

# Secondary Products of Arsenopyrite in the Terrubias Mining Area (Salamanca, Spain)

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## INTRODUCTION.

Oxidation of arsenopyrite can result in the mobilisation and migration of As into the environment. This study considers the arsenopyrite-rich mine wastes that have undergone more than three decades of oxidation in the Terrubias mining area. In this area two Sn-W mineralization types are present: stratiform with calcosilicate bands, and in subvertical veins of NNE-NE and N100-130E directions, cutting the scheelite-rich calcosilicate bands. The paragenesis of these veins is dominated by quartz, mica, turmaline, wolframite, scheelite, casiterite and arsenopyrite. The aim of this work is to identify the arsenopyrite oxidation products in the Terrubias mining area in order to evaluate if arsenic is fixed by them or, on the contrary, is easily released, with the consequent risk of contamination of surrounding ecosystem compartments.

## MATERIALS AND METHODS.

Samples of arsenopyrite from the Terrubias wastes, showing different weathering stages, have been studied by X-ray powder diffraction (XRD), polarizing microscopy, electron microprobe analysis and Raman and Mössbauer spectroscopies.

## RESULTS AND DISCUSSION.

### X-Ray Diffraction.

The identified weathering minerals are scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) and goethite ( $\text{Fe}^{3+}\text{O}(\text{OH})$ ).

### Polarizing Microscopy.

Microscopically, the minerals identified by XRD and different weathering products have been observed.

Arsenopyrite is the opaque mineral more abundant. It appears as unweathered euhedral crystals embedded in quartz, as partial or totally weathered crystals that keep their original shape, and in relicts with corroded borders.

Scorodite is the oxidized mineral more abundant and presents different textures (Fig. 1): microcrystalline, around the arsenopyrite and filling small cracks in quartz, botroidal, very abundant, and spherulitic, located in zones of higher porosity. Microcrystalline scorodite appears locally aggregating the spherulites.

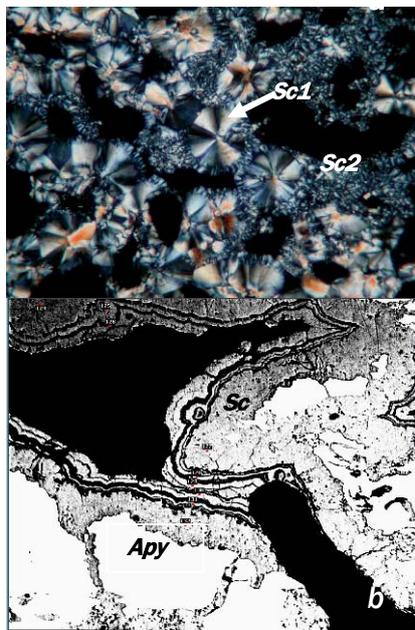


fig 1. Scorodite textures: (a) spherulitic (Sc1) and microcrystalline (Sc2) (polarized transmitted light XP, 20x), (b) botroidal (Sc) (backscattered electron image). Apy: arsenopyrite.

Goethite and other red-blackish phases occur bordering the scorodite. These latter phases are isotropes, with

numerous internal reflections that seem to correspond to highly hydrated Fe oxides. Orange-reddish products of cracked appearance generally occur embedded in scorodite masses and, more rarely, in direct contact with corroded relicts of arsenopyrite.

Macroscopically and microscopically, a simple weathering sequence of arsenopyrite is observed (Fig. 2): firstly, to scorodite and, secondly, to goethite and hydrated Fe oxides (HFO).

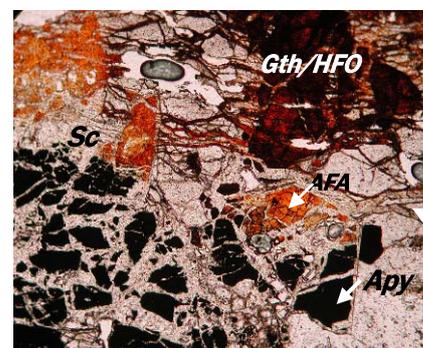


fig 2. Photomicrograph in polarized transmitted light (PP 4x) of secondary products of arsenopyrite (Apy): scorodite (Sc), amorphous Fe arsenates (AFA) and goethite (Gth)/hydrated ferric oxides (HFO).

## Electron Microprobe Analysis.

### Fe(III) Arsenates.

The scorodite chemical composition varies within a short range, displaying traces of S, Ba and Cu. Its Fe/As molar ratio is close to 1. In acidic conditions, scorodite is the secondary mineral more frequent in the Fe(III)-As(V) system. In addition to this well-crystallised Fe(III) arsenate, those poorly crystallised (usually considered as the amorphous equivalents of scorodite) are habitually cited as important As-carriers in very contaminated places. Phases that under the polarizing microscope show a cracked appearance seem to

correspond to these Fe (III) arsenates (Fig. 2). In the studied area these phases are very rare. Their chemical composition is very variable, without clear stoichiometry, and, occasionally, with impurities such as Al, Si, and, in a lesser extent, P, K and Ba. These phases are amorphous gels with the typical mudcrack-type texture, developed by sample dehydration. These phases are called amorphous ferric arsenates (AFA) (Salzsauler et al., 2005) or "pitticite" (Dunn, 1982). AFA with elevated S contents are denominated amorphous iron sulphoarsenates (AISA) (Gieré et al., 2003; Salzsauler et al., 2005). In the studied area, their S contents are relatively low ( $\text{SO}_3$ : < 2%wt), therefore, these compounds cannot be considered as AISA.

According to Paktunc et al. (2008) AFA are absent in precipitates with Fe/As molar ratios > 5, and in negligible amounts in precipitates with Fe/As molar ratios about 4. In the precipitates present in the Terrubias mining area this ratio is < 3. Several studies have proven that the solubility of Fe(III) arsenates decreases with their increasing Fe/As molar ratio (Courtin-Nomade et al., 2002). This is in accordance with the low solubility of scorodite. This propriety limits the As concentration in the acid mine drainage in numerous mining areas, making this mineral a desired phase (Pichler et al., 2001).

#### Goethite and Hydrated Fe Oxides.

Goethite and HFO display a Fe/As molar ratio very high and variable. Their  $\text{As}_2\text{O}_5$  content is roughly 21 %wt, being lower in goethite than in the amorphous phases. The As content of these phases is explained by the incongruent dissolution of scorodite and the subsequent As fixation by the precipitated Fe compounds. Scorodite dissolves incongruently forming Fe hydroxide and arsenate oxyanions.

#### Raman Spectroscopy.

To identify the Raman spectra the RRUFF database (<http://rruff.info>) and several articles (e.g., Filippi et al., 2009) were employed. The obtained Raman spectra (Fig. 3) correspond to scorodite and goethite. The first one is characterised by two bands of higher intensity about  $800\text{ cm}^{-1}$  ( $\nu_1$ , symmetry stretching mode) and  $890\text{ cm}^{-1}$  ( $\nu_3$ , asymmetric stretching mode) in the arsenate stretching region, and by several bands in the region of low wavenumber at  $335$  and  $383\text{ cm}^{-1}$  ( $\nu_2$

symmetric bending mode) and at  $422$ ,  $450$  and  $490\text{ cm}^{-1}$  (asymmetric bending modes). The second one is characterised by several bands at  $243$ ,  $299$ ,  $385$ ,  $479$ ,  $550$  and  $685\text{ cm}^{-1}$ . In many points of analysis no spectrum was obtained, indicating their amorphous or low-crystalline nature, as is the case of the so-called AFA and the red-blackish material corresponding to HFO.

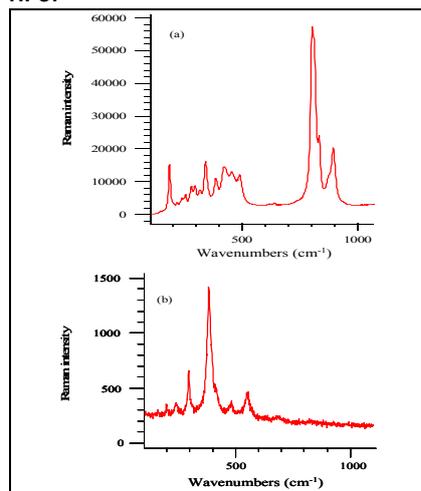


fig 3. Raman spectra: scorodite (a) and goethite (b).

#### Mössbauer Spectroscopy.

Two Mössbauer spectra (Fig. 4) were obtained. In one of them the main component comes from Fe and has values of  $\text{IS}=0.40\text{ mm/s}$  and  $\text{QS}=0.43\text{ mm/s}$ , corresponding to scorodite. The second component has values of  $\text{IS}=0.36\text{ mm/s}$  and  $\text{QS}=0.98\text{ mm/s}$ , corresponding to arsenopyrite. In the other obtained spectrum the approximate hyperfine parameters are  $\delta=0.3\text{ mm/s}$ ,  $2\varepsilon=-0.35\text{ mm/s}$ ,  $B_{\text{hf}}=37.0\text{ T}$ , and width of  $0.45\text{ mm/s}$ . The isomeric as well as the square polar displacement are consistent to goethite.

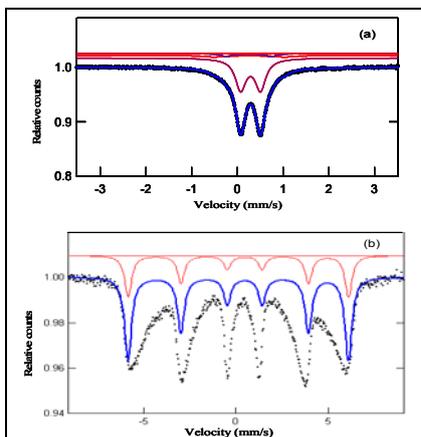


fig 4. Mössbauer spectra of scorodite (a) and goethite (b).

#### CONCLUSIONS.

The arsenopyrite weathering products in the Terrubias mining area are crystalline Fe(III) arsenates (scorodite, the most abundant), amorphous Fe(III) arsenates (AFA, very rare), Fe oxyhydroxides (goethite) and hydrated Fe oxides (HFO) with high As fixation capacity. All this contributes to limit importantly the As dispersion into the environment.

#### ACKNOWLEDGMENTS.

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