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

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ABSTRACT

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; $Eh \approx 0$ 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.

1. Introduction

The Iberian Pyrite Belt (IPB) has been continuously explored and mined for more than 4500 years (Nocete et al., 2005; Sáez et al., 2003) and includes precious metals within massive sulfide weathering profiles. Examples of gossans mined for Au and Ag since prehistoric times are Riotinto and Filón Sur-Tharsis. Las Cruces is a recently discovered volcanic-hosted massive sulfide deposit in the IPB whose supergene profile differs from others known and contains large resources of precious metals.

Supergene precious metal ores occur essentially as the result of concentration during the weathering of hypogene deposits. In near-surface environments, Ag and Au are released during the oxidative dissolution of primary sulfides. These metals are concentrated and redistributed through the oxidation profile by residual concentration processes.

The mobilization and enrichment of precious metals in oxidizing and acidic environments are well documented (Benedetti and Bouleguè, 1991; Boyle, 1979; Freyssinet et al., 2005; Hough et al., 2009; Reich et al., 2005; Webster and Mann, 1984). Under extreme conditions, precious metals are mobilized through the weathering profile via complexation by different anions, such as a CN^{2-}, OH^-, NH_3, Cl^-, I^-, Br, and HS^- (Groen et al., 1990) until reaching an environment with physical–chemical conditions favorable for precipitation.

Under oxidizing conditions, native Au is the only specie stable (Krupp and Weiser, 1992), whereas Ag can occur as a native element, as halides such as chlorargyrite [ClAg], iodargyrite [IAg], and bromargyrite [BrAg]; or as sulfates of the jarosite group (i.e., argentojarosite $[AgFe_3(SO_4)_2(OH)_6]$) (Dutrizac and Jambor, 1987).

Regarding the supergene profiles of the IPB, native Au has been reported in Filón Sur-Tharsis (Capitán, 2006) and Riotinto (Viñals et al.,

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1995) and the main Ag-bearing phases are halides, acanthite, and argentojarosite, in both Riotinto (Capitán, 2006; Viñals et al., 1995) and Tharsis (Capitán, 2006). The burial of the Las Cruces deposit after oxidation resulted in significant changes that make it very different to common models of precious metal concentration during gossan formation. The most important concerns the formation of Au–Ag–Hg amalgams as the main precious metal minerals at Las Cruces. Hg–Ag amalgams have also been reported in the Lagoa Salgada gossan (Oliveira et al., 2011), whose supergene evolution is similar to that of the Las Cruces deposit. The occurrence of Au–Ag amalgams has consequences regarding the mechanisms of mobilization and precipitation of precious metals in supergene environments.

2. Au, Ag, and Hg mobilization and fixation in supergene profiles

The physico-chemical conditions of precious metal redistribution in weathering profiles have been well documented (Benedetti and Bouleguè, 1991; Krupp and Weiser, 1992; Mann, 1984; Webster and Mann, 1984). Different mechanisms for Au and Ag dissolution, mobilization, and precipitation have been proposed. In oxygenated aqueous solutions, Au and Ag are soluble and transported by organic complexes (Boyle et al., 1975), halogen complexes (Mann, 1984), hydroxide complexes (Wood, 1990), and sulfur ligand complexes (Webster, 1986).

Supergene redistribution of Au and Ag through the weathering profile is dependent on the nature and stability of anionic complexes and their behavior under near-surface weathering conditions (Webster and Mann, 1984). Au and Ag released from the oxidation of primary sulfides are slightly mobilized when the environmental conditions are extremely acidic. These species can be transported down short distances along the weathering profile to environments where the conditions are less acidic. Mann (1984) proposed that in an acidic, oxygenated, saline and Fe-rich aqueous stream environments ($pH < 5.5$; $Eh > 0.9$ V; activity $Cl^- > 10^{-3.2}$), precious metals are mobilized through the weathering profile as Au– and Ag–chloride complexes (Webster and Mann, 1984). These conditions are common in oxidized meteoric waters containing abundant chlorine derived from the dissolution of salts (Ross, 1997). The dissolution of Au and Ag to form chloride complexes is expressed by the following chemical reactions:

$$4Au + 16Cl^- + 3O_2 + 12H^+ = 4AuCl_4^- + 6H_2O(\text{Mann, 1984}) \quad (1)$$

$$4Ag + 4Cl^- + O_2 + 4H^+ = 4AgCl^0 + 2H_20(\text{Mann, 1984}). \quad (2)$$

Au precipitation can be produced by inorganic reduction of Au-chlorides by a slight decrease in Eh (Hough et al., 2008), and also by the reduction of the $AuCl_4^-$ ion with Fe^{2+} by the reaction:

$$4AuCl_4^- + 3Fe^{2+} + 6H_2O = Au^0 + 3FeOOH + 4Cl^- + 9H^+(\text{Mann, 1984}). \quad (3)$$

This reaction involves the simultaneous deposition of both native Au and iron hydroxide. However, $AgCl^0$ is not precipitated as native Ag by the oxidation of Fe^{2+} because the redox potential for $Ag^0/AgCl^0$ is below that of the Fe^{2+}/Fe^{3+} couple (Mann, 1984). Therefore, $AgCl^0$ remains in solution, migrating downward (Saunders, 1993) until reaching an environment where the physico-chemical conditions are less extreme, allowing its precipitation as chlorargyrite.

The sulfide breakdown during weathering processes releases a number of metastable sulfur species as SH^-, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} (Freyssinet et al., 2005). All of them can favor precious metal transport through the profile and can be transformed according to pH and oxygen fugacity (Krupp and Weiser, 1992). Au bisulfide complex $[Au(SH)_2^-]$ can occur in supergene environments under reducing conditions (Anthony et al., 2009; Webster, 1986) and pH near to neutral (Vlassopoulos and Wood, 1990), for example during early supergene alteration stages (Gray et al., 1992). Hence, SH^- ligand is not so important in supergene environments (Freyssinet et al., 2005) although it can be particularly significant in hydrothermal systems (Boyle, 1979; Seward, 1973).

At near-neutral conditions ($pH = 6–7$; $Eh \approx 0$ V) and in the presence of weathered carbonate rocks, the formation of thiosulfate and/or sulfite ions during sulfide oxidation favors the migration of Au and Ag along the weathering profiles as $Au–Ag(S_2O_3)_2^{3-}$ and $Au–Ag(SO_3)_2^{3-}$ (Benedetti and Bouleguè, 1991; Boyle, 1979; Webster and Mann, 1984). Due to its slow kinetic transformation (Rolla and Chakrabarti, 1982), thiosulfate could remain in solution over relatively long periods. Thus, thiosulfate is the most probable complex under near-surface environment and neutral conditions (Webster and Mann, 1984).

The dissolution of Au and Ag to form thiosulfate complexes is expressed by the chemical reactions:

$$2Au^0 + 4S_2O_3^{2-} + 2H^+ + 0.5O_2 = 2Au(SO_3)_2^{3-} + H_2O\,(\text{Freyssinet et al., 2005}) \quad (4)$$

$$2Ag^0 + 4S_2O_3^{2-} + 2H^+ + 0.5O_2 = 2Ag(SO_3)_2^{3-} + H_2O. \quad (5)$$

In addition, the precious metal mobilization as thiosulfate complexes have been successfully used to Au and Ag industrial extraction and recovery of different ore types (Aylmore and Muir, 2001).

However, if the redox conditions increase, thiosulfates are readily oxidized and converted to sulfates (Benedetti and Bouleguè, 1991; Freyssinet et al., 2005). Au — sulfate complexes would rapidly decompose, leaving Au as an uncomplexed Au^+ ion, which would be precipitated by reduction to Au^0 as submicroscopic particles (Benedetti and Bouleguè, 1991) or within the mineralized structures (Freyssinet et al., 2005).

The Au precipitation can be expressed by the following chemical reaction:

$$Au^+ + Fe^{2+} + 2H_20 = Au^0 + FeOOH + 3H^+(\text{Stroffregen, 1986}). \quad (6)$$

Moreover, Ag sulfate remains as stable species in solution (Krupp and Weiser, 1992). The high solubility of Ag_2SO_4 makes its occurrence as a stable oxidation product of Ag unlikely, although more complex sulfate phases (i.e., argentojarosite) are common in sulfide weathering profiles (Dutrizac and Jambor, 1987). Hence, Ag_2SO_4 is transported through the oxidation profile to the water table, where Ag_2SO_4 becomes destabilized through reduction and Ag can be reprecipitated as sulfide below the redox front.

Hg mobilization during the massive sulfide weathering is less well documented. Therefore, little is known about the mechanisms of Hg dissolution and re-precipitation in these environments.

During sulfide weathering, mercurous compounds (Hg^+) are rapidly oxidized to mercuric forms (Hg^{2+}) and are slightly mobilized through the weathering profiles as $HgCl_2^0$, which is the stable species in solution under oxidizing and acidic conditions (Davis et al., 1997). The oxidative dissolution of Hg to form chloride complexes could occur through the reaction:

$$Hg^{2+} + 2Cl^- + 3O_2 + 12H^+ = HgCl_2^0 + 6H_2O. \quad (7)$$

Under neutral and high pH conditions, Hg^{2+} is stable in solution and is easily complexed by OH^-, enhancing its solubility by the reactions:

$$Hg^{2+} + 0.5O_2 + H_2O = Hg(OH)_2^0 + H^+ \quad (8)$$

$$HgCl_2 + 2H_2O = Hg(OH)_2^0 + 2H^+ + Cl^-(\text{Hepler and Olofsson, 1975}). \quad (9)$$

The redistribution and fixation of secondary Hg-minerals through the weathering profile are dependent on the redox and pH conditions. Under oxidizing and acidic conditions, Hg^{2+} can be precipitated as