, several partial objectives are outlined. These shape the 6 chapters that make up this report, and are indexed in a simplified way in the following lines:

- To perform a comprehensive study of the Las Cruces deposit based on the geological and structural data obtained at the open pit as well as on data achieved from the numerous drill cores conducted by CLC during the exploration and evaluation phases.
- To study the bulk mineralogy and geochemistry all along the deposit, including the primary mineralization, Cu-rich supergene mineralization and the gossan cap.
- The characterization of the different facies and lithologies at the gossan profile based on the geological observations at the open pit and on the bulk gossan mineralogy and geochemistry.

- The detailed determination of the newly-formed mineralogy at the current gossan and its textural relationships based on optical microscopy, SEM and XRD analysis.
- The evaluation of the mineral chemistry of the main minerals forming the Las Cruces gossan based on EPMA analysis.
- To establish a paragenetic sequence, based on the mineralogical data, that constraints the metallogenic processes responsible for the Las Cruces gossan system.
- To recognize and differentiate the genetic stages that explains the formation and transformations of the weathering profile.
- The identification of the physical-chemical conditions in each genetic stages based on its paragenesis and mineral stabilities.
- To integrate the identified processes within the regional geological context.
- To determine the distribution of precious metals and its relationship with the different supergene facies and lithologies based on the geological observation at the open pit and on the bulk gossan mineralogy and geochemistry.
- The characterization of the mineralogical and textural features of the different Au and Ag ores by optical microscopy and SEM analysis.
- To study the chemical make-up of the different Au and Ag particles by EPMA analysis.
- The identification of suitable mechanisms of precious metals transport and precipitation in the supergene profile.

#### **1.4. OUTLINE OF THE PHD THESIS**

This PhD thesis includes an introduction, a geological context, three main chapters and the general conclusions. Each of the main chapters is based on one or two international publications. The structure of these principal chapters includes: introduction, methodology, results, discussion and conclusions; thereby, they can be read independently.. The general structure of the PhD thesis is as follows:

Chapter 1. Introduction

It includes the general context and geological issues concerning to weathering profiles and its related precious metal concentration. In this introductory section, the current knowledge on this issue is analysed and the main aims of this PhD thesis summarized.

## Chapter 2. Geological context

This chapter provides an updated summary of the IPB geology, including the general features of the ore deposits and their genesis, as well as their structure, mineralogy and geochemistry.

## Chapter 3. The Las Cruces deposit, Iberian Pyrite Belt, Spain

This chapter is based on the paper:

Yesares, L., Sáez, R., Nieto, J.M., Almodóvar, G.R., Gómez, C., and Escobar, J.M., 2015. The Las Cruces deposit, Iberian Pyrite Belt, Spain: *Ore Geology Reviews*. 66: 25–46.

This third chapter, presents a general study of the Las Cruces deposit focussed on the geological and structural data obtained at the open pit, on the geochemical interpretation of data from the drill holes conducted by CLC during the exploration and evaluation phases, and on the mineralogical studies of the different primary and supergene mineralization. A comprehensive genetic model for the Las Cruces deposit is also proposed in this chapter. The model tries to give an explanation of the whole Las Cruces deposit, from the origin of the primary sulfides to the final evolution of the supergene profile.

## Chapter 4. Mineralogical evolution of the Las Cruces Gossan Cap (Iberian Pyrite Belt): from subaerial to underground conditions

This chapter is based on the paper:

Yesares, L., Sáez, R., Almodóvar, G.R., Nieto and J.M., Gómez, C. Mineralogical evolution of the Las Cruces Gossan Cap (Iberian Pyrite Belt): from subaerial to underground conditions: Submitted to *Ore Geology Reviews*.

This chapter deals in detail with the intricate mineralogy of the Las Cruces gossan cap. It includes the mineral associations, textures and mineral chemistry characteristics of the Las Cruces gossan. All these data provide valuable information regarding the paragenetic ore sequence, contributing therefore to the understanding of the distribution of ore minerals and associated mineralizations.

## Chapter 5. The precious metals occurrences in the Las Cruces gossan, Iberian Pyrite Belt, Spain

This chapter is based on the papers:

Yesares, L., Sáez, R., Nieto, J.M., Almodóvar, G.R, and Stephen Cooper, S., 2014. Supergene enrichment of precious metals by natural amalgamation in the Las Cruces weathering profile (Iberian Pyrite Belt, SW Spain): *Ore Geology Reviews*. 58: 14-26.

Yesares, L., Aiglsperger, T., Sáez, R., Almodóvar, G.R., Nieto and J.M., Proenza, J.A., Gómez, C., Escobar, J.M., 2015. Gold Behavior in Supergene Profiles Under Changing Redox Conditions: The Example of the Las Cruces Deposit, Iberian Pyrite Belt: *Economic Geology*. 110: 1-18.

This chapter analyses all together the features of the three different precious metals supergene mineralizations recognized in the Las Cruces deposit. It determines also the Au and Ag distributions and the relationship between the different supergene facies and lithologies. Further characterization of the chemical composition of the different Au and Ag particles is achieved. Finally, the chapter proposes the mechanisms of precious metals transport and precipitation in the Las Cruces supergene profile.

#### Chapter 6. General conclusions

In this final chapter, the most relevant results and interpretations achieved in this PhD thesis are summarized.

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## CHAPTER 2. GEOLOGICAL CONTEXT

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**The Iberian Pyrite Belt (IPB)** is located in the southwest part of the Iberian Peninsula and extends for about 230-km-long and 40-km-wide, from Seville (Spain), to south of Lisbon (Portugal) (Fig. 1).

The IPB constitute the central domain of the South Portuguese Zone (SPZ), which is the southernmost one of the Iberian Variscan Massif (Julivert et al., 1974; Carvalho, 1976). This zone has been interpreted as a tectonostratigraphic terrane sutured to the Iberian Massive during Variscan times (Quesada, 1991; Leistel et al., 1998).

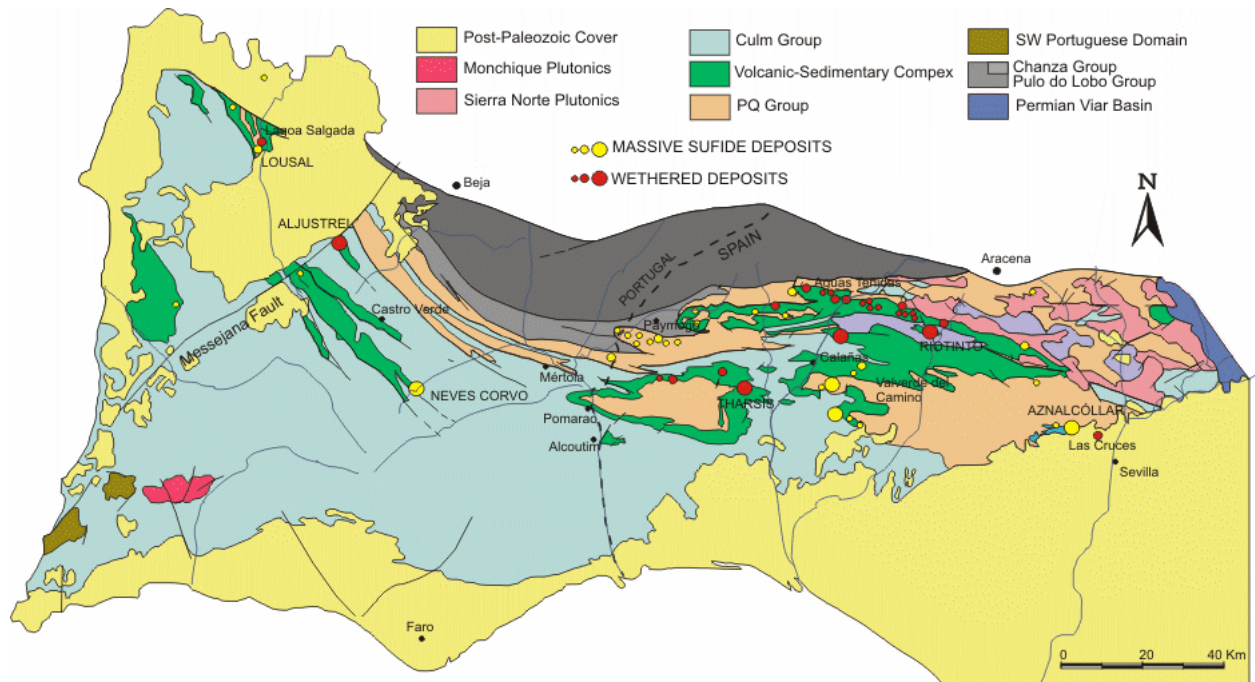


Fig. 1. Geologic map of the South Portuguese zone including the massive sulfide deposits and the wethered deposits (modified from Sáez, 2010).

The stratigraphic record of the IPB consists of Upper Palaeozoic sedimentary and igneous rocks which include, from footwall to hanging wall, three main lithostratigraphic units: the Pre-Volcanic Phyllite-Quartzite Group (PQ Group), the Volcano-Sedimentary Complex (VSC) and the Post-Volcanic Culm Group (Culm Group) (Schermerhorn, 1971). The limits of the three units are depositional, although locally they are masked by tectonic.

The PQ Group have been dated as Late Givetian to Late Famennian (Van den Boogaard and Schermerhorn, 1975; González et al., 2004) and represents the footwall of the IPB series. It consists of a thick detrital sequence of shales and sandstones representative of the sedimentation in a shallow marine platform that evolved near the top in response to basin shallowing (Moreno and Sáez, 1990; Moreno et al., 1996).

The VSC is Late Famennian to Middle Viséan in age according to paleontological data (Oliveira, 1990). It is mostly composed of volcanic and subvolcanic rocks interbedded in a detrital sedimentary sequence of shales and volcano-derived sandstones. The VSC is characterized by bimodal volcanism (Schermerhorn, 1975; Mitjavila et al., 1997).

Toward the top the VSC gradually evolves into the shaly sequence of the Culm Group (Moreno, 1987; Moreno and Sequeiros, 1989). This unit, Late Viséan-Moscovian in age, consists of a thick turbidite sequence of shales and sandstones representing the basin infill after tectonic uplift. The

Ossa-Morena Zone and the IPB itself have been interpreted as the main source areas (Moreno, 1993).

Geodynamic interpretations suggest that during Late Devonian-Early Carboniferous the IPB was affected by an extensional tectonic, which has been proposed as responsible for the breakdown and compartmentation of the basin and the beginning of the volcanic activity (Moreno et al., 1996). This palaeogeographic environment favoured the formation of the massive sulfide deposits (Sáez et al., 1996). The episodic ascent of magma just below the compartmentalized basin could trigger the establishment of hydrothermal systems. Large volumes of seawater with connate water trapped in the volcanic pile and the Devonian sediments could be the source of the fluids necessary for the transport and deposition of metals (Sáez et al., 1999; Tornos and Heinrich, 2008).

The massive sulfide deposits of the IPB occur within the Volcano-Sedimentary Complex associated mainly with felsic volcanoclastic and/or black shale sequences (Routhier et al., 1978; Barriga, 1990, Sáez et al., 1996). Radiometric ages obtained in hosting rocks and the massive sulphides themselves indicate that the massive sulfide deposits in the IPB were deposited between Late Famennian and Early Viséan (Nesbit et al., 1999; Nieto et al., 2000; Barrie et al., 2002). In addition, palynological data obtained from the hosting black shales of the main ore deposits suggest a massive sulfide event linked to the Devonian-Carboniferous boundary (González, 2002; González et al., 2006; Sáez, et al., 2008).

The massive sulfide deposits occur as lens-shaped stratabound bodies interbedded with black shales and, in minor extent, with volcanoclastic rocks from the first two felsic volcanic episodes (Routhier et al., 1978; Barriga, 1990), or their stratigraphic equivalents (Lécolle and Roger, 1973; Aye, 1974; Strauss and Madel, 1974; Routhier et al., 1978; Barriga, 1990; Almodóvar and Sáez, 1992; Sáez et al., 1999).

During the Variscan orogeny, the IPB was intensely deformed. During the Pennsylvanian, the inversion of the tectonic regime from transtensional to compressional (Simancas et al., 2003) resulted in the deformation according to a thin-skinned tectonic model (Silva et al., 1990) and the very low-grade metamorphism recorded in the IPB rocks. The Variscan deformation occurs along three main stages. The first stage, dated as Middle Westphalian (Schermerhorn, 1971; Silva et al., 1990) resulting in the main regional structures and responsible for the stacking of tectonic slices, with S-verging asymmetric folds and thrust. The second and third phases were distensives resulting in the late-Variscan fractures (Simancas, 1983). The older one gently folded the main F1 foliation, with vertical, N-S axial planes. Finally, the younger deformation stage was related to the late-Variscan fracturing phase, and consisted of two fault systems, an E-W set and a conjugated NNW/SSE and NE/SW system.

The massive sulfide deposits in the IPB are composed mostly of pyrite, with subordinated sphalerite, galena, chalcopyrite, tetrahedrite-tennantite, arsenopyrite, pyrrhotite and many other minor phases as Bi- and Pb-sulfosalts, cassiterite, magnetite, stannite, electrum and cobaltite (García de Miguel, 1990; Marcoux et al., 1996; Sáez et al., 1996 and 1999; Leistel et al., 1998; Almodóvar et al., 1998; Gaspar, 2002; Inverno et al., 2008; Oliveira et al., 2011).

**Weathered deposits in the Iberian Pyrite Belt.** The uplifting and erosion of the part of the IPB up to the Lower Miocene, gave room to the exhumation of some massive sulfide deposits (Essalhi et al., 2011; Velasco, et al., 2013). The exposition of massive sulphides under subaerial conditions promoted its oxidation, weathering and the formation of gossan caps under arid and semiarid climatic conditions (Velasco et al., 2013). Some examples of gossans in the IPB are: Tharsis, Riotinto, San Miguel and São Domingos (García Palomero et al., 1986; Arribas, 1998; Capitán 2006; Velasco et al., 2013).

The gossan caps in the IPB show similar features than other described elsewhere. According to Capitán (2006) and Velasco et al. (2013), the gossans in the IPB are made of goethite, hematite, quartz and jarosite as the main forming minerals. These are distributed along three horizons: the lowermost one is formed by goethite and minor jarosite, showing enrichment in S, As, P, Pb, Sn, Sb, Ag and Au; ii) the intermediate horizon constitute the main of the gossan. It is comprised largely by goethite involving strong depletion in S, As, and heavy and precious metals; iii) and the upper horizon, located near the surface, is mainly composed of hematite and quartz, being strongly leached.

**Post-variscan sedimentary cover.** Owing to the Neogene marine transgression (Abad, 2007), the south and western parts of the IPB were buried under the Neogene-Quaternary sediments of the Guadalquivir and Sado basins in Spain and Portugal respectively (Strauss and Madel, 1974). Both, Las Cruces (in Spain) and Lagoa Salgada (in Portugal) represent examples of recently discovered massive sulfide deposits hidden below the Neogene-Quaternary sedimentary cover.

The sedimentary record of the Guadalquivir Basin is comprised mostly by a carbonate and detrital sequence that unconformably overlies the Palaeozoic basement (Sierro, 1990; González-Delgado, 2004). In Las Cruces area the sedimentary sequence is circa 150-m-thick and can be divided in two main formations. The lowermost one, the Niebla Formation, consists of a calcarenite series overlaying a basal conglomerate. This unit, of continental to shallow marine origin, has a thickness range of 5-to-15-m, and is gently wedging to the south. Conformably over this unit the marine Arcillas de Gibraleón Formation comprises a 100-150-m-thick sequence of semi-consolidated glauconitic sands interbedded with marls and silts. Upper formations of the Guadalquivir Basin (e.g.

Arenas de Huelva, and Arenas de Bonares) do not outcrop in the Las Cruces area. The basal conglomerate, calcarenites and glauconitic sands, jointly with the upper part of the Palaeozoic weathering cap constitute the “Niebla-Posadas” aquifer.

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## CHAPTER 3. THE LAS CRUCES DEPOSIT, IBERIAN PYRITE BELT, SPAIN

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*This chapter is based on the paper:*

Yesares, L., Sáez, R., Nieto, J.M., Almodóvar, G.R., Gómez, C., and Escobar, J.M., 2015. The Las Cruces deposit, Iberian Pyrite Belt, Spain: *Ore Geology Reviews*. 66: 25–46.

Este capítulo representa un **estudio general del depósito de Las Cruces**. Este trabajo está basado en las observaciones geológicas y estructurales, a diferentes escalas, realizadas en los afloramientos exhumados durante las labores mineras y la testificación de testigos de sondeos realizados por CLC S.A. durante las fases de evaluación y explotación del yacimiento. Este trabajo también aborda un estudio mineralógico y textural de las diferentes mineralizaciones primarias y supergénicas del depósito de Las Cruces. Los datos obtenidos permitieron establecer un modelo genético para la formación del yacimiento. Este modelo explica el origen de los sulfuros primarios, su posterior supergénesis y su evolución bajo la cobertera sedimentaria de la Cuenca del Guadalquivir.

### CHAPTER 3. THE LAS CRUCES DEPOSIT, IBERIAN PYRITE BELT, SPAIN

Debido a restricciones relativas a los derechos de autor, el artículo que forma parte de este apartado ha sido retirado de la tesis. Dicho artículo ha sido sustituido por la referencia bibliográfica, enlace al texto y resumen.

Yesares Ortiz, M.D., Sáez Ramos, R., Nieto Liñán, J.M., Ruiz de Almodovar Sel, G., Gómez, C., Escobar, J.M.: "The Las Cruces deposit, Iberian Pyrite Belt, Spain". Vol. 66, págs.. 25-46, (2015). DOI: 10.1016/j.oregeorev.2014.10.019

Enlace al texto completo del artículo (solo para miembros de la UHU):

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Acceso Abierto a la versión post-print del artículo en Arias Montano, Repositorio Institucional de la Universidad de Huelva:

<http://hdl.handle.net/10272/12205>

#### **RESUMEN:**

The Las Cruces deposit is located at the eastern margin of the Iberian Pyrite Belt (IPB), beneath the Neogene-Quaternary deposits of the Guadalquivir Basin. These sediments covered and preserved the supergene profile somewhat after its generation until its recent discovering. For this reason, the Las Cruces ore deposits, together with Lagoa Salgada in Portugal, are the only known deposits in the IPB that preserve the entire weathering profile, including both the gossan and the enrichment zone. In that sense, the present study provides new data on the IPB ore deposits and their post-Palaeozoic evolution.

The primary mineralization consists of massive and semi-massive polymetallic sulfides overlaying a cupriferous and pyritic stockwork. The supergene enrichment extends from the primary zone to gossan and consists of a thick cementation zone characterized by intense replacement of part of the primary sulfides by Cu-rich supergene sulfides.

At present, the only economic resource of Las Cruces is the cementation zone, with initial reserves of 17.6 Mt @ 6.2% Cu, but the orebody also includes significant contents of Cu and Zn within the primary mineralization, and Au, Ag, and Pb in the gossan.

Mineralogical and geochemical data confirm that the primary mineralization at Las Cruces resembles other IPB deposits in terms of distribution and evolution, however the gossan and cementation zone show an uncommon evolution for this kind of

supergene profile. The major singularity that makes the Las Cruces supergene mineralisation noticeably different from others in the IPB or elsewhere resides in its unusual mineralogical composition, mostly comprised of newly-formed siderite, calcite, Fe-sulfides and galena.

The genetic model proposed for the Las Cruces deposit includes three main stages: (1) ore genesis and evolution of primary mineralization, which seems to be comparable to other IPB deposits; (2) genesis of Cu-rich secondary mineralization and gossan by weathering, after Miocene exhumation, of the upper part of the massive sulfide deposit, under oxidizing and acidic conditions; and (3) late evolution of supergene profile below the carbonated-rich sediments of the Guadalquivir Basin, with the subsequent change in the redox conditions due to water–rock interaction between the supergene profile and basinal fluids.



## CHAPTER 4. MINERALOGICAL EVOLUTION OF THE LAS CRUCES GOSSAN CAP (IBERIAN PYRITE BELT): FROM SUBAERIAL TO UNDERGROUND CONDITIONS

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*This chapter is based on the paper:*

Yesares, L., Sáez, R., Almodóvar, G., Nieto, J.M., Gómez, C., Ovejero, G. Mineralogical evolution of the Las Cruces Gossan Cap (Iberian Pyrite Belt): from subaerial to underground conditions: Submitted to Ore Geology Reviews.

En este capítulo se realiza un **análisis mineralógico detallado** del gossan de Las Cruces. Desde el punto de vista metodológico se han aplicado técnicas analíticas como microscopía óptica para las determinaciones petrográficas de minerales y análisis textural, Difracción de Rayos X, SEM-EDS y EPMA. Los datos obtenidos permitieron establecer detalles respecto a la inusual mineralogía que compone esta mineralización única y establecer una secuencia de evolución mineral que permite definir las condiciones fisicoquímicas de los fluidos mineralizadores. Una de las conclusiones más importantes que se presentan es la interacción de la cobertera sedimentaria suprayacente y el depósito como un sistema abierto.

#### **CHAPTER 4. MINERALOGICAL EVOLUTION OF THE LAS CRUCES GOSSAN CAP (IBERIAN PYRITE BELT): FROM SUBAERIAL TO UNDERGROUND CONDITIONS**

Debido a restricciones relativas a los derechos de autor, el artículo que forma parte de este apartado ha sido retirado de la tesis. Dicho artículo ha sido sustituido por la referencia bibliográfica y resumen.

Yesares Ortiz, M.D., Sáez Ramos, R., Ruiz de Almodóvar Sel, G., Nieto Liñaán, J.M., Gómez, C., Ovejero, G.: "Mineralogical evolution of the Las Cruces Gossan Cap (Iberian Pyrite Belt): from subaerial to underground conditions". Submitted to *Ore Geology Reviews*

##### **RESUMEN:**

The Las Cruces VMS deposit is located at the eastern corner of the Iberian Pyrite Belt (SW Spain) and is overlaid by 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 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, fulloppite, plagionite, boulangerite, plumosite, jordanite-geocronite series, Ag-Hg-Sb sulfides and sulfosalts including miargyrite, pyrargyrite, sternbergite, acanthite, freibergite cinnabar, Ag-Au-Hg amalgamas; 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 appears 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 derived in the carbonatization and sulfidation of the gossan, and thus 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.



## CHAPTER 5. THE PRECIOUS METALS OCCURRENCES IN THE LAS CRUCES GOSSAN, IBERIAN PYRITE BELT, SPAIN

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*This chapter is based on the papers:*

Yesares, L., Sáez, R., Nieto, J.M., Almodóvar, G.R, and Stephen Cooper, S., 2014. Supergene enrichment of precious metals by natural amalgamation in the Las Cruces weathering profile (Iberian Pyrite Belt, SW Spain): *Ore Geology Reviews*. 58: 14-26.

Yesares, L., Aiglsperger, T., Sáez, R., Almodóvar, G.R., Nieto and J.M., Proenza, J.A., Gómez, C., Escobar, J.M., 2015. Gold Behavior in Supergene Profiles Under Changing Redox Conditions: The Example of the Las Cruces Deposit, Iberian Pyrite Belt: *Economic Geology*. 110:2109-2126.

Este capítulo analiza conjuntamente las características de las tres **mineralizaciones supergénicas de metales preciosos** encontradas en el perfil supergénico del depósito de Las Cruces. Con este objetivo, se han determinado la distribución de Au y Ag y la relación entre estos metales y las diferentes facies y litologías del perfil supergénico. Además, se han caracterizado la composición química de las diferentes partículas de metales preciosos. Finalmente, este capítulo propone los diferentes mecanismos de transporte de Au y Ag y su concentración en el perfil supergénico de Las Cruces.



## **Supergene enrichment of precious metals by natural amalgamation in the Las Cruces weathering profile (Iberian Pyrite Belt, SW Spain)**

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Yesares, L., Sáez, R., Nieto, J.M., Almodóvar, G.R. and Stephen Cooper, S.  
Ore Geology Reviews.  
58: 14-26 (2014)

El objetivo de este trabajo es conocer las **concentraciones de metales preciosos del depósito de Las Cruces**. Con este fin, se estudiaron de manera comparada la distribución geoquímica de oro y plata, las litologías que contienen estos elementos y su mineralogía. Los datos obtenidos muestran que la mayor parte de los metales preciosos del depósito de Las Cruces se encuentran concentradas como amalgamas de Au-Ag-Hg en la parte baja del gossan, principalmente asociados a un horizonte de pizarras negras intensamente lixiviadas. Este trabajo propone dos etapas para la formación de esta mineralización de metales preciosos: (1) liberación, movilización, precipitación de los metales durante la exhumación del yacimiento y meteorización de parte de este; y (2) movilización y fijación de Au, Ag y Hg durante la evolución del perfil supergénico bajo la Cobertera sedimentaria de la Cuenca del Guadalquivir.



## Gold Behavior in supergene profiles under changing redox conditions: the example of the Las Cruces deposit, Iberian Pyrite Belt

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Yesares, L., Aiglsperger, T., Sáez, R., Almodóvar, G.R., Nieto and J.M., Proenza, J.A., Gómez, C., Escobar, J.M.  
Economic Geology.  
110: 1-18 (2015)

El objetivo de este trabajo es caracterizar las mineralizaciones de **metales preciosos contenidas en la parte alta del gossan y en la zona de cementación**, ambas del depósito de Las Cruces. Para ello se estudiaron los contenidos en oro y plata de las diferentes litologías y se realizaron concentrados por gravedad por hidroseparación. Los datos obtenidos muestran significantes diferencias entre las mineralizaciones de metales preciosos. Las principales diferencias radican en las litologías que contienen estos elementos, las asociaciones minerales, las texturas y la pureza de las partículas de metales preciosos. Los mecanismos propuestos de movilización y precipitación de metales preciosos en el perfil supergénico de Las Cruces consisten en: (1) liberación, movilización, precipitación de oro y plata durante la exhumación del yacimiento y meteorización de parte de este; y (2) movilización y fijación de oro y plata durante la evolución del perfil supergénico bajo la Cobertera sedimentaria de la Cuenca del Guadalquivir.

## CHAPTER 5. THE PRECIOUS METALS OCCURRENCES IN THE LAS CRUCES GOSSAN, IBERIAN PYRITE BELT, SPAIN

Debido a restricciones relativas a los derechos de autor, los artículos que forman parte de este apartado han sido retirados de la tesis. Dichos artículos han sido sustituidos por la referencia bibliográfica, enlace al texto y resumen.

- Yesares Ortiz, M.D., Sáez Ramos, R., Nieto Liñán, J.M., Ruiz de Almodóvar Sel, G., Cooper, S.: "Supergene enrichment of precious metals by natural amalgamation in the Las Cruces weathering profile (Iberian Pyrite Belt, SW Spain)". *Ore Geology Reviews*. Vol. 58, págs. 14-26, (2014). DOI: 10.1016/j.oregeorev.2013.10.004

Enlace al texto completo del artículo (solo para miembros de la UHU):

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Acceso Abierto a la versión post-print del artículo en Arias Montano, Repositorio Institucional de la Universidad de Huelva:

<http://hdl.handle.net/10272/12210>

### RESUMEN:

Natural Au–Ag–Hg alloys occur in the Las Cruces ore deposit, in the eastern part of the Iberian Pyrite Belt. They are mainly concentrated in the lower part of the gossan profile including a sheared black shale level where the gossan makes contact with a barren pyrite zone within the supergene Cu-rich mineralization.

Drill core analyses show a heterogeneous distribution of Au, Ag, and Hg within the weathering profile, with mean values of 5.1 ppm, 155 ppm, and 52 ppm, respectively. In general, the absolute tenures increase towards the bottom of the weathered profile. Mineralogical studies conducted on samples from the active mine workings indicate that Hg and precious metals occur mainly as Au–Ag–Hg alloys. These associations constitute the best potential resource for precious metals at the Las Cruces deposit.

This paper describes how this unusual precious metal enrichment is produced along the weathering profile by supergene processes. Combining paragenetic information, mineral chemistry and the data pertaining to the solubilities of Au, Ag, and Hg in a weathering profile, we suggest a two-stage genetic model for the formation of the Las Cruces Au–Ag–Hg mineralization: (1) release of Au, Ag, and Hg from the massive sulfide deposit by weathering processes during the gossan formation. At pH < 5.5 and Eh > 0.9 V conditions, Au, Ag and Hg are mobilized downward through the weathering profile as chloride complexes and fixed as elemental Au, halides, oxides, and sulfates; and (2) remobilization of Hg, Ag, and Au in the gossan after the deposit was buried beneath the Neogene carbonate-rich sedimentary cover. The buffering capacity of the percolating fluids due to their interaction with the carbonate-rich sedimentary pile

leads to significant mineralogical and geochemical changes. At near-neutral conditions (pH = 6–7; Eh ≈ 0 V), Hg, Ag, and Au are newly-remobilized as thiosulfate, sulfate, and hydroxide complexes and newly-fixed by sorption during ferric hydroxide formation and as sulfates. Several cycles of dissolution–precipitation of Au, Ag, and Hg near the redox front occur by oscillations in the water table and changes in the pH–Eh conditions. The interaction of downward migrating fluids with high reductant lithologies (black shales and massive sulfides) seems to be responsible for the reduction of different complexes and for the precipitation of cinnabar, Ag-sulfides and sulfosalts as well as the precipitation of Au–Ag–Hg amalgams.

- Yesares Ortiz, M.D., Aiglsperger, T., Sáez Ramos, R., Ruiz de Almodóvar Sel, Nieto Liñán, J.M., Proenza, J.A., Gómez, C., Escobar, J.M.: “Gold Behavior in Supergene Profiles Under Changing Redox Conditions: The Example of the Las Cruces Deposit, Iberian Pyrite Belt”. *Economic Geology*. Vol. 110, págs. 2109-2126, (2015). DOI: 10.2113/econgeo.110.8.2109

Enlace al texto completo del artículo (solo para miembros de la UHU):

<http://econgeo.geoscienceworld.org/content/110/8/2109.short?related-urls=yes&legid=econgeo;110/8/2109>

Acceso Abierto a la versión post-print del artículo en Arias Montano, Repositorio Institucional de la Universidad de Huelva:

<http://hdl.handle.net/10272/12204>

## **RESUMEN:**

The Las Cruces deposit is in the eastern end of the Iberian Pyrite Belt (SW Spain). It is currently being mined by Cobre Las Cruces S.A. The main operation is focused on the supergene Cu-enriched zone (initial reserves of 17.6 Mt @ 6.2% Cu). An Au-Ag-Pb-rich gossan resource (3.6 Mt @ 3.3% Pb, 2.5 g/t Au, and 56.3 g/t Ag) occurs in the upper part of the deposit. The Au grade ranges from 0.01 ppm to >100 ppm, and occurs as three different Au ore types: (1) Au mineralization in the upper part of the gossan linked to Fe-oxides lithofacies, (2) Au concentration in the lower part of the gossan associated with leached black shales, and (3) Au ore in the cementation zone related to subvertical fractures.

A hydroseparation device has been used to obtain heavy mineral concentrates from selected samples of different ore types. Reflected-light microscopy, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and electron probe microanalysis (EPMA) were used to study the separated Au particles. Significant differences between the defined ore types include the Au-bearing lithologies, mineral

associations, textural features, particle sizes, morphologies, and fineness. Au-rich minerals include native Au, Au-Ag electrum, and Au-Ag-Hg amalgams. Gold-bearing mineral associations include Pb-oxihalides, Fe-oxides, galena, pyrite, cinnabar, and Ag-sulfosalts.

The Au enrichment mechanism in the supergene profile involves (1) dissolution of Au from the primary sulfides as chloride-rich ionic complexes during the weathering of the deposit under subaerial exposure; dissolved Au is transported downward through the supergene profile under acidic and oxidized conditions; (2) destabilization of the Au complexes by Fe-controlled redox reactions; as a consequence, coarse-grained, high-fineness Au particles precipitated in association with Fe-oxyhydroxides. This resulted in secondary concentration in the upper gossan; and (3) after deposition of cover sediments took place a progressive change in the system conditions resulting in a later Au remobilization as hydroxidehalide, hydroxide, thiosulfate, and bisulfide complexes in the lowermost gossan and cementation zone. The main pathways for migration of enriched fluids to the cementation zone are secondary permeability zones linked to Alpine reactivated faults. Deposition of Au seems to be related to fluid interaction with reductant lithologies, including black shales and the primary sulfides.



## CAPÍTULO 6. CONCLUSIONES

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De acuerdo con los objetivos propuestos en este estudio y tras la evaluación de los resultados obtenidos en los diferentes capítulos, las conclusiones se presentan agrupadas según **los aspectos geológicos del depósito, la mineralogía del gossan y las mineralizaciones supergénicas de metales preciosos.**

### **Conclusiones relacionadas con los aspectos geológicos del depósito**

- ✓ Los sulfuros primarios del yacimiento de Las Cruces presentan muchas analogías con respecto a otros depósitos de tipo VMS, pero sin embargo, el perfil de alteración supergénica difiere de otros conocidos.
- ✓ En común con otros yacimientos de sulfuros masivos de la Faja Pirítica Ibérica, los sulfuros primarios del depósito de Las Cruces presentan: la mineralogía, el estilo tectónico, el tipo de roca encajante, las zonaciones geoquímicas y los diferentes tipos de mineralizaciones que presenta.
- ✓ Las principales peculiaridades del depósito de Las Cruces radican en su perfil supergénico, siendo las más significativas: las características geométricas como su estructura interna o el espesor de la mineralización supergénica de cobre, y las características mineralógicas del gossan. Estas peculiaridades tienen como consecuencia las elevados tonelajes y leyes del yacimiento.
- ✓ La característica más significativa del perfil supergénico del depósito de Las Cruces es la mineralogía. Las primeras asociaciones minerales identificadas en la zona de cementación y en el gossan están relacionadas con la alteración de los sulfuros primario en condiciones superficiales. Estas son las asociaciones descritas habitualmente en los perfiles supergénicos. Sin embargo, las últimas asociaciones identificadas no son comparables con este tipo de mineralizaciones.
- ✓ De acuerdo con los datos basados en la geología del depósito de Las Cruces, se propone un modelo de genético general en el que se explica: (1) la formación de los sulfuros primarios similar al del resto de yacimientos de la Faja Pirítica Ibérica; y (2) las anomalías mineralógicas y geoquímicas presentes en el perfil de alteración se atribuyen a la evolución del yacimiento bajo la cobertera sedimentaria.
- ✓ Los eventos regresivos y transgresivos que tuvieron lugar en el Mioceno provocaron cambios en el flujo hidrogeológico y cambios de las condiciones físico-químicas del medio. Esto afectó directamente a los procesos de interacción agua-roca dando lugar a dos etapas genéticas en el perfil supergénico de Las Cruces: (1) La oxidación en condiciones subaereas y la lixiviación de una parte de los sulfuros primarios. Esto dio lugar a la formación de Fe-oxihidroxidos en la zona vadosa, y la precipitación de sulfuros de cobre secundarios en la zona saturada a partir de las soluciones descendientes ricas en cobre; y (2) los eventos transgresivos del Mioceno y la sedimentación asociada dieron lugar a un periodo de interacción agua marina-gossan y a la neutralización de los fluidos de cuenca. Estos procesos favorecieron la reducción del gossan y el reemplazamiento de las fases primarias del gossan por siderita, sulfuros

de Fe y galena. Estos procesos reactivaron la zona de cementación resultando en una segunda generación de sulfuros de cobre asociados a calcita, sulfuros de Ag y cinabrio.

### **Conclusiones referentes a la mineralogía del gossan**

- ✓ La mineralogía que compone el gossan de Las Cruces es completamente diferentes a otros perfiles de meteorización conocidos en la Faja Pirítica Ibérica y en otras provincias metalogenéticas. La mineralogía mayoritaria consiste en: carbonatos, incluidos siderita, calcita y cerusita; sulfuros de Fe, como piritita, marcasita, greigita y pirrotina; y galena. La mineralogía subordinada está formada por: sulfuros y sulfosales de Pb y Sb, como galena, stibina, fulopita, plagionita, bulangerita, plumosita, jordanita-geocronita y sulfosales de Fe, Pb y Sb sin identificar; sulfuros y sulfosales de Ag, Hg y Sb, incluyendo miargirita, pirargyrita, esternbergita, acantita, freibergita, cinabrio, imiterita, amalgamas de Ag-Au-Hg; y por ultimo minerales de Bi, como bismutinita, galenobismutinita, Bi nativo y sulfosales de Bi y Pb sin identificar. Paradójicamente, hematites y goethita aparecen como fases subordinadas.
- ✓ La compleja secuencia mineralógica reconocida en el gossan de Las Cruces, se puede explicar con un mínimo de tres asociaciones minerales:

(1) La primera compuesta por relictos del gossan primario formados durante la meteorización de los sulfuros en condiciones subaereas. Esta asociación está compuesta por fragmentos de oxihidroxidos de Fe dispersos por el perfil de alteración meteórica. Esta asociación muestras características mineralógicas y geoquímicas comunes a otros gossans conocidos;

(2) La segunda asociación mineral está formada por una primera generación de siderita y una segunda generación de goethita y hematites. Esta asociación está relacionada con la carbonatación del gossan durante el enterramiento del depósito bajo los sedimentos ricos en carbonatos de la Cuenca del Guadalquivir. Esta modificación mineralógica está controlada por la interacción del gossan primario con los fluidos de cuenca;

(3) La tercera asociación está formada por sulfuros generados durante la última etapa de carbonatación. Los principales minerales que la forman son calcita, sulfuros de Fe, galena, estibina, sulfosales de Pb, Fe y Sb, sulfuros y sulfosales de Ag y sulfuros y sulfosales de Bi.

- ✓ El escenario más probable para la precipitación de estos minerales incluye una etapa temprana de transformación del gossan debida la interacción agua marina-gossan tras la subida del nivel del mar durante el Mioceno superior. La evolución mineralógica del gossan continúa bajo la cobertera sedimentaria y por la interacción de los fluidos de cuenca reducidos y ricos en S y el gossan.
- ✓ Tanto la distribución mineral como la variabilidad composicional sugieren que los procesos de carbonatización y sulfidización fueron sistemáticamente controlados por fallas subverticales tardivaricas reactivadas durante la orogenia Alpina. La permeabilidad secundaria asociada con estas fallas proporcionó el camino para la migración de los fluidos de cuenca y su interacción con el gossan primario. La mineralización siderítica y la mineralización de calcita y sulfuros se formaron en relación con esta etapa.
- ✓ En general, se podría decir que las modificaciones en el perfil supergénico de Las Cruces son resultado de la alteración diagenética (sensu estricto) del gossan primario. Esto es congruente con la estrecha relación entre la evolución de los sedimentos carbonatados de la cobertera Neógena y el gossan de Las Cruces, así como su conexión por fracturas. En este sentido, los procesos generales implicados en la modificación del gossan primario son: la removilización de los fluidos mineralizantes dependiendo de las fluctuaciones del nivel freático; la disolución y removilización de carbonatos de la cobertera; la disolución reductiva de los minerales del gossan primario; y la precipitación de minerales neoformados estables con las nuevas condiciones del medio.
- ✓ Las singulares características mineralógicas del perfil meteórico de Las Cruces, sostienen que esta mineralización merece una categoría diferente en los sistemas supergénicos.

### **Conclusiones relacionadas con las mineralizaciones supergénicas de metales preciosos**

- ✓ Las mineralizaciones supergénicas de metales preciosos del depósito de Las Cruces difieren notablemente de las conocidas en otros gossan ricos en Au y Ag. Las diferencias más significativas son:
  - (1) El depósito de Las Cruces tienen leyes muy superiores de metales preciosos comparando con otros depósitos de la Faja Pirítica Ibérica;

(2) La distribución de los metales preciosos en el perfil supergénico y las litologías que lo contienen son más variables que las de otros depósitos de este tipo. Entre las litologías ricas en Au y Ag se incluyen las facies ricas en oxihidroxidos de Fe que se encuentran dispersas en la parte alta del gossan, niveles de pizarras negras lixiviadas que se localizan en la base del gossan y breccias de fallas en la zona de cementación;

(3) El tamaño de las partículas, su composición química, sus texturas, y sus asociaciones minerales son diferentes en Las Cruces en comparación con otros depósitos de este tipo.

- ✓ Las partículas de Au contenidas en las facies formadas por oxihidroxidos de Fe son de tamaño de grano grueso, de alta pureza y están asociadas a nadorita. Por otro lado, las partículas de metales preciosos que se encuentran en los niveles lixiviados de pizarra negra son amalgamas de Au Ag y Hg, de tamaño de grano grueso, asociadas a sulfuros y sulfosales de Ag y Hg. Por último, los metales preciosos contenidos en la zona de cementación aparecen como electrum, de tamaño de grano fino y asociados a proustita.
- ✓ Como en otros depósitos de la Faja Pirítica Ibérica, la concentración supergénica de metales preciosos en Las Cruces es el resultado de la lixiviación de estos durante la meteorización del depósito, mientras que la evolución tardía de Las Cruces bajo los sedimentos de la Cuenca del Guadalquivir hace a las mineralizaciones de Au y Ag de Las Cruces únicas.
- ✓ La existencia de tres mineralizaciones diferentes de metales preciosos en el perfil supergénico de Las Cruces, sugiere que más de un mecanismo estuvo implicado en la disolución, movilización y precipitación de Au y Ag. La presencia de partículas de Au de alta pureza, implica una refinación química producida por la movilización de los metales preciosos vía complejos de haluros durante la oxidación de los sulfuros primarios. Estos procesos tuvieron lugar durante la exhumación del depósito en el Mioceno. Las partículas de Au precipitaron asociadas a oxihidroxidos de Fe, los cuales fueron reemplazados después por carbonatos y sulfuros.
- ✓ Tras la deposición de los sedimentos suprayacentes, las condiciones redox del perfil supergénico cambiaron. Estas fueron progresivamente más reductoras debido a la subida del frente redox, y más alcalinas por la neutralización de los fluidos de cuenca. Los fluidos de cuenca circularon por los sedimentos y el perfil supergénico a través de fracturas subverticales que conectan la cobertera sedimentaria y el depósito. Los cambios progresivos de las condiciones físico-químicas de las soluciones portadoras de metales preciosos, dieron lugar a la movilización de Au y Ag como complejos de

varios tipos incluyendo hidroxihaluros, hidróxidos, tiosulfatos y bisulfuros. De esta manera, los metales preciosos llegaron a la base del gossan y a la zona de cementación, dando lugar a la desestabilización de los complejos y la subsecuente precipitación de amalgamas de Au, Ag y Hg y electrum, los dos asociados a litologías reductoras como las pizarras negras de la base del gossan y las breccias piríticas de la zona de cementación.

