Preliminar study of a mineralization at Gallinero de Cameros (La Rioja, Spain)

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INTRODUCTION

The Cameros Basin has a great mining tradition as evidenced by different documents and mining vestiges, however there are hardly any studies of mineralization. The stratigraphy of the basin consists in sequences of conglomerates, sands, muds and lacustrine limestone at the top. These sequences have been affected by a very low to low metamorphism during the Middle-Upper Cretaceous and no magmatic signs have been observed (Mas et al., 2002). The mining vestige is located in the vicinity of Gallinero de Cameros (La Rioja), and it consists of a collapsed pithead (Fig. 1A), situated in a silicified conglomerates and quartzites level coated by green and blue patinas, and a dump composed of several centimetric blocks of these rocks. The history of this mining evidence is uncertain because there are no documents in the Regional Historic Archive of La Rioja. The aim of this work was the preliminary study of the mineralization of this mine.

SAMPLES AND METHODS

The samples were obtained from a chosen block of the dump containing the aforementioned lithologies with disseminated millimetric metallic minerals and patinas as alteration products of them (Fig. 1B). Samples of host rocks, metallic minerals and patinas were examined by X-ray diffraction (XRD) at the X-ray Diffraction Service of the University of Salamanca. Five polished thin sections were obtained and studied by polarizing microscopy (transmitted and reflected light) and analyzed by electron microprobe (Al, Sb, As, S, Ca, Cu, Fe, Ag, Pb and Si). Two samples of the blue and green patina were metallized in gold to be observed and analyzed by scanning electron microscopy.

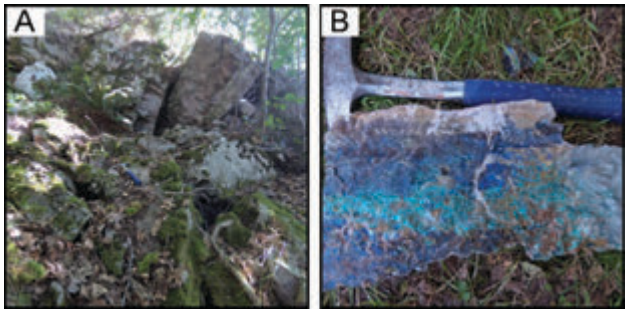

***Fig 1**. Collapsed pithead (A). Block with the blue and green patinas (B).*

RESULTS AND DISCUSSION

The phases detected by XRD in the host rocks were: quartz, albite, muscovite in quartzite and conglomerates, and, in addition, dolomite and calcite in these latter. Other minerals identified were tennantite ($Cu_{12}As_4S_{13}$) and azurite ($Cu_3(CO_3)_2(OH)_2$), corresponding to the metallic mineral and the blue patina, respectively. Alotriomorphic tennantite (the most abundant mineral) and chalcopyrite ($CuFeS_2$) (which were both associated and isolated), a very scarce white phase and bornite (Cu_5FeS_4) appeared microscopically disseminated in quartzites and conglomerates. Chalcopyrite was surrounded and corroded by tennantite (Fig. 2). The white phase was only observed inside tennantite; occasionally, close to chalcopyrite, bornite was also found.

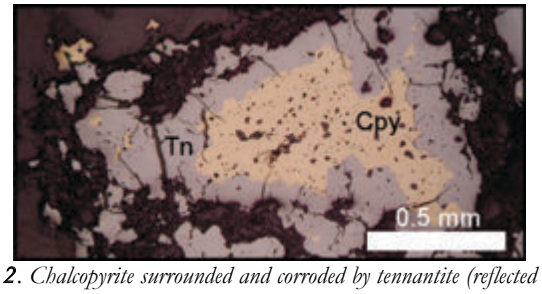

***Fig 2**. Chalcopyrite surrounded and corroded by tennantite (reflected light microscopy, uncrossed polarizers).*

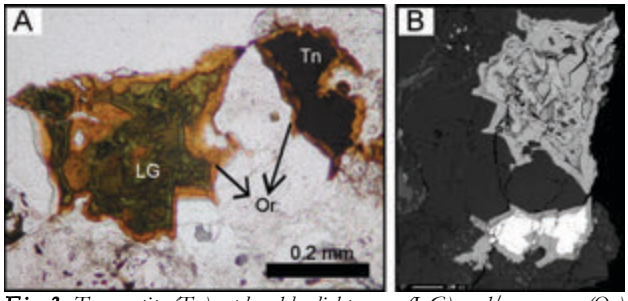

***Fig 3**. Tennantite (Tn) replaced by light green (LG) and/or orange (Or) phases in transmitted light microscopy, uncrossed polarizers (A) and backscattered electron image (B). Image B is rotated 90º with respect to image A.*

Tennantite was replaced pseudomorphically by isotropic and cracked orange and/or light green phases (Fig. 3A and B) in conglomerates and quartzites. Chalcopyrite was replaced pseudomorphically by ringed and cracked Fe (oxyhydr)oxides in quartzites (Fig. 4A and B) and, rarely, bornite and chalcopyrite borders were altered to covellite (CuS). Azurite and a dark green phase appeared associated filling small fractures in conglomerates and the latter also in quartzites filling small holes in tennantite.

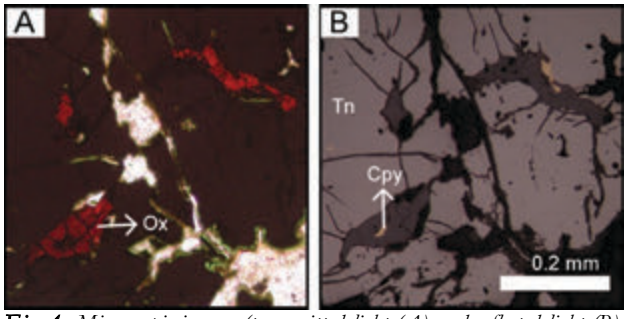

***Fig 4**. Microscopic images (transmitted light (A) and reflected light (B), uncrossed polarizers) of Fe (oxyhydr)oxides (Ox) replacing chalcopyrite (Cpy) inside tennantite (Tn).*

Spot chemical analysis of tennantite showed S, As and Cu contents (wt%) between 28.29 and 30.08, between 17.31 and 20.00, and between 42.45 and 44.88 respectively; other elements, Fe, Sb and Ag, were presented as trace (contents between 0.02 and 0.10). Chalcopyrite exhibited Fe contents between 29.52 and 30.32, S contents between 35.53 and 36.35, and Cu contents between 33.31 and 33.90; minor contents of Pb (0.18-0.24) and Sb (0.07-0.20) and trace of Ag (<0.04). The white phase presented Pb contents between 85.12 and 86.05, and S contents between 13.47 and 13.70, corresponding to galena (PbS), remarkable elements such as Fe (0.04-0.18), Cu (0.05-1.69), Sb (0.12-0.23) and Ag showed contents under the detection limit.

The analysis of the alteration products revealed that the main oxides of the light green phase (LG) were Fe_2O_3 whose contents (wt%) varied between 12.06 and 18.55, As_2O_5, between 23.52 and 32.53, and CuO, between 37.73 and 47.45, corresponding to Cu and Fe arsenates, similar to those studied by Borčinová Radková et al. (2017). The Fe (oxyhydr)oxides showed Fe_2O_3 contents between 60.07 and 62.12, in addition, exhibited high contents of CuO (16.53-22.20), As_2O_5 (1.37-9.60) and SO_3 (2.17-3.87), probably due to an adsorption process (Lindsey et al., 2015). Orange phases corresponded to Cu-Fe-Ca arsenates (CuO (wt%): 25.35-30.96, Fe_2O_3: 18.73-21.30, CaO: 7.35-9.14, As_2O_5: 29.17-30.95) and dark green phases to likely carbonate-arsenates of Cu and Ca (As_2O_5: 15.57-25.66, CuO: 47.28-50.59, CaO: 4.38-4.93).

Secondary electron images of the green patina (Fig. 5A) showed like-rosettes aggregates of platy crystals, whereas the image of the blue patina revealed botroidal aggregates (Fig. 5B). The analysis (wt%) on the green patina exposed C contents from 4.30 to 12.28, Ca contents between 2.98 and 4.79, Cu contents between 24.06 and 51.54, As contents from 9.88 to 16.23 and O contents from 29.50 to 44.81 (possible tyrolite), whereas the analysis on the blue patina presented C contents from 13.00 to 17.21, Ca contents between 1.49 and 2.45, Fe contents from 0.66 to 8.39, Cu contents from 8.15 to 18.92, As contents from 11.74 to 13.63 and O contents from 47.08 to 55.05 (possible carbonate-arsenates of Cu, Fe and Ca).

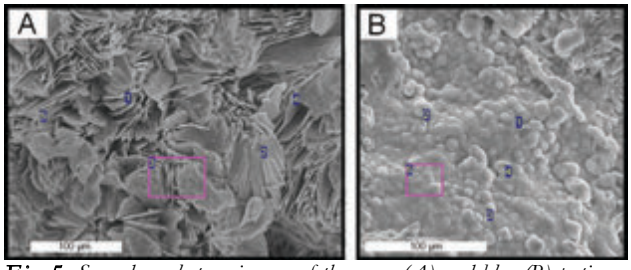

***Fig 5**. Secondary electron images of the green (A) and blue (B) patinas. Spot analyses (numbers) and area analyses (numbers with pink square).*

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