

# Simple Efflorescent Sulphates from Iberian Pyrite Belt (Portugal)

/ NUNO DURÃES <sup>(1)</sup> / IULIU BOBOS <sup>(2)</sup> / EDUARDO FERREIRA DA SILVA <sup>(3)</sup>

(1.) Centro de Geologia da Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

(2.) Departamento de Geologia, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

(3.) GeoBioTec - Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

Simple efflorescent sulphates were studied by X-ray diffraction, infrared spectroscopy and secondary electron microscopy. Zn, Cu - melanterite was formed after the dissolution of green melanterite. Melanterite is one of the simple sulphates which stored rapidly the heavy metals solubilized in acid mine waters. Rozenite and szomolnokite have resulted from melanterite dissolution caused by humidity decreasing and temperature increasing as well.

## INTRODUCTION

Poorly- and well-crystallized efflorescent sulphates sequences beginning with the simple hydrated salts from divalent to trivalent cations are described in acid mine drainage (AMD) elsewhere (Alpers et al., 1994; Nordstrom, 1999; Nordstrom and Alpers, 1999; Buckby et al., 2003; Romero et al., 2006; among others). Weathering of pyrite and pyrrhotite produces acidity and Fe, followed by precipitation of the simple hydrated divalent sulfates. The Fe<sup>+2</sup> may be substituted by other divalent cations (i.e., Cu, Pb, Zn, Co, Mg, Mn, Ca, etc) generating isomorphous substitutions in the crystal-chemistry structure of each simple hydrated sulphates groups. Efflorescent sulphates may occur in AMD as monomineralic or mixture phases, and their crystal-chemistry variety suggests a short evolution in time and space, depending to the environmental geochemistry related area and the seasonal climatic conditions.

The main goal of this paper is to describe the crystal-chemistry of the simple efflorescent sulphates precipitated in the Portuguese Iberian Pyrite Belt.

## GEOLOGY

The Iberian Pyrite belt extends about 230 Km along strike-faults with a width ranging from 35 to 50 km, which forms a roughly back-arc through southern Portugal and Spain (Fig. 1). The polymetallic massive sulfide mines of Lousal, Aljustrel and São Domingos are situated in the NW region of the Iberian Pyrite Belt (IPB) along an alignment of the Volcano - Sedimentary Complex (VSC)

within the Volcanic Hosted Massive Sulfides (VHMS) province (Oliveira et al., 2001). Accordingly, the Lousal mineralization is related to an exhalative deposit probably formed in brine pools within the lower VSC (Upper Devonian - Lower Carboniferous). The Aljustrel mine area is a Late Devonian - Early Carboniferous polymetallic volcanogenic massive sulphide deposits, which commonly shows an overall metal zoning from a zinc-rich zone near the hanging wall and a copper-rich zone near the footwall, separated by low grade to barren massive pyrite. The massive sulphide horizon in the Aljustrel mine area occurs at or near the top of the Lower Rhyolite unit in two linear belts that trend from northwest to southeast. In the São Domingos, a unique ore body occur at the contact between metasedimentary and volcanic rocks with a Upper Devonian - Lower Carboniferous age. Intense wall-rock hydrothermal alteration occurs surrounding the ore body and a big gossan, covers the top of the ore body and extends until the surface.



Fig. 1. Geological sketch of the Iberian Pyrite Belt (adapted from Carvalho et al., 1976)

## MATERIALS AND METHODS

Efflorescent sulphates samples with lighter colours from blue, green, pale-green, yellow and white were collected from several abandoned mines located

at the Lousal, Aljustrel and São Domingos. Samples were gently ground and mixed for X-ray diffraction (XRD) and Fourier-Transform Infrared spectroscopy (FTIR). The XRD patterns of randomly oriented aggregates were obtained with a Philips X'Pert MPD machine equipped with CuK $\alpha$  radiation. Infra-Red spectra in transmittance technique were recorded in the 4000 - 400 cm<sup>-1</sup> frequency region using a Bruker Tensor-27 Infra-Red spectrometer equipped with a room temperature TGC - detector. Morphology of simple efflorescent sulphates was carried out with an environmental scanning electron microscope (ESEM) FEI Quanta 400FEG, equipped with a X-ray energy dispersive (EDAX Genesis X4M).

## RESULTS

X-ray diffraction. Simple efflorescent sulphates identified by XRD are: melanterite (Fe<sup>+2</sup>SO<sub>4</sub>·7H<sub>2</sub>O), siderotil (Fe<sup>+2</sup>SO<sub>4</sub>·5H<sub>2</sub>O), hexahydrite (MgSO<sub>4</sub>·7H<sub>2</sub>O), chalcantite (CuSO<sub>4</sub>·5H<sub>2</sub>O), rozenite (Fe<sup>+2</sup>SO<sub>4</sub>·4H<sub>2</sub>O) and szomolnokite (Fe<sup>+2</sup>SO<sub>4</sub>·H<sub>2</sub>O). The d(111) peak of green or blue melanterite, as well as siderotil, occurs at about 4.90 Å, whereas for rozenite at 4.47 Å for szomolnokite at 3.44 Å. X-ray diffraction pattern of chalcantite (CuFeSO<sub>4</sub>·7H<sub>2</sub>O) was now acquired due to its small amounts collected.

## Infrared spectroscopy.

Chalcantite, green and blue melanterite and rozenite were analyzed by infrared spectroscopy (Fig. 2). Sulphate minerals analyzed contain loosely adsorbed water molecules showing a strong O - H bending at 1630 cm<sup>-1</sup> and

**palabras clave:** sulfatos simples eflorescentes, difracción de rayos-X, espectroscopia de infrarrojos, mapas de rayos-X, Faja Pirítica Ibérica

**key words:** simple efflorescent sulphates, X-ray diffraction, Infrared spectroscopy, X-ray maps, Iberian Pyrite Belt.

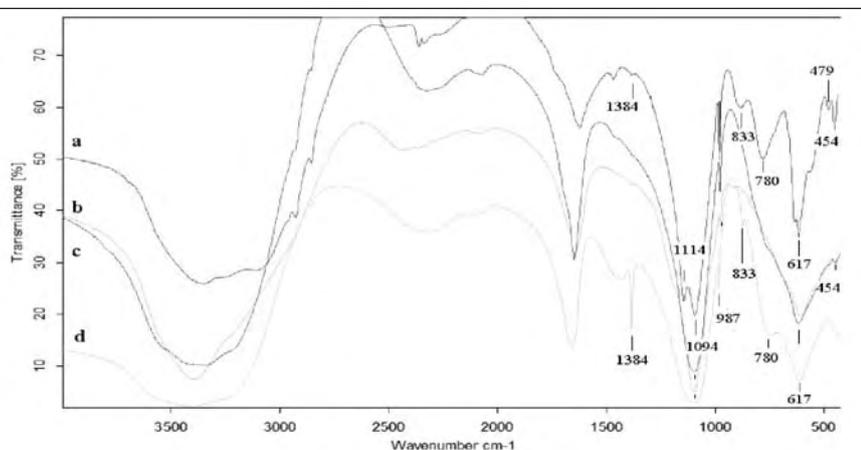


Fig. 2. Infrared spectroscopy spectra of simple efflorescent sulphates: chalcantinite (a), green melanterite (b), blue melanterite (c) and rozenite (d).

a very large O - H stretching at about  $3400\text{ cm}^{-1}$ . The IR spectra exhibit features resulting from the fundamental vibrations of the  $\text{SO}_4^{2-}$  anion. Fundamental vibrational bands (some of which are split into 2 components) for chalcantinite occur at  $\sim 1114 - 1094$  ( $\nu_3$ ),  $\sim 987$  ( $\nu_1$ ),  $\sim 700$  ( $\nu_4$ ), and  $\sim 479 - 454$  ( $\nu_2$ )  $\text{cm}^{-1}$ . The  $\nu_1$  vibration mode at  $987\text{ cm}^{-1}$  show the sulfate sorbed on metal (i.e., Cu). The intensity band decreases either green or blue melanterite and disappeared in the samples of rozenite. Also, the  $\nu_3$  vibration corresponding to sulphate did not exhibit dis-

ting splitting in melanterite and rozenite.

#### Secondary electron microscopy.

Blue melanterite morphology exhibits pseudo-octahedral crystals with short prismatic or tabular habit (Fig. 3a). Incipient dissolution is characterized by pit-etch and holes observed on the surface and cleavage planes of melanterite (Fig. 3b). Rozenite crystals occur jointed with melanterite (Fig. 3c). Chalcantinite exhibit the platy shape morphology (Fig. 3d).

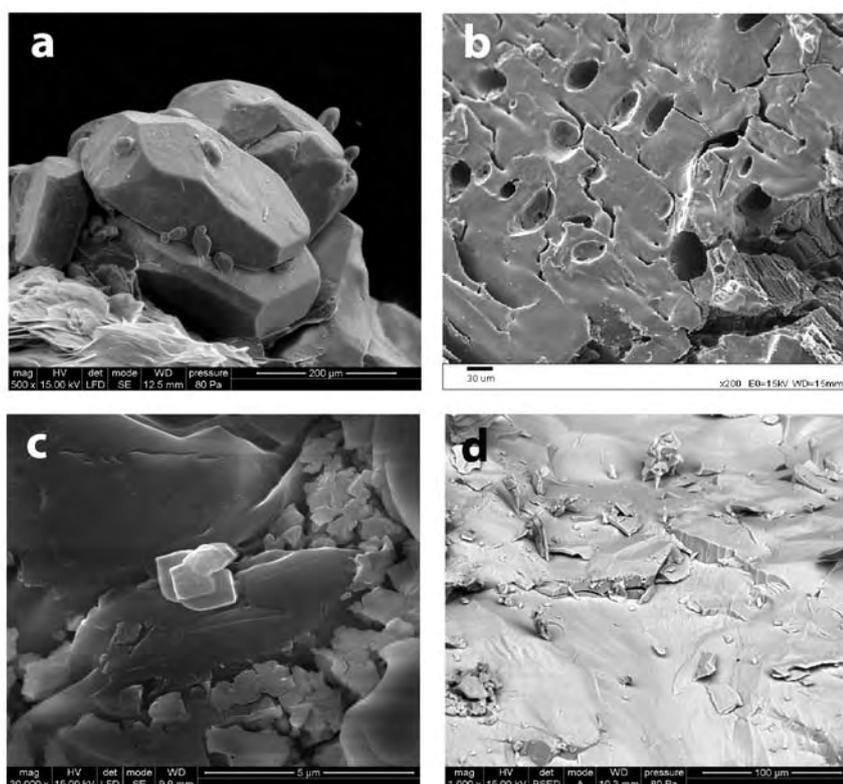


Fig. 3. Secondary electron microscopy images of blue melanterite (a), incipient dissolution of melanterite (b), initial stage of rozenite precipitation from melanterite dissolution (c) and chalcantinite (d).

#### Back-scatter images and X-ray maps.

X-ray maps of blue melanterite correspond to Fe and S distributions (Fig. 4a and b). This blue melanterite incorporates Zn and Cu from solid solution (Fig. 4c and d). X-ray maps of chalcantinite show a homogeneous S and Cu distribution (Fig. 4e and f).

#### DISCUSSION

The more common hydrated iron-sulfate minerals that occur as simple efflorescent salts on the surfaces of weathering pyrite include melanterite, rozenite and szomolnokite. Melanterite is one of the first soluble sulfate forms in acid mine drainage areas studied. Usually, stalactite of green melanterite up to 30–40 cm could be observed in the flotation plant of the Lousal mine.

The dehydration process of melanterite is accompanied by dissolution of melanterite which is always with acid production:



These efflorescent salts are highly soluble and provide an instantaneous source of acidic water upon dissolution and hydrolysis (Nordstrom 1982). The dissolution of melanterite is independent of the oxygen fugacity (Jerz & Rimstidt). Zinc- or Zn - (Cu) melanterite was formed after the dissolution of green melanterite. Isomorphic substitution of  $\text{Fe}^{+2}$  for  $\text{Cu}^{+2}$  or  $\text{Zn}^{+2}$  affects the melanterite dehydration producing a structural reorganization of the sulphate tetrahedral. The transformation is accompanied by color changes from green to blue. According to equation (1) more acid is produced and the heavy metals (i.e.,  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$ , etc) from solution will trap in a new structure corresponding to or Zn-(Cu) melanterite or Cu-(Zn) melanterite.

Melanterite dehydrates and an incipient dissolution does occur with increasing temperature or decreasing humidity, where rozenite or szomolnokite precipitated jointed with green melanterite. Siderotil results either from melanterite or from chalcantinite due to Cu for Fe substitution.

During the first stage of heavy metals geochemical cycle in acid mine drainage areas, melanterite is one of the simple sulphates which stored rapidly the heavy metals solubilized in acid mine waters.

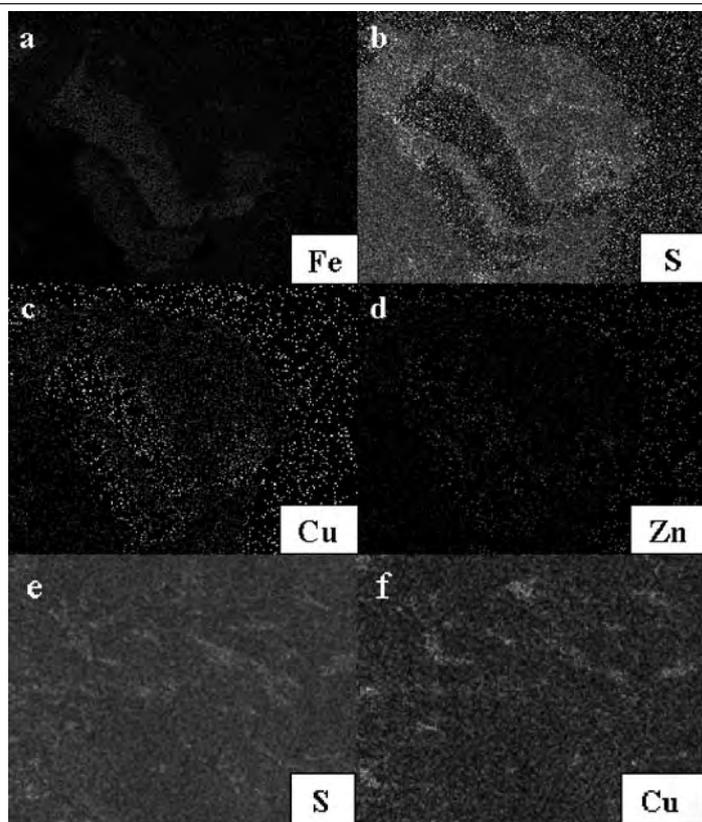


Fig. 4. X-ray maps for blue melanterite (a,b,c and d) related to Fig.3a and chalcantite (e and f) related to Fig.3.d.

## REFERENCES

- Alpers, C.N., Blowes, D.W., Nordstrom, D.K. & Jambor, J.L. (1994): Secondary minerals and acid mine-water chemistry. in "The Environmental Geochemistry of Sulfide Mine-Wastes" J.L. Jambor & D.W. Blowes, eds. Mineralogical Association of Canada., Short-Course Handbook, 22, 247-270.
- Buckby, T., Black, S., Coleman, M.L. & Hodson, M.E. (2003): Fe-sulfate-rich evaporative mineral precipitates from the Río Tinto, southwest Spain. *Mineralogical Magazine*, 67, 263-278.
- Carvalho, D., Conde, L., Enrile, J.H., Oliveira, V., Schermerhorn, L. (1976): Livro-Guia das excursões geológicas na Faixa Piritosa Ibérica. *Comunicações dos Serviços Geológicos de Portugal*, 6, 271-315.
- Jerz, J.K. & Rimstidt, J.D. (2003): Efflorescent iron sulfate minerals: Paragenesis, relative stability, and environmental impact. *American Mineralogist*, 88, 1919-1932.
- Nordstrom, D.K. (1982): Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. in "Acid Sulfate Weathering" J.A. Kittrick, D.S. Fanning & L.R. Hossner, eds. Soil Science Society of America, Spec. Publ., 10, 37-56.
- \_ (1999): Sulfates. in "Encyclopedia of Environmental Science" D.E. Alexander & R.W. Fairbridge, eds., Kluwer Academic Publishers, 580-585.
- \_ & Alpers, C.N. (1999): Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. *Proceedings of the National Academy of Sciences*, 96, 3455-3462.
- Oliveira, V.M.J., Matos, J.X., Rosa, C. (2001): The NNW sector of the Iberian Pyrite Belt – new exploration perspectives for the next decade. *Geode Workshop – Massive sulphide deposits in the Iberian Pyrite Belt: new advances and comparison with equivalent systems*, Aracena, Spain, 34-37.
- Romero, A., González, I., Galán, E. (2006): The role of efflorescent sulfates in the storage of trace elements in stream waters polluted by acid mine-drainage: The case of Peña Del Hierro, southwestern Spain. *The Canadian Mineralogist*, 44, 1431-1446.