

Preliminary study of the Candelaria mine mineralization in Gallinero de Cameros (La Rioja)

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INTRODUCTION

The Candelaria mine is located in the Valoria river valley in Gallinero de Cameros (La Rioja), WGS84 30T 531550 E 4668600N, within the Cameros Basin. This was formed during the second extensional stage of the Iberian Mesozoic rift (Upper Jurassic-Lower Cretaceous) and, later, in the Alpine Orogeny, underwent a tectonic inversion, constituting the current positive relief (Salas et al., 2001). The host rocks of the mineralization are quartzitic conglomerates and sandstones of fluvial environments laterally related to shallow carbonate lakes belonging to the Tera Group (Purbeck facies). This basin has a great mining tradition as evidenced by different documents; however, there are hardly any studies of its mineralizations.

The Candelaria mine was exploited in 1889 by Don Braulio de Pablo after confirmation by the Civil Government of the Province of Logroño. In the Municipal Archives of Gallinero de Cameros, it is described as a "argentiferous lead" mine. Nowadays, only a small gallery and a dump of small dimensions remain in the area. The aim of this work was to perform a preliminary chemical-mineralogical study of the Candelaria mine mineralization.

MATERIALS AND METHODS

Different samples were taken from the surface of the dump (fragments of conglomerates, metaconglomerates and quartzites with mineralization disseminated in carbonate and quartz veins) and inside the gallery (patinas, stalactites, gours and flags of white, blue turquoise and ochre colors) (Fig.1). These were characterized by X-ray diffraction, polarizing microscopy (transmitted and reflected light) and electron microprobe (Centro Nacional de Microscopía Electrónica, Madrid). The following elements were analyzed: Al, Sb, As, S, Ca, Cu, Fe, Ag, Pb and Si.

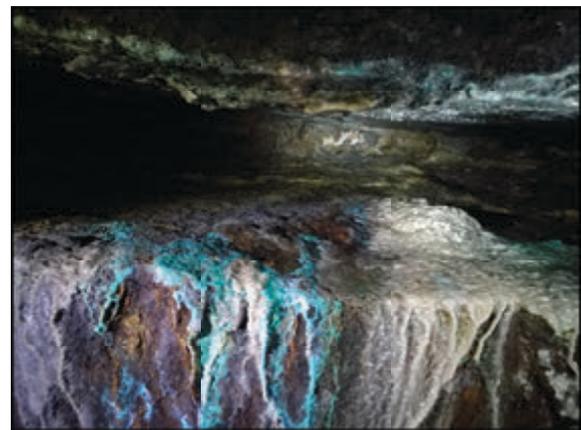


Fig. 1. Endokarstic forms in the gallery of the Candelaria mine.

RESULTS

Dump samples

Arsenopyrite (FeAsS), galena (PbS), tennantite ((Cu,Fe)₁₂As₄S₁₃), chalcopyrite (CuFeS₂) and pyrite (FeS₂) were identified in conglomerates and metaconglomerates. These minerals appeared finely disseminated in these rocks and in small veins together with calcite or quartz. Galena, allotriomorphic and interclastic, (Fig.2.a) and arsenopyrite, idiomorphic, (Fig.2.b) occurred rimmed by tennantite and, sometimes, by chalcopyrite. This latter also occurred in the conglomerate brecciated zones filled with quartz and dolomite. Either idiomorphic or subidiomorphic pyrite crystals appeared crosscutting clasts and inside them. Except for galena, the same minerals have been identified in quartzite samples. In these rocks chalcopyrite appeared inside idiomorphic arsenopyrite crystals. Both arsenopyrite and idiomorphic pyrite appeared cracked and rimmed by chalcopyrite and tennantite. There were brecciated zones with quartz and sericite where disseminated chalcopyrite was also present.

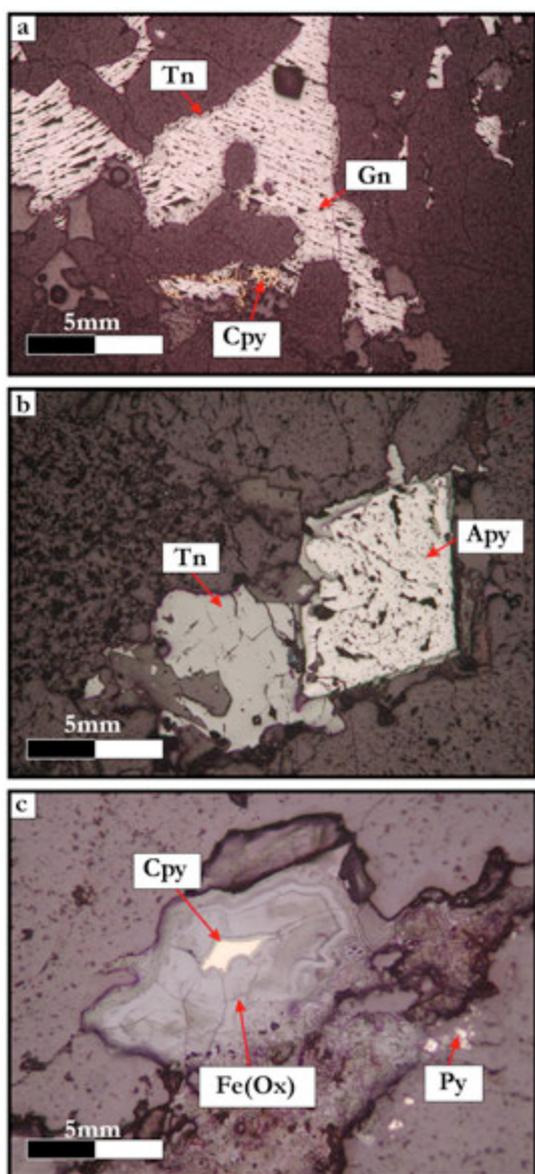


Fig. 2. Microscopic images (reflected light-uncrossed polarizers): a) interclastic galena (Gn) rimmed by tennantite (Tn), and chalcopyrite (Cpy), b) idiomorphic arsenopyrite (Apy) surrounded by tennantite, and c) chalcopyrite altered to iron (oxyhydr)oxides (Fe(Ox)), and framboidal pyrite (Py).

Spot chemical analyses performed on these minerals revealed significant contents (wt.%) of Sb (0.47-2.04), Pb (0.11-0.21) and Ag (up to 1) in tennantite, Pb (0.11-0.15), Sb (0.11-0.19), Cu (up to 0.16) and Ag (up to 0.04) in arsenopyrite, and Pb (0.16-0.41), Sb (0.04-0.3) and Ag (0.01-0.11) in chalcopyrite. Remarkable were also the contents of Pb (0.27-1.07), Sb (up to 0.31), Ag (up to 0.35), As (up to 0.43) and Cu (up to 1.54) in pyrite. Galena reached Sb, Cu and Fe contents up to 0.38, 0.39 and 0.24, respectively, whereas those of Ag were below the detection limit.

In addition to sulfides, the following minerals have been identified as secondary products: azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$), jarosite ($\text{KFe}(\text{SO}_4)_2(\text{OH})_6$) and iron (oxyhydr)oxides. Malachite was the most abundant and appeared with a fibrous

radial habit filling cracks. Jarosite occurred forming masses constituted by microscopic spheres, surrounded by iron (oxyhydr)oxides. These also appeared forming cracked concentric bands of different grayish colors, isotropic, substituting for chalcopyrite occurring in corroded relicts inside them (Fig.2.c). Spot chemical analyses on malachite showed relatively significant contents (wt.%) of As_2O_5 (0.37-0.99), PbO (0.31-0.56), Sb_2O_5 (0.09-0.23) and Fe_2O_3 (0.01-0.09), whereas those carried out on iron (oxyhydr)oxides substituting for chalcopyrite revealed considerable contents of PbO (5.42-7.79), CuO (5.78-6.97), As_2O_5 (2.62-4.13) and Sb_2O_5 (0.15-0.28). Studies performed on the chalcopyrite oxidation mechanism have concluded that at high pH there is a preferential oxidation of Fe with respect to Cu, giving rise to the precipitation of iron (oxyhydr)oxides over its surface (Xionga et al., 2018).

Gallery samples

The following minerals were identified in these samples: calcite, gypsum, malachite, brochantite ($\text{Cu}_4(\text{SO}_4)(\text{OH})_6$), chalcantite ($\text{Cu}_4(\text{SO}_4) \cdot 5\text{H}_2\text{O}$) and scarbroite ($\text{Al}_5(\text{OH})_{13}(\text{CO}_3) \cdot 5\text{H}_2\text{O}$). Some of the stalactites showed a concentric zonation: iron (oxyhydr)oxides (core)-brochantite/malachite-micritic and sparitic calcite (border). Brochantite and malachite presented a botryoidal and fibrous radial habit, respectively.

CONCLUSIONS

The bibliographic search has allowed the mine name assignment (Candelaria) which was known so far as Valoria mine. This mine presents a Cu-Pb-Fe mineralization. Although historic documents described it as a "argentiferous lead" (argentiferous galena) mine, its Ag contents were below the detection limit, with only tennantite reaching values up to 1%.

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