

Arsenic and Cadmium-Bearing Minerals in the La Parrilla Mine Wastes (Cáceres, Spain)

/ SANDRA BARRIOS-DE-PEDRO (1), ASCENSIÓN MURCIEGO-MURCIEGO (1*), ESTHER ÁLVAREZ-AYUSO (2), ANTONIO GARCÍA-SÁNCHEZ (2), ENCARNACIÓN PELLITERO-PASCUAL (1)

(1) Department of Geology. Plaza de los Caídos s/n. Salamanca University. 37008 Salamanca (Spain)

(2) Department of Environmental Geochemistry. IRNASA (CSIC). Apdo. 257. 37071 Salamanca (Spain)

INTRODUCTION

La Parrilla deposit is located at the municipal district of Almoharín (Cáceres province, Spain). This is a quartz-scheelite vein deposit with patterns of "stockwork" type. The mineral association mainly consists of scheelite, the most important economic mineral, arsenopyrite, cassiterite, wolframite, sphalerite, chalcopyrite, pyrite, pyrrhotite, quartz, muscovite and tourmaline as primary minerals, and scorodite, tungstite, limonite, covellite, marcasite and meymacite as secondary minerals (Gumiel and Pineda, 1981). Mining activity peaked in this area during the 1940–1987 period, producing huge amounts of wastes composed of various barren rock types (mostly schists) and vein fragments, the latter mainly containing arsenopyrite, pyrite, marcasite, sphalerite and their weathering products. The waste dumps have high As contents (610–1285 mg/kg) and continue to be a source of pollution to the surrounding environment (Anawar et al., 2006).

The aims of this work were to characterize the As and Cd mineral occurrences in the La Parrilla mine wastes and to estimate the potential of these minerals to act as sources or scavengers of these toxic elements.

MATERIALS AND METHODS

Twenty five samples of vein fragments of the surface of waste dumps of this mine containing sulfides and weathering products were studied by X-ray powder diffraction, polarizing microscopy and electron microprobe analysis.

RESULTS AND DISCUSSION

X-Ray Diffraction

The detected gangue minerals are:

quartz, muscovite, phlogopite, chamosite, halloysite, talc and sulfides (arsenopyrite, pyrite, marcasite and sphalerite).

The identified weathering minerals of sulfides are: goethite, the most abundant mineral resulting from the pyrite (and marcasite) oxidation, scorodite, quite scarce, and sulphates such as jarosite, syngenite and coquimbite, very scarce.

Polarizing Microscopy

Microscopically, the minerals identified are: arsenopyrite, pyrite, sphalerite, pyrrhotite, chalcopyrite, bismuthinite, quartz, mica, chlorite and minor apatite. The phyllosilicates appear sometimes coated by Fe oxyhydroxides. Arsenopyrite, pyrite and sphalerite are the opaque minerals more abundant. Arsenopyrite and pyrite appear as unweathered euhedral crystals embedded in quartz-mica assemblages and as partially weathered crystals that generally keep their original shape. Pyrite crystals appear much more oxidised than arsenopyrite. Relicts of pyrite in masses of Fe oxyhydroxides are frequent. Microcrystalline scorodite is around and filling small cracks in arsenopyrite (Fig. 1).

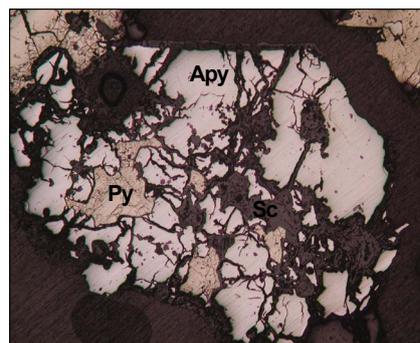


fig 1. Photomicrograph in polarized reflected light (4x) of unweathered pyrite (Py) and arsenopyrite (Apy) partially altered to scorodite (Sc).

Sphalerite appears as anhedral crystals showing an intense red colour when observed in transmitted light and it is very cracked (Fig. 2).

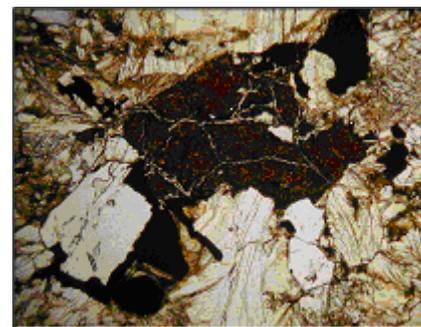


fig 2. Photomicrograph in polarized transmitted light (4x) of cracked sphalerite (red), micas and opaque minerals (pyrite).

Electron Microprobe Analysis.

Chemical compositions of arsenopyrite and pyrite are very close to the ideal formula. Arsenic content in pyrite is very low (< 0.14 wt.%), indicating that this mineral does not actually represent a source of As in this area.

The scorodite chemical composition varies within a short range, showing S contents up to 1.9 wt.% SO₃, and traces of P. The slight S enrichment may be explained by the direct contact of scorodite with pyrite (Fig. 3). Nevertheless, its Fe/As molar ratio is close to 1. Scorodite is considered to have low solubility and relatively high stability under oxidising conditions. The solubility of scorodite is minimum at pH slightly less than 3, being the secondary mineral more frequent in the Fe(III)-As(V) system in acidic conditions. Scorodite should limit greatly the release of As into the surrounding environment, unless drastic condition changes (mainly redox and pH changes) take place.

The analyses carried out on goethite

(Fig. 4) show Fe₂O₃ contents comprised in the range 76.1–88.9 wt.% and As₂O₅ contents up to 0.8 wt.%. The indicated As₂O₅ values agree well with the As(V) adsorption capacities reported in literature for this mineral (García-Sánchez et al., 2002; Lakshminathiraj et al., 2006) and with values reported in other similar mining areas (Murciego et al., 2011a, 2011b). The important occurrence of goethite in this area represents a significant sink for As released from the weathering and/or dissolution of As-minerals.

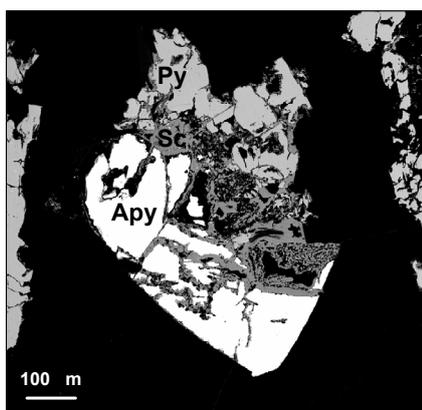


fig. 3. Electron backscattered image of arsenopyrite (Apy) altered to scorodite in contact with pyrite (Py).

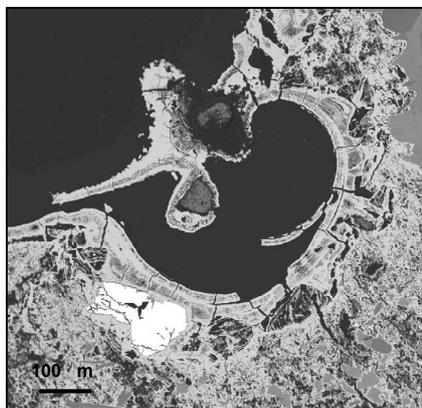


fig. 4. Electron backscattered image of goethite (grey) with relicts of pyrite (white).

Exposure assessment of As in soils around the La Parrilla mine was realised by Anawar et al. (2006). Arsenic concentrations in such soils varied from 148 to 2540 mg/kg, with a mean value of 1015 mg/kg. Water-soluble As concentrations in these soils ranged from 0.10 to 4.71 mg/kg. Although these values exceed the maximum level of soluble As permitted in agricultural soils (0.04 mg/kg) (Bohn et al. 1985), such contents represent < 0.2% of the total As amounts. The low breakdown of arsenopyrite, the low solubility of scorodite and the important occurrence

of goethite limit the As mobility in the studied area.

Chemical analyses of selected sphalerite crystals show high Fe and Cd contents in this mineral. Usually Zn content in sphalerites is comprised in the range 41–67 wt.% (Deer et al., 1962). Sphalerite from La Parrilla shows a relatively low Zn content, between 50 and 55 wt.%. Iron is almost always present in natural sphalerite, from trace levels up to more than 15 wt.% (Lepetit et al., 2003). The sphalerite of the studied mine presents a very high Fe content (up to 10.5 wt.%), showing a black colour in hand specimen. This colour is normally related to high Fe contents (> 6 wt.%) (Cook et al., 2009). Cadmium contents in sphalerite are commonly rather uniform in a given deposit, typically within the range 0.1–0.5 wt.%, although sometimes higher (Cook et al., 2009). The sphalerite from La Parrilla shows Cd contents between 0.7 and 1.4 wt.% that exceed the typical range and the values found in other Spanish sphalerites (Martínez-Frías, 1991; Murciego et al. 2010). This high Cd content could represent a serious threat to surrounding ecosystems if geo-environmental conditions promote the weathering of this mineral, as cadmium is one of the most hazardous toxic elements. Sphalerite is generally considered less reactive than pyrite, but dissolution rates for the two minerals may nevertheless be comparable. Unlike pyrite, sphalerite may even continue dissolving in non oxidising conditions (Acero et al., 2007), increasing, therefore, the risk of toxic element release into the environment.

CONCLUSIONS

Arsenopyrite and the weathering products of arsenopyrite and pyrite, (scorodite and goethite), are the As-bearing minerals in La Parrilla mine wastes. The abundance of goethite represents an important sink for As released from the weathering and/or dissolution of As-minerals. Sphalerite is the main Cd-bearing phase in this mining area. The high Cd content in this mineral represents a potential environmental hazard, especially if geo-environmental conditions (acid oxidising conditions) favour its release.

ACKNOWLEDGMENTS

Authors acknowledge Alfredo Fernández Larios from the ICTS “Centro Nacional de

Microscopía Electrónica”, Complutense University of Madrid for performing the electron microprobe analyses.

REFERENCES

Acero, P., Cama, J., Ayora, C. (2007): Sphalerite dissolution kinetics in an acidic environment. *Appl. Geochem.*, **22**, 1872–1883.

Anawar, H.M., García-Sánchez, A., Murciego, A., Buyolo, T. (2006): Exposure and bioavailability of arsenic in contaminated soils from the La Parrilla mine, Spain. *Environ. Geol.*, **50**, 170–179.

Bohn, H.L., McNeal, B.L., O'Connor, G.A. (1985): *Soil chemistry*. 2nd ed, John Wiley & Sons, New York, 341 p.

Cook, N.J., Ciobanu, C.L., Pring, A., Skinner, W., Shimizu, M., Danyushevsky, L., Saini-Eidukat, B., Melcher, F. (2009): Trace and minor elements in sphalerite: A LA-ICPMS study. *Geochim. Cosmochim. Acta*, **73**, 4761–4791.

Deer, W.A., Howie, R.A., Zussman, J. (1962): *Rock-forming minerals*, 5, non silicates, New York, John Wiley and Sons, 371 p.

García-Sánchez, A., Álvarez-Ayuso, E., Rodríguez-Martin, F. (2002): Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soil. *Clay Miner.*, **37**, 187–194.

Gumiel, P. & Pineda, A. (1981): Estudio del yacimiento de scheelita de La Parrilla (Cáceres-Badajoz). *Tecniterrae*, **39**, 16–38.

Lakshminathiraj, P., Narasimhan, B.R.V., Prabhakar, S., Bhaskar Raju, G. (2006): Adsorption of arsenate on synthetic goethite from aqueous solution. *J. Hazard. Mater.*, **136**, 281–287.

Lepetit, P., Bente, K., Doering, T., Luckhaus, S. (2003): Crystal chemistry of Fe-containing sphalerites. *Phys. Chem. Miner.*, **30**, 185–191.

Martínez-Frías, J. (1991): Sulphide and sulphosalts mineralogy and paragenesis from the Sierra Almagrera veins, Betic Cordillera (SE, Spain). *Estudios Geol.*, **47**, 271–279.

Murciego Murciego, A., Álvarez Ayuso, E., García Sánchez, A., Pellitero Pascual, E. (2010): The Occurrence of Cd and Tl in the Sphalerite from El Losar del Barco Mine (Ávila, Spain): a Potential Environmental Hazard. *Macla*, **13**, 163–164.

—, —, Pellitero, E., Rodríguez, M.A., García-Sánchez, A., Tamayo, A., Rubio, J., Rubio, F., Rubin, J. (2011a): Study of arsenopyrite weathering products in mine wastes from abandoned tungsten and tin exploitations. *J. Hazard. Mater.*, **186**, 590–601.

—, Pellitero Pascual, E., Álvarez Ayuso, E., García Sánchez, A. (2011b): Arsenic-bearing secondary products of arsenopyrite and pyrite in the EL Cabaco mining area (Salamanca, Spain). *Macla*, **15**, 147–148.