

# Arsenic-Bearing Secondary Products of Arsenopyrite and Pyrite in the El Cabaco Mining Area (Salamanca, Spain)

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## INTRODUCTION.

The El Cabaco mining district, located in the southwest of the Salamanca province (Spain), is characterised by W-As-Au mineralization in subvertical quartz veins of NW-SE direction, enclosed in granites and metamorphic rocks. The main minerals are arsenopyrite, pyrite and wolframite, together with other minor minerals such as scheelite, chalcopyrite, pyrrhotite, sphalerite, galena, bismuthinite, gold, and bismuth (Antona et al., 1993, 1994). The mining activities developed in this area for the exploitation of the economic ore minerals produced important amounts of As-containing waste rocks and tailings, with the consequent risk of As release and dispersion to surrounding environment.

The aims of this work are to identify and characterise the As-bearing secondary products generated from the weathering of arsenopyrite and pyrite present in mine wastes and to assess their potential environmental hazard.

## MATERIALS AND METHODS.

Ore samples containing arsenopyrite and pyrite from the El Cabaco mining area have been studied by X-ray powder diffraction (XRD), polarizing microscopy and electron microprobe analysis.

## RESULTS AND DISCUSSION.

### X-Ray Diffraction.

The identified secondary minerals are mainly scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) and goethite ( $\alpha\text{-FeO(OH)}$ ). Other minor phases include hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). The presence of primary minerals such as quartz, tourmaline (schorl), muscovite,

arsenopyrite and pyrite was also detected.

### Polarizing microscopy.

Polarizing microscopy in transmitted and reflected light shows that arsenopyrite and pyrite are the opaque minerals more abundant, appearing as unweathered euhedral crystals embedded in quartz, as totally weathered crystals that keep their original shape, and in relicts with corroded borders. Chalcopyrite, pyrrhotite, gold and bismuth occur in minor amounts.

The secondary products more abundant are scorodite, goethite and reddish phases that could correspond to hydrous ferric oxides (HFO) (Fig. 1). Scorodite occurs on the arsenopyrite crystal borders, along small cracks, inside of arsenopyrite, and presents different textures: microcrystalline aggregates, colloform, and prismatic crystals (with size varying from tens to hundreds of  $\mu\text{m}$ ) occurring into cavities. Goethite occurs as needle-like crystals, in colloform textures and in microcrystalline aggregates, replacing arsenopyrite and pyrite crystals.

### Electron microprobe analysis.

The As content in pyrite is negligible ( $< 0.03\% \text{As}_2\text{O}_5$ ), revealing that arsenopyrite is the only mineral source of As in this area. The main general differential characteristics of scorodite are: relatively high Al contents (up to  $10.4\% \text{Al}_2\text{O}_3$ ), moderately low contents of S and Cu (up to  $1.33\% \text{SO}_3$  and  $1.28\% \text{CuO}$ ) and minor or trace concentrations of other elements (P, Si, K, Ca and Mn). The highest Al contents are present in scorodite crystals, whereas microcrystalline and colloform scorodites show negligible Al contents. The Fe/As molar ratios in scorodite crystals varies in the range  $0.86\text{--}1.03$ , differing from the scorodite theoretical value. Such composition denotes that this mineral is an intermediate term between scorodite and mansfieldite ( $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ ), corresponding to aluminian scorodite ( $(\text{Fe, Al})\text{AsO}_4 \cdot 2\text{H}_2\text{O}$ ). Scorodite and mansfieldite are end members of an isomorphic series (Allen et al., 1948). The electron backscatter images also suggest such elemental composition. Thus, zonation is observed in scorodite crystals (Fig. 2a), showing intensified grey tonalities when enriched with Al. Zonation is not present in

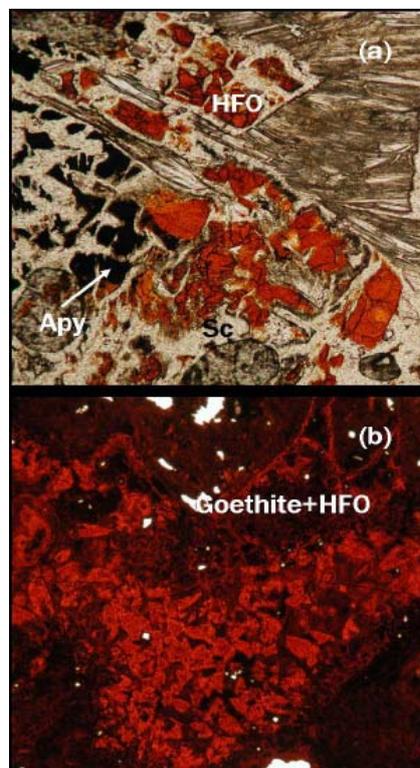


fig 1. Photomicrograph in polarized transmitted light (4x) of secondary products: (a) scorodite and hydrous ferric oxides (HFO), and (b) goethite+HFO. Sc: scorodite and Apy: arsenopyrite.

**palabras clave:** Arsenopirita, Pirita, Al-eskorodita, HFO, Goethita.

**key words:** Arsenopyrite, Pyrite, Al-scorodite, HFO, Goethite.

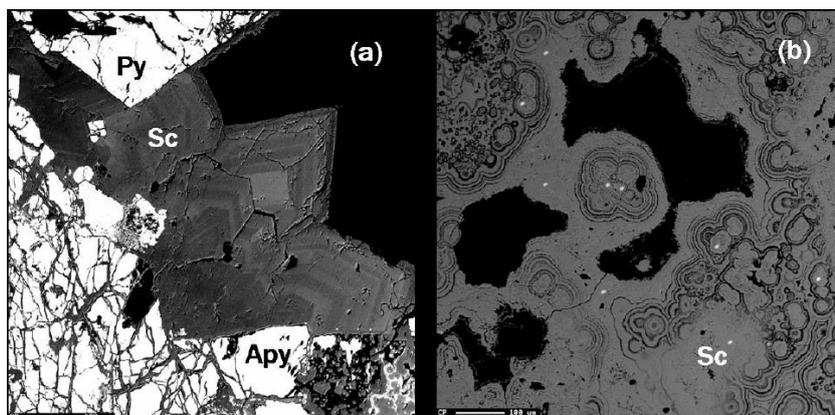


fig 2. Electron backscatter images of (a) zoned crystals of scorodite (intensified grey tonalities correspond to higher Al contents), and (b) colloform scorodite. Sc: scorodite, Apy: arsenopyrite and Py: pyrite.

colloform scorodite (Fig. 2b). The study of the stability of the scorodite-mansfieldite solid solution compounds has revealed that the increase of Al fraction in the scorodite structure causes its destabilization, being scorodite a better material for the long-term immobilization of its As than Al-containing counterparts (Le Berre et al., 2007a, 2007b).

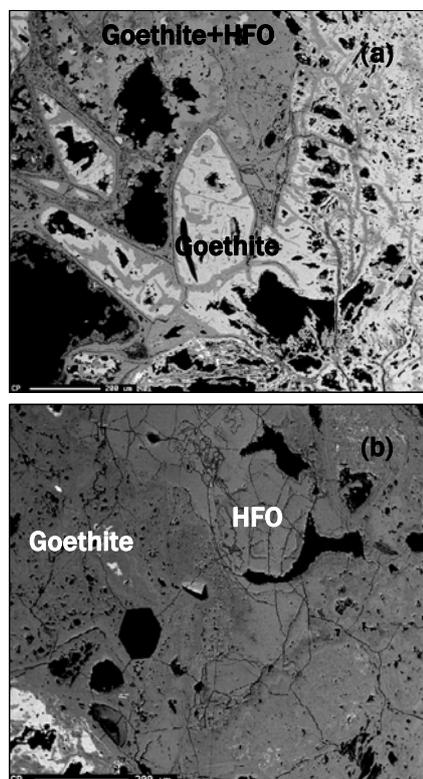


fig 3. Electron backscatter images of (a) goethite replacing arsenopyrite and pyrite crystals, and (b) goethite and HFO, the latter showing a mudcrack-type texture when highly hydrated.

The chemical environment or the surrounding rock mineralogy plays an

important role in the composition and stability of scorodite. Thus, the occurrence of schorl and muscovite in the quartz veins and in the surrounding rocks explains the Al enrichment in this scorodite.

In this regard, phosphoscorodite was the variety found in the Barruecopardo (Salamanca, Spain) mine wastes in relation to the occurrence of apatite in this area (Murciego et al., 2011). Also the presence of phosphate in the structure of scorodite leads to a mineral of somewhat reduced stability (Singhania et al., 2006).

The analyses carried out on goethite, which replaces arsenopyrite and pyrite crystals (Fig. 3a), show  $Fe_2O_3$  and  $As_2O_5$  contents comprised, respectively, in the ranges 76.2–91.8% and 0.02–2.05%. These  $As_2O_5$  values agree well with the As adsorption capacities reported in literature for this mineral (García-Sánchez et al., 2002; Lakshminathiraj et al., 2006). The chemical composition of the other reddish phases indicates that these correspond to HFO or mixtures of HFO and goethite. The maximum  $As_2O_5$  contents reach values up to 27.0%. Such high  $As_2O_5$  values are found in the most highly hydrated phases which show a mud crack-type texture (Fig. 3b) and low  $Fe_2O_3$  contents (< 50%) and important  $Al_2O_3$  levels (up to 6.52%).

#### CONCLUSIONS.

The As-bearing secondary products generated from the weathering of arsenopyrite and pyrite present in wastes from the El Cabaco mine include mostly Al-scorodite, goethite and HFO. These phases contribute

importantly to mitigate the migration of As to the surrounding environment, especially Fe oxides and oxyhydroxides due to their important presence in this area.

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