

Weathering Products of Pb, Sb, As and Fe-Bearing Sulfides in the Losacio Mining Area (Zamora, Spain)

/ ASCENSIÓN MURCIEGO-MURCIEGO (1*), ESTHER ÁLVAREZ-AYUSO (2), ANTONIO GARCÍA-SÁNCHEZ (2), ENCARNACIÓN PELLITERO-PASCUAL (1), AURELIO SANZ-ARRANZ (3), JESÚS MEDINA-GARCÍA (3), FERNANDO RULL-PÉREZ (3).

(1) Departamento de Geología. Plaza de los Caídos s/n. Universidad de Salamanca. 37008 Salamanca (Spain)

(2) Department of Environmental Geochemistry. IRNASA (CSIC). Apdo. 257. 37008 Salamanca (Spain)

(3) Unidad Asociada Universidad de Valladolid-CSIC al Centro de Astrobiología. CSIC.

INTRODUCTION

The Losacio vein field (Zamora, Spain) is located near a small granitic stock hosted in the "Serie de los Cabos". Around granites there are Sb-Pb-Zn-Ag deposits which show a zoned disposition. Mineralization is present in quartz veins of E-W direction with a dip of 35°S. Such veins have a typical length of 300 m and an unknown depth. The mineral association is composed of stibnite, galena, sphalerite, arsenopyrite, manganite, antimony ochres (cervantite, senarmontite, stibiconite, bindheimite and others, filling cavities in quartz), arsenates (mimetite) and phosphates (pyromorphite and apatite).

Mineral deposits were exploited mainly for antimony ochres from around the middle of the XIX century until the beginning of the XX century (De la Escosura, 1846; Gumiel, 1983; SIEMCALSA, 2007). At present, in the Losacio area there are hardly vestiges of the mines (the pits have been covered), and the mineral wastes appear disseminated on the land.

The aim of this work is to identify the weathering products of sulfides in the Losacio mining area in order to estimate the risk of Sb, As and Pb release and dispersion into the surrounding environment.

MATERIALS AND METHODS

Samples of vein fragments containing carbonates (siderite), quartz, micas, chlorite, sulfides (pyrite, the most abundant, arsenopyrite, quite scarce, and stibnite, the rarest), Fe oxyhydroxides, showing collomorph textures, and sulphates (jarosite) were collected. Such vein fragments were

studied by X-ray Powder Diffraction (XRD), polarizing microscopy (in transmitted and reflected light), electron microprobe analysis and microRaman spectroscopy.

RESULTS AND DISCUSSION

X-ray Diffraction

The XRD analyses performed on the bulk samples of the waste rocks allowed to identify the following weathering minerals from sulfides: scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), goethite ($\alpha\text{-FeOOH}$), the most abundant, hematite ($\alpha\text{-Fe}_2\text{O}_3$), natrojarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$) and Sb oxides and oxyhydroxides (senarmontite, Sb_2O_3 , bindheimite, $\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$).

Sulfides (arsenopyrite, pyrite and stibnite) and gangue minerals such as quartz, chamosite, siderite, chlorapatite, mimetite and vermiculite were also identified.

Polarizing Microscopy

Microscopically, the following minerals were observed:

- Galena (PbS), present as corroded relicts included in pyrite.
- Coronadite ($\text{Pb}(\text{Mn}^{4+}, \text{Mn}^{3+})_8\text{O}_{16}$), mineral of the cryptomelane group. Appears as a mineral whose colour in reflected light is nearly galena-white, showing a strong anisotropism.
- Goethite, which presents collomorph textures (Fig. 1), very abundant, and as pseudomorphs after pyrite (Fig. 2). The oxidation of some pyrite crystals was mainly limited to the grain boundary and fractures.
- Natrojarosite, which is very fine grained, massive, and with numerous fine inclusions, appears in contact with goethite and hematite (Fig. 3).

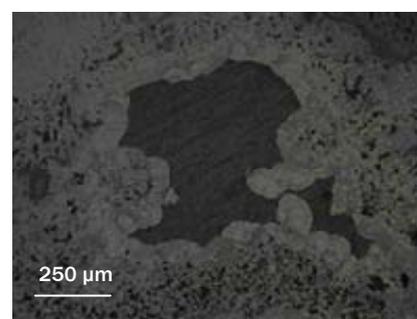


fig 1. Photomicrograph in reflected light of collomorph goethite.

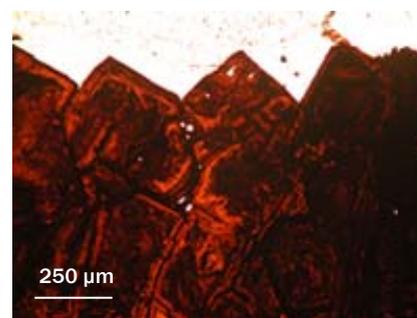


fig 2. Photomicrograph in polarized transmitted light of goethite pseudomorphs after pyrite cubes.

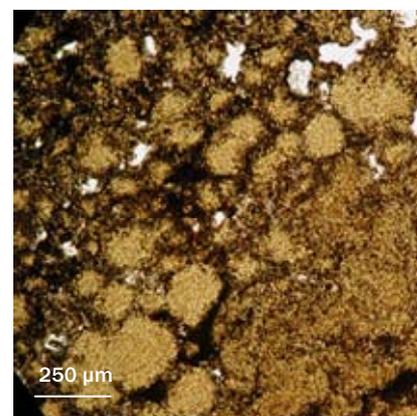


fig 3. Photomicrograph in polarized transmitted light of natrojarosite with numerous microinclusions.

palabras clave: Goethita, Natrojarosita, Coronadita, Escorodita.

key words: Goethite, Natrojarosite, Coronadite, Scorodite.

Electron microprobe analysis

Arsenic contents in unaltered pyrite are comprised in the range 0.01-1.93 wt.% As_2O_5 ; traces of Pb and Sb are also present. Therefore, in addition to arsenopyrite, relatively scarce, pyrite, which is very abundant, also represents a source of As.

Collomorph goethite presents As contents ranging between 0.06 and 2.0 wt.% As_2O_5 and Pb contents between 0.24 and 4.2 wt.% PbO. Traces of Zn, Sb, Cu, Al and P were also detected. Goethite replacing idiomorphic crystals exhibits As contents ranging from 0.15 to 1.6 wt.% As_2O_5 and Pb contents between 0.2 and 2.3 wt.% PbO.

Goethite is an efficient adsorbent of As and Pb. The important occurrence of this mineral in the studied mining area represents a significant sink for such toxic elements.

Coronadite (Fig. 4), with Pb contents of 24-28 wt.% PbO, shows minor contents or traces of Cu and Sb (1-1.5 wt.% CuO and 0.2-0.3 wt.% Sb_2O_5 , respectively). Impurities of Fe and Al are also common.

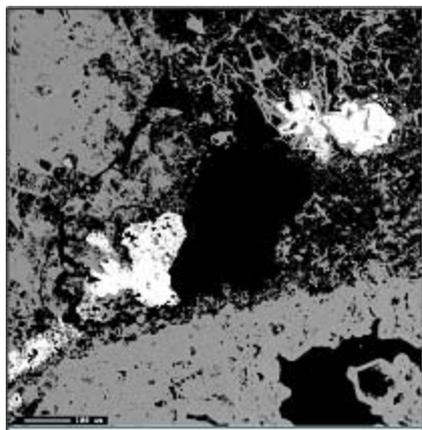


fig 4. Electron backscattered images of coronadite (white) and goethite replacing pyrite crystals (grey).

Coronadite is characterized by tunnel-type structure, based on double chains of edge-shared $[MnO_6]$ octahedra. Lead is situated in such structural tunnels (Vassileva et al., 2004). Coronadite is fairly rare mineral and in most cases is the product of simultaneous weathering of Mn and Pb-minerals. This mineral constitutes, therefore, an important scavenger of Pb.

Jarosite has the chemical formula $KFe_3(SO_4)_2(OH)_6$, but its structure can

accommodate many other elements to produce chemically diverse varieties like natrojarosite $[NaFe_3(SO_4)_2(OH)_6]$ (Jambor, 1999; Desborough et al., 2010). In the studied area natrojarosite shows Na contents varying in a wide range (3.5-6.4 wt.% Na_2O). Although Na is dominant, both Pb and K are significant components of this natrojarosite (up to 1.4 wt.% PbO and up to 2.5 wt.% K_2O , respectively). Likewise, small amounts of Al substituting for Fe are present (up to 0.9 wt.% Al_2O_3). Traces of other elements (As and Sb) were also found.

MicroRaman Spectroscopy

MicroRaman spectra of natrojarosite were obtained. To identify these the RRUFF database (<http://rruff.info>) and several articles (Frost et al., 2006; Casas et al., 2007; Murphy et al., 2010) were employed. A representative spectrum is shown in Fig. 5.

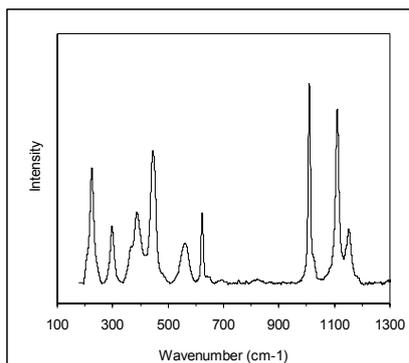


fig 5. MicroRaman spectrum of natrojarosite.

The spectrum is characterized by five bands of higher intensity situated at about 225, 447, 623, 1010 and 1111 cm^{-1} . The band at about 623 cm^{-1} (ν_4 bending mode) is present in all the jarosite spectra (Frost et al., 2006).

The jarosite mineral group can be characterized by their microRaman spectra. Nevertheless, the natural jarosite microRaman spectra show complexity with overlapping bands. It is probable that this is caused by low concentrations of other ions incorporated into the structure (Frost et al., 2006).

CONCLUSIONS

Mineralogical studies of the waste rocks from the Losacio mining area confirm the presence of goethite, natrojarosite, coronadite, scorodite and Sb ocras as

secondary minerals. Scorodite and goethite act as the main mineral scavengers for As, and coronadite, goethite and jarosite for Pb. These minerals limit the release and dispersion of the mentioned toxic elements.

ACKNOWLEDGMENTS

This work was supported by the research project from MICINN (Ref. CGL2008-06357). Authors acknowledge Alfredo Fernández Larios from the ICTS "Centro Nacional de Microscopía Electrónica", Complutense University of Madrid for performing the electron microprobe analyses.

REFERENCES

Casas, J.M., Paipa, C., Godoy, I., Vargas, T. (2007): Solubility of sodium-jarosite and solution speciation in the system $Fe(III)-Na-H_2SO_4-H_2O$ at 70 °C. *J. Geochem. Explor.*, **92**, 111-119.

De la Escosura, L. (1846): De los minerales de antimonio de Losacio en la provincia de Zamora. *Boletín Oficial de Minas del 1 de agosto de 1846*.

Desborough, G.A., Smith, K.S., Lowers, H.A., Swayze, G.A., Hammarstrom, J.M., Diehl, S.F., Leinz, R.W., Driscoll, R.L. (2010): Mineralogical and chemical characteristics of some natural jarosites. *Geochim. Cosmochim. Acta*, **74**, 1041-1056.

Frost, R.L, Wills, R.A., Weier, M.L., Martens, W., Mills, S. (2006): A Raman spectroscopic study of selected natural jarosites. *Spectrochimica Acta Part A*, **63**, 1-8.

Gumiel, P. (1983): Metalogenia de los yacimientos de antimonio de la Península Ibérica. *Tecniterrae*, **54**, 6-120.

Jambor, J.L. (1999): Nomenclature of the alunite supergroup. *Can. Mineral.*, **37**, 1323-1341.

Murphy, P.J., Smith, A.M.L., Hudson-Edwards, K.A., Dubbin, W.E., Wright, K. (2010): Raman and ir spectroscopic studies of alunite-supergroup compounds containing Al, Cr^{3+} , Fe^{3+} and V^{3+} at the B site. *Can. Mineral.*, **47**, 663-681.

SIEMCALSA (2007): La minería en Castilla y León. Junta de Castilla y León. Valladolid, 402 p.

Vassileva, M., Dobrev, S., Kolkovski, B. (2004): Chalcophanite and coronadite from Au-polymetallic Madjarovo deposit, Eastern Rhodopes. *Annual Of University Of Mining And Geology St. Ivan Rilski, Part I, Geology And Geophysics*, **47**, 57-62.