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. 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 relics with corroded borders. Scordite 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 scordite appears locally aggregating the spherulites.

RESULTS AND DISCUSSION.

X-Ray Diffraction.

The identified weathering minerals are scordite (FeAsO$_2$2H$_2$O) and goethite (Fe$_3$O(OH)).

Polarizing Microscopy.

Microscopically, the minerals identified by XRD and different weathering products have been observed. Goethite and other red-blackish phases occur bordering the scordite. 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 scordite masses and, more rarely, in direct contact with corroded relics of arsenopyrite. Macroscopically and microscopically, a simple weathering sequence of arsenopyrite is observed (Fig. 2): firstly, to scordite and, secondly, to goethite and hydrated Fe oxides (HFO).

Electron Microprobe Analysis.

Fe(III) Arsenates.

The scordite 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, scordite 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 scordite) 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 (SO3 < 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 AsO5 content is roughly 21 1wt, 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 oxanions.

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 cm⁻¹ (ν₁, symmetry stretching mode) and 890 cm⁻¹ (ν₃, asymmetric stretching mode) in the arsenate stretching region, and by several bands in the region of low wavenumber at 335 and 383 cm⁻¹ (ν₂ symmetric bending mode) and at 422, 450 and 490 cm⁻¹ (asymmetric bending modes). The second one is characterised by several bands at 243, 299, 385, 479, 550 and 685 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.

**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.

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**REFERENCES.**


