Groundwater-Gossan Interaction at the Las Cruces Ore Deposit (SW Spain)

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INTRODUCTION

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. The primary mineralization consists of massive and semi-massive polymetallic sulfides overlaying a cupriferous and pyritic stockwork. The supergene mineralization extends from the primary sulfides 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, 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 that of other IPB deposits in terms of distribution and evolution.
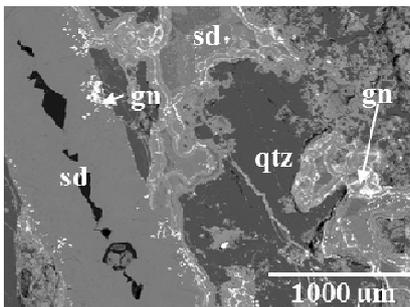

Figure 1. Reflected light microscope image of the sideritic facies: qtz= quartz; sd= siderite; gn= galena

The gossan, however, shows an uncommon mineralogy for this kind of supergene profile. There, goethite has been almost entirely replaced by siderite and minor amounts of calcite, galena, pyrite/marcasite and precious
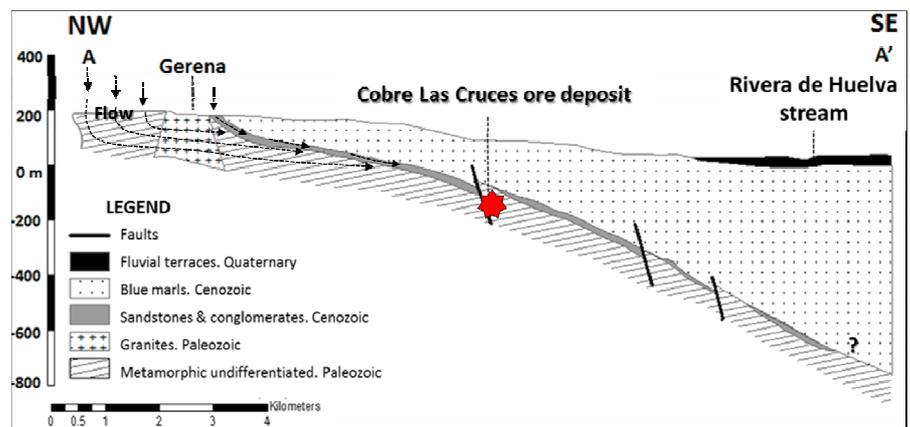

Figure 2: Generalized cross section NW-SE of the study area.

metals (Figure 1) (Yesares et al., 2014). We postulate here that such unusual mineralogy can be the result of the interaction of present day groundwater with an ancient goethite gossan.

HYDROGEOLOGICAL SETTING

The study area is located in the Northern edge of the south-western Guadalquivir basin, about 20 km North of Sevilla between the Guadiamar and the Rivera de Huelva rivers.

The geology in the study area is made up of Cenozoic materials constituting a bluish marl "FM arcillas de Gibraleón" of marine origin wedge that thickens toward the south and below conglomerates, detrital limestones and sandstones forming the aquifer Niebla-Posadas (NP). The NP materials outcrop on the northern margin of the basin and become confined below the bluish marls that increases in thickness to the south. The Paleozoic materials of the basement form a paleorelief and are affected by a series of SW-NE oriented fractures and other less relevant NW-SE fractures (Figure 2). Recharge to the NP aquifer takes place by rainwater infiltration in the northern part of the area, close to Gerena and Guillena, and

by upward flow from the underlying Paleozoic aquifer when conditions are favorable. Groundwater flow is dominantly north-west to south-east (Figure 2). Temperature also increases from NW to SE, reaching 38°C around the deposit.

Groundwater was dated using ^{3}H, ^{14}C and ^{36}Cl, and the following NW-SE zonation was obtained: recharge (<0.06 ky), intermediate (0.06 to 20 ky), deeper 1 (20 to 30 ky) and deeper 2 (> 30ky). The deeper 2 waters were sampled close to the ore body.

HYDROCHEMICAL SETTING

46 samples in wells/piezometers were collected during a field campaign and the physico-chemical parameters as temperature, pH, Eh, Electrical Conductivity (EC) and alkalinity (TAC) were measured in the field. Major and trace elements, dissolved gases (CH_4 and H_2S) and stable isotopes ($\delta^{34}S/\delta^{18}O$ in sulfate, $\delta^{13}C_c$,) were also determined in the laboratory.

Following the flow direction, groundwater evolves from Ca-HCO3 to Na-HCO3 and finally NaCl. The Na-Cl and Br-Cl ratios suggest mixture of fresh
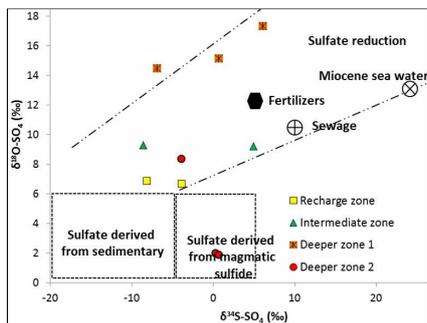
Figure 3: Representation of the isotopic content of sulfates in groundwater.

relict syndepositional water trapped in the pores. Concomitantly, pH increases to around 10 and Eh decreases to around -300 mV close to the ore deposit.

The sulfate isotope values show a distinct variation from the recharge to the deeper zones (*Figure 3*). Samples from the recharge zone evolve towards lighter ^{34}S and heavier ^{18}O values compatible with oxidation of sulfides either in granites, massive sulfide deposits or dispersed in the sedimentary materials. Samples from the intermediate and especially from the deeper 1 zone show a distinct trend towards heavier δ^{18}O and δ^{34}S values indicating that there is sulfate-reduction. This is confirmed by the sulfate isotope, the low sulfate concentrations and the presence of dissolved H$_2$S in the gas samples.
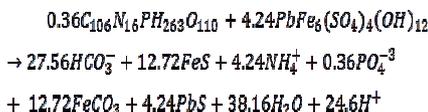
WATER-ROCK INTERACTION

When present day groundwater reaches a goethite gossan, the following reaction triggered by the decomposition of organic matter is thermodynamically favored: (R1)

$$C_{106}N_{16}PH_{263}O_{110} + 424FeOOH + 331H^+ + HCO_3^-$$
$$\rightarrow 424FeCO_3 + 16NH_4^+ + PO_4^{-3} + 636H_2O$$
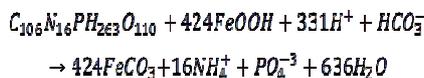
Since groundwater transports very low content of Pb (< 1ppb), an additional source of the element to form galena is assumed to be present in the initial gossan. Plumbojarosite has been described very often as the mineral limiting the low Pb concentrations of massive sulfide oxidation sites, and particularly in the Iberian Pyrite Belt (Figueiredo et al., **2011**). Therefore, a supplementary reaction taking place in a lower extent (two orders of magnitude less) has been assumed: (R2)

Tª	Eh	pH	Cl	Al	Ba	Ca	Fe	K	Mg	Mn	Na	S[-2]	S(6)	Sl	Sr	Zn	Cu	C(4)	C(-4)
37.5	-300	7.33	1581	-0.3	25.5	95	0.01	15	30	0.11	1061	0.11	0.98	10.6	5.59	0.01	0.01	390	4.6

Table 1: Chemical composition of deep groundwater from CLC-well 308 (concentration in ppm)

$$0.36C_{106}N_{16}PH_{263}O_{110} + 4.24PbFe_6(SO_4)_4(OH)_{12}$$
$$\rightarrow 27.56HCO_3^- + 12.72FeS + 4.24NH_4^+ + 0.36PO_4^{-3}$$
$$+ 12.72FeCO_3 + 4.24PbS + 38.16H_2O + 24.6H^+$$

The reduction of plumbojarosite by the Fe-reducing bacteria (S. putrefaciens) has been described in the laboratory (Smeaton et al. **2012**).

The evolution of the water-gossan interaction is described in Figure 4. It has been modeled with the code PHREEQC and the WATEQ database (Parkhurst and Appelo, **2014**). Thermodynamic data for plumbojarosite have been extracted from Forray et al. (**2010**).
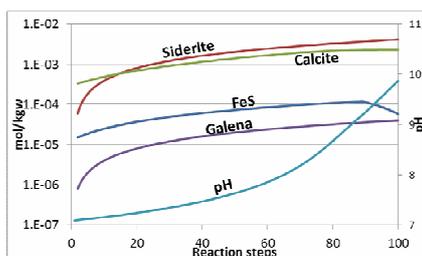

Figure 4: Evolution of the reaction of 1 kg of water from the area close to the deposit (Table 1) with 4 mmol goethite and 0.04 mmol plumbojarosite.

Amorphous FeS is also initially formed as a precursor phase for greigite, marcasite and pyrite (Rickard and Morse, **2005**), which are the phase actually found in the paragenesis. This hypothesis is supported by the following evidences from deep groundwaters:

- Unusually high pH values (up to 10).
- Unusually high concentration (up to 9 ppm) of NH$_4^+$ from the anoxic oxidation of organic matter (R1).
- Presence of As (III) in some sample as product of FeOOH dissolution.
- Saturation indices of siderite close to equilibrium.
- Very low amount of Fe (< 10 ppb) is detected in groundwater.
- The δ^{13}C values of siderite range from -13.4 and -47.95 per mil (Capitan, 2006), pointing to the origin of the C from organic matter oxidation.

CONCLUSION

The reduction of gossan minerals (goethite and possibly plumbojarosite) at expenses of the organic matter dissolved in present day deep groundwater is able to form the unusual mineralogy (siderite, galena) of the Las Cruces gossan deposit. This conceptual idea is consistent with the features observed in the solid and aqueous phases.

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