

Magnesium and aluminum sulfates in salt efflorescences from acid mine drainage in the Iberian Pyrite Belt (SW Spain)

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Abstract

The current study is focused on AMD-precipitates that compose the typical magnesium and aluminum sulfate assemblages in the Spanish sector of the Iberian Pyrite Belt (SW Spain). The main objectives are identify and describe the composition, morphology and paragenetic relationships of these sulfate phases.

From the methodological point of view, sampling procedure covered the entire metallogenic province, including five selected representative mines and eight river basins, which are the main receptors of the acid mine drainage discharges. The mineralogical analyses were performed by X-Ray diffraction and electron microscopy. The obtained results showed the extraordinary abundance of aluminum sulfates with acicular habit, from the series pickeringite-apjohnite-halotrichite. They form typical assemblages with other aluminum sulfates, such as alunogen and tamarugite, and with the Mg sulfates: epsomite and hexahydrate. Moreover, the paragenetic relationships indicate the late occurrence of acicular Al-sulfates from the halotrichite group.

Key words: Salt efflorescences, soluble salts, magnesium and aluminum sulfates, mineral assemblage

Introduction

Secondary soluble salts form ubiquitous assemblages in acid mine drainage (AMD) affected systems. They occur commonly as complex mixtures of very fine grained minerals, mainly sulfates. (e.g. Nordstrom and Alpers, 1999). The properties of the sulfate efflorescences, regarding morphology, chemistry and paragenesis, are important for understanding the environmental conditions of the affected systems as well as the evolution processes undergone by AMD (Valente et al., 2013). Therefore, the ability of the soluble sulfates to indicate the prevailing conditions in which they form contributes to their monitoring relevance. Moreover, environmental significance is enhanced by their role in controlling pollutants mobilized by acid mine drainage solutions.

The Iberian Pyrite Belt (IPB) is a paradigmatic metallogenic province, well-known by the magnitude of the AMD processes (Grande, 2013). In this region there are many works investigating various aspects of AMD-precipitates (e.g., Buckby et al, 2003; Valente et al., 2013). The present study is focused on the mineralogical assemblages dominated by aluminum and magnesium sulfates. It documents data from the entire metallogenic province, covering sampling sites in the most representative sulfide mines as well as in the receiving watercourses. The main objectives are (i) to identify the most common assemblages, (ii) to describe typical habits, occurrence modes and spatial distribution; (iii) to obtain chemical composition; and (iii) to understand possible paragenetic relationships between the Mg and Al sulfate phases that compose some of the most common efflorescences.

The mineralogical highlighted the role of aluminum and magnesium sulfates in the Pyrite Belt river network. These minerals, especially from the groups of pickeringite-halotrichite and epsomite, are extraordinary abundant, mainly in distal positions. Mineralogical identification, chemical composition

and morphological description also allowed some paragenetic interpretations, revealing the late occurrence of acicular aluminum sulfate phases.

Methods

Study area

The Iberian Pyrite Belt (IPB), located in the southwest of Iberian Peninsula, is well-known by the historic mining activity, especially for copper in volcanic-hosted massive sulfide deposits. It extends from north of Seville – in Spain – to southern of Portugal, being known for its large massive sulfide ore deposits within the Volcano-Sedimentary Complex. In general, the ore deposits are classic volcanic-hosted massive deposit (VHMS). Although with variable ore paragenesis, the most important deposits consist of ore lenses located in the lowermost volcanosedimentary complex overlying a thick siliclastic sequence from the Phyllite-Quartzite Group (Tornos et al., 2008; Mantero et al., 2011). The sulfides mineralization is mainly represented by massive pyrite, followed by chalcopyrite, sphalerite, and galena. Gangue minerals include abundant quartz and aluminum silicates (mainly chlorite), with minor amounts of carbonates.

The study area, located in the Huelva province, has a Mediterranean climate, which can be classified as semi-arid, due to low precipitation rates. Annual precipitation is about 630 mm/year, being mostly concentrated in the wet season from October to May. Monthly precipitation ranges from 3 to 121 mm, corresponding to June and December, respectively. Average annual temperature is 17.1 °C, January being the coldest month (mean 9.8 °C), while in the summer, July and August have the highest temperatures (mean 25.7 °C) (Instituto Nacional de Meteorología; unpublished data). July also has higher evapotranspiration (162 mm) than January (19 mm). It should be noted that sampling for this study was performed in July, with temperature and relative humidity readings consistent with the typical mean annual values (temperature up 25°C and relative humidity around 50%) (Instituto Nacional de Meteorología; unpublished data).

As a consequence of historic mining legacy, the IPB is characterized by strong environmental contamination by AMD. Nowadays, there are more than 4800 ha occupied by waste dumps, open pits, tailing dams, and mining facilities, corresponding to 88 sulfide mines (Grande et al. 2013). The present research was focused on the entire Spanish sector of the Iberian Pyrite Belt, covering different situations: abandoned mining sites, with their waste dumps and seepages, and the receiving river network. So, there are soluble salt samples from contaminated rivers and from selected representative mines, which locations are presented in Table I. The following abandoned mines were selected in order to represent the diversity of the main sources of AMD. In turn, the receiving river network comprises eight major river basins: Trimpancho, Cobica, Meca, Oraque, Olivargas, Odiel, Tinto and Guadiamar (Table 1).

Sampling and analyses

The sampling campaign was performed under strong evaporation and low flow hydrological conditions (July 2015). The sampling network comprised two distinctive environments. One refers to waste-dumps, seepages and leachates in the abandoned mines. The other environment corresponds to the watercourses, which represent the receiving river network. For this, eight sampling areas were established, in order to represent the sub-basins defined in the IPB by Perez-Ostale (2014) (Table 1). At each sampling area, the AMD-precipitates were collected in order to represent the field variability, given rise to approximately 200 complex samples. Air temperature and relative humidity were measured in the field.

Efflorescent salts and crusts were examined for morphology, photographed and sorted by binocular microscopy. Afterwards, samples were lightly ground in preparation for mineralogical analysis. The samples were analyzed by X-ray powder diffraction (XRD) with a Philips X'pert Pro-MPD diffractometer, using Cu Ka radiation at 40 kV and 30 mA. Morphological and compositional features were analyzed by scanning electron microscopy with a LEICA S360 microscope, combined with an energy dispersive system (SEM-EDS, 15 keV). The samples were coated with platinum or Au/Pa, in order to allow high resolution images. The XRD data were processed with the X'pert Pro-MPD

software, which help to identify the most probable phases. However, this type of sample poses particular problems, which imply the use of an iterative procedure to accomplish mineralogical identification. (Jerz and Rimstidt, 2003; Hammarstrom et al. 2005). Sample preparation procedures and the appropriate XRD and SEM conditions for dealing with fine grain size, high hydration states, and impurity have been described by Valente and Leal Gomes (2009).

Table 1 Location of the study sites (rivers and mines)

	River waters – Location (coordinates)
Tinto	N-37° 40' 59"; W-06 32' 56"
Meca	N-37° 29' 10; W-7° 04' 12"
Cobica	N-37° 38' 50"; W-07° 16" 46"
Trimpancho	N-37° 42' 40"; W-07° 26' 52"
Oraque	N-37° 31' 16" W-06° 59' 40"
Odiel	N-37° 29' 49"; W-03° 56' 59"
Olivargas	N-37° 46' 17"; W 06° 47' 24"
Guadamar	N-37° 41' 06"; W-06° 22' 35"
Mine sites for AMD-precipitates	
Herrerías mine	Waste-dumps N-37° 37' 51"; W-07° 18' 59"
Riotinto Mines	Waste dumps Seepages; surface drainages N-37° 40' 54" ; W-06° 33' 59"
Lazunazo Mine	Mine pond N-37° 37' 34"; W 07° 10' 08"
Tharsis Mine	Waste dumps and AMD-emergences N-37° 35' 13"; W-07° 06' 27"
San Telmo Mine	Waste dumps and pit lake banks N-37° 48' 50"; W-06° 58' 55"

Results and discussion

Most of the samples occurred as powder or crusted efflorescences as shown in figure 1. The XRD data provided identification of several iron, copper, magnesium, calcium and aluminum sulfates. These efflorescences are mainly complex assemblages since pure minerals are rare.

Magnesium and aluminum sulfates occur mainly in the river network, hence with distal distribution regarding the mine waste dumps. Nevertheless, sometimes they may appear near the main focus of AMD (e.g., Herrerias, Tharsis and San Telmo mines). In these cases, they are often in association with copper and iron sulfates.

The mineralogical study by SEM has led to the chemistry of the secondary minerals and to the morphological characterization of the typical associations (Fig. 2). The study has revealed the extraordinary abundance of aluminum sulfates with acicular habit (mainly pickeringite and halotrichite) as well as magnesium sulfates (mainly epsomite and hexahydrate) (Figure 1) which had already been detected in XRD.



Figure 1 Field images showing the occurrence modes of typical efflorescences, composed by aluminium and magnesium sulfates. a) General view of Meca River with white powder efflorescences; b) crustified efflorescences dominated by aluminocopiapite ; c) Orange plate efflorescences dominated by magnesium sulfates (epsomite); d) Blue-green globular efflorescences with magnesium sulfates (hexahydrate) and copper sulfates (chalchantite).

They form typical assemblages with other aluminum sulfates, such as alunogen and tamarugite, and sometimes with iron sulfates, such as copiapite and aluminocopiapite or copper sulfates (chalchantite and alpersite). The SEM images presented in fig. 2 show the morphology of some of the most typical assemblages, namely:

Epsomite+pickeringite

Epsomite+tamarugite

Hexahydrate+pickeringite

Tamarugite+pickeringite

Hexahydrate+alpersite+chalchantite

copiapite+Aluminocopiapite+Alunogen+Holotrichite

The morphological relationships suggest that aluminum sulfates have late occurrence. This paragenetic relationship is evident in the SEM images presented in figs... The acicular aluminum sulfates, mainly pickeringite or halotrichite, are ubiquitous over epsomite or hexahydrate. Other aluminum sulfates, such as tamarugite, also occur often covering the crystals of epsomite, as shown in fig.

Epsomite and hexahydrate are the most abundant magnesium sulfates. They appear generally in different assemblages. Epsomite occurs more often nearest the water bodies, in accordance to its higher hydration state.

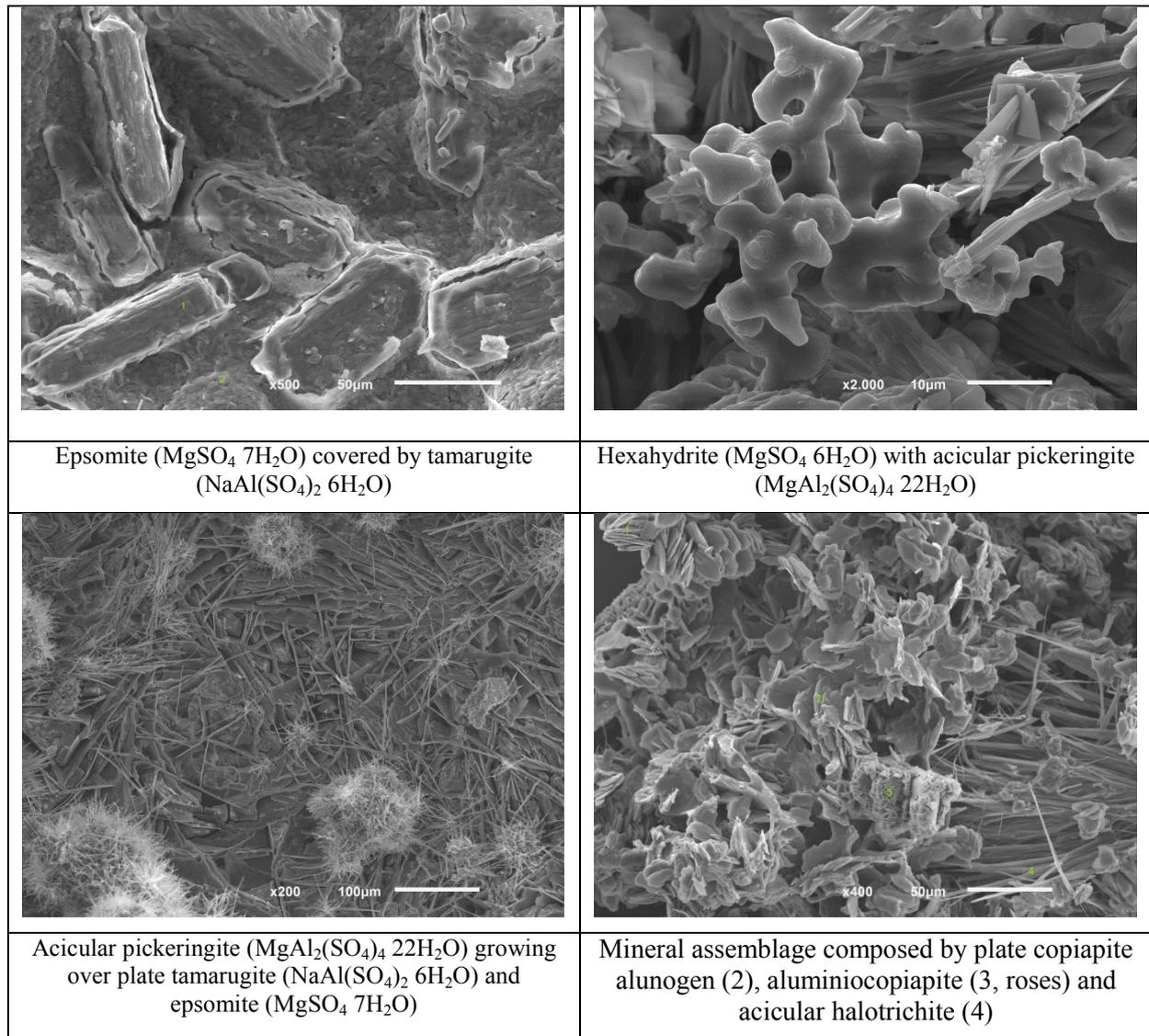


Figure 2 SEM images showing morphology of typical mineralogical assemblages composed by aluminium and magnesium sulfates.

Conclusions

The present study showed the extraordinary abundance of aluminium and magnesium sulfates in the AMD-precipitates from the Iberian Pyrite. These minerals dominate the mineralogical assemblages in the receiving environment, as a fingerprint of the abundant Mg and Al-silicates that compose the host rocks of the sulfide ores in the Iberian Pyrite Belt. The late occurrence of acicular aluminium sulfates from the halotrichite group is typically noticeable in the paragenetic relationships. Tamarugite and alunogen are other typical aluminium sulfates composing the mineralogical associations. Near the AMD sources, in the abandoned mines, the aluminium and magnesium sulfates occur more often in assemblage with iron and copper sulfates.

Acknowledgements

Financial support for this research was provided by the Andalusian Autonomous Government Excellence Project, code P06-RNM-02167. This work was also co-funded by the European Union through the European Regional Development Fund, based on COMPETE 2020 (Programa Operacional da Competitividade e

Internacionalização), project ICT (UID/GEO/04683/2013) with reference POCI-01-0145-FEDER-007690 and national funds provided by Fundação para a Ciência e Tecnologia.

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