

Preliminary study of the Serrana Segunda copper mine (Gallinero de Cameros, La Rioja).

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INTRODUCTION

The Cameros Basin, situated in the NW of the Iberian mountain range, is one of the basins belonging to the Mesozoic Iberian Rift system in which four megacycles have been distinguished with different stages of rift and postrift, as well as a low-grade metamorphism stage (Mas et al., 2002). In this basin there are some small size mines, barely documented and investigated. One of these is the Serrana Segunda copper mine, located in the Gallinero stream valley, next to the road that connects Gallinero de Cameros with Pradillo. Its last acquisition date back to the beginning of the 20th century (registered in 1909 in the Provincial Historic Archive of La Rioja). In this mining area a gallery and waste heaps are present, with the latter being visible from the road (Fig. 1A and B). The gallery is in a fining upward sequence composed of conglomerates with centimetric clasts in the base and fine to medium grained sandstones, crossed by small, thin carbonate veins, alternated with banded black shales. Occasionally, grey marls appear between the sandstones and shales.

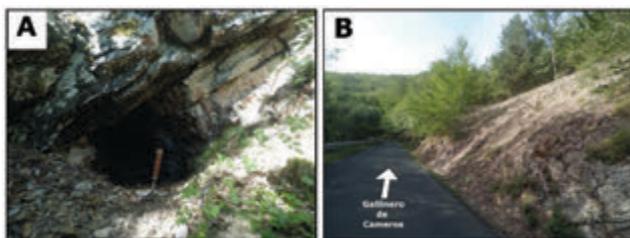


Fig. 1. Gallery's pithead (A) and waste heaps (B)

The aim of this work was the preliminary study of the mineralization of the cited mine.

MATERIALS AND METHODS

The samples under study, taken from the waste heaps and inside the gallery, are fragments of different rocks and carbonate veins. All of them had millimetric metallic minerals finely disseminated (except for the shales where they appeared orientated following deformation planes), and bluish and greenish patinas on their surface, with these later being alteration products of metallic minerals.

All the collected samples were studied by X-ray diffraction (XRD), polarizing microscopy (in transmitted and reflected light) and electron microprobe for the analysis of Al, Sb, As, S, Ca, Cu, Fe, Ag and Pb. A representative patina sample was analysed by Scanning Electron Microscopy. Both spot chemical analyses and secondary electron images were obtained at the National Electronic Microscopy Centre (Madrid)

RESULTS AND DISCUSSION

The minerals identified by XRD in marls, shales and sandstones were quartz, calcite, dolomite, muscovite and albite, in addition to illite and montmorillonite in sandstones, and kaolinite and microcline in shales. The identified metallic mineral corresponded to tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), and as oxidation product azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) was detected. Microscopically, all rocks had tennantite and chalcopirite (CuFeS_2) anhedral, finely disseminated, both alone or associated; in this last case, tennantite rimmed partially or completely chalcopirite and galena (PbS) (this last mineral only in marls and sandstones) (Fig. 2A). Covellite (CuS) and bornite (Cu_5FeS_4), occasionally bordering chalcopirite, appeared in shales and inside carbonate veins (calcite/dolomite). Bornite also appeared occasionally in contact with tennantite (Fig. 2B).

The identified oxidation products were: azurite, mainly filling small and fine fissures, a pistachio-green phase with cracked appearance, isotropic and amorphous (confirmed by XRD data) replacing pseudomorphically tennantite. (Fig. 3) and iron (oxyhydr)oxides with cracked appearance, filling cracks inside chalcopirite (Fig. 2A). Tennantite showed contents (wt%) of Cu, S, As and Fe comprised within the ranges: 40.58-47.61, 27.61-29.77, 18.01-20.29 and 3.67-8.02, respectively. Contents of Sb and Ag varied between 0.02 and 2.06 and 0.01 and 3.81, respectively; the highest contents of Sb belonged to tennantite of marls and those of Ag to tennantite of medium grain size sandstones with carbonate veins. In chalcopirite, S, Cu and Fe contents were between 35.15 and 36.08, 33.21 and 35.74 and

27.40 and 30.19, respectively. It is worth highlighting the contents of Ag (up to 0.44) and Pb (up to 0.21). Bornite contents of Cu, Fe and S ranged from 59.77 to 66.34, 8.36 to 10.34 and 24.64 to 27.22, respectively. Covellite had contents of Cu and S as much as 66.20 and 31.05, respectively. Pb and S in galena were between 84.66 and 85.64 and 13.32 and 14.08, respectively. The contents of Cu, Sb, and Fe were also remarkable, up to 2.11, 0.31 and 0.20, respectively. According to George et al. (2017), when the minerals of tetrahedrite-tennantite series co-crystallizes with galena, chalcopyrite and sphalerite (ZnS), the former are the first to host Ag.

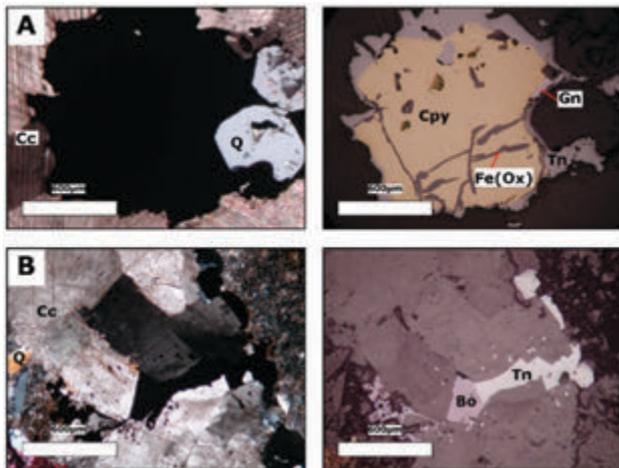


Fig. 2. Images in transmitted light with two polarizers (left) and in reflected light with one polarizer (right): A) chalcopyrite (Cpy) with Fe(oxyhydr)oxides filling small cracks (Fe (Ox)) in contact with galena (Gn) and surrounded by tennantite (Tn), B) Bornite (Bo) and tennantite in a carbonate vein. Q: Quartz and Cc: Calcite

The pistachio-green phase, alteration product of tennantite, showed contents of CuO (wt%) comprised between 13.35 and 18.58, As₂O₅, 30.23 and 33.73, and Fe₂O₃, 13.35 and 18.58. They were amorphous Cu and Fe arsenates. The contents of CuO in azurite were between 62.07 and 62.52. Iron (oxyhydr)oxides had contents of Fe₂O₃ varying between 53.58 and 63.90. In addition, CuO, PbO, As₂O₅ and Sb₂O₅ contents showed values up to 18.43, 1.63, 2.87 and 0.62, respectively. These concentrations could be due to the adsorption of these elements by iron (oxyhydr)oxides (Lindsey et al., 2015). Their formation may be linked to the preferential oxidation of Fe with respect to Cu at high pH (Xiong et al., 2018). Secondary electron images showed greenish

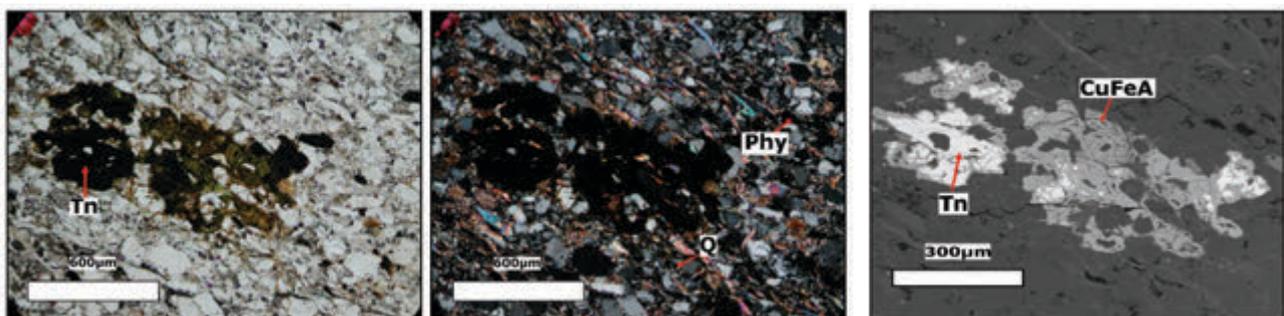


Fig. 3. Images in transmitted light with one (left) and two (middle) polarizers and back-scattered electron image (right) of tennantite (Tn) and copper and iron arsenates (CuFeA) in sandstones. Q: Quartz, Phy: Phyllosilicates.

patinas formed by aggregates of laminar crystals, sometimes, with cracked appearance (Fig. 4). In them the contents (wt%) of C varied between 11.67 and 24.99, O 34.86 and 41.58, Cu 15.84 and 36.14, Ca 2.41 and 4.64 and As 10.76 and 17.71, that may correspond to carbonate-arsenates of copper and calcium.

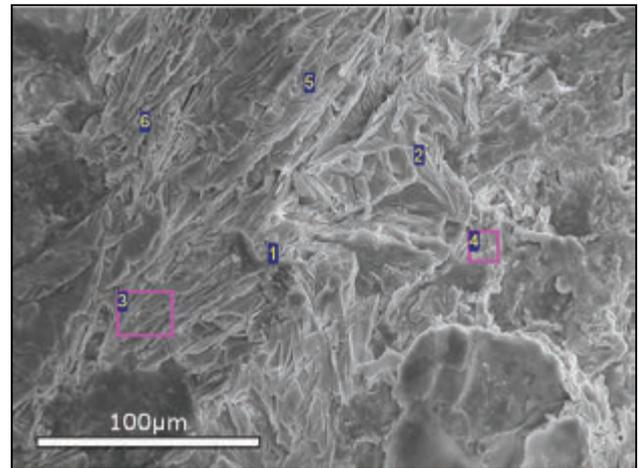


Fig. 4. Image of secondary electrons of greenish patinas. Spot analyses (1, 2, 5 and 6) and area analyses (3 and 4).

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