

# Evaporation-Dissolution Cycles in Highly Acidic Mine-Influenced Waters and Their Control over the Secondary Paragenesis of Sulfate Salt Efflorescences

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## Abstract

Sulfate salt efflorescences are typical minerals associated with acid mine waters. These efflorescences play relevant roles in mining environments since they are highly soluble and contain potentially toxic elements. Therefore, information about the stability and thermodynamics of these secondary minerals is essential to comprehend the possible behavior in dehydration reactions and, consequently, previewing seasonal cycles of retention-mobilization of toxic elements in mine-influenced waters. The present work aims to characterize the transition phases related to dehydration processes of mine-influenced water collected in a mine site with extreme contamination the Rio Tinto mining area (Spain).

**Keywords:** Sulfate Salt Efflorescences, Mine-Influenced Water, Monitoring, Dehydration Process

## Introduction

Halotrichite ( $\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ) and melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) are typical sulfate efflorescent salts associated with acid mine waters. Rhomboclase ( $\text{HFe}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$ ) and voltaite ( $\text{K}_2\text{Fe}^{2+}5\text{Fe}^{3+}3\text{Al}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$ ), although rarer, may also form from the precipitation of dissolved ions. These secondary minerals are highly soluble and can store and transport acidity and potentially toxic elements (Alpers *et al.* 2000). The evaporation-dissolution cycles control the crystallization process of these salts, which dissolution during the wet seasons might lead to an increase of contamination in the ecosystems (Valente *et al.* 2013). Therefore, information about the stability and thermodynamics of these mineral phases is essential to comprehend the possible behavior in dehydration reactions and, consequently, previewing seasonal cycles of retention-mobilization of toxic elements. Such information can help to develop adequate monitoring and remediation schemes for metal-sulfide mine sites (Gomes *et al.* 2017).

To investigate the stability of hydrated metal sulfates several studies used the humidity-buffer technique proposed by Chou *et al.* 2002, which revealed that temperature (T) and relative humidity (RH) are the main control variables for the mineral stability (Chou *et al.* 2013). In the present work, the mineral precipitation process was promoted and accompanied through the air drying of mine-influenced water in the laboratory, with T and RH monitorization. The main goal was to characterize the paragenesis sequence related to the dehydration process and the stability of the neoformed minerals. Mine-influenced water was collected in the mining complex of Rio Tinto (fig. 1), which belongs to the Iberian Pyrite Belt (IPB), one of the largest metallogenic provinces in the world (Valente *et al.* 2013; Olías *et al.* 2020). This mining complex constitutes an extreme case of pollution by acid mine drainage (AMD) (Olías *et al.* 2020), characterized by abundant blooms of secondary sulfate minerals. Buckby *et al.* (2003), in Rio Tinto, identified the following sulfate salts: melanterite, rozenite,

rhomboclase, szomolnokite, halotrichite, and others. The chemical analysis of the mixture of these minerals showed concentrations of Fe (up to 31 wt.%), Mg (up to 4 Wt.%), Cu (up to 2 wt.%), and Zn (up to 1 wt%), suggesting ability to store metals (especially Zn and Cu). Knowledge of the paragenesis associated with these mine-waters is essential for assessing the environmental impact of the minerals, predicting the evolution of AMD sites, and identifying effective AMD remediation procedures.

## Methods

A sample of mine-influenced water was collected around Zarandas (Rio Tinto district, Spain) at a channel that receives leachates from a rehabilitated heap rich in sulfide wastes (fig. 1). At the time of collection, typical efflorescent salts were observed, such as melanterite and copiapite. The sample was collected in polyethylene bottle (Kartel) and stored in cool and dark conditions (at 4°C) until laboratory analysis. It was characterized in the field for pH, electrical conductivity (EC), temperature, and oxidation-reduction potential (ORP) with portable multiparametric equipment. In the laboratory, acidity and sulfate were obtained using volumetric titration and turbidimetry methods (Standard method 2310 B and 4500-SO<sub>4</sub><sup>-2</sup> E), respectively.

The air dehydration experiment of this AMD-water was conducted for 135 days, to evaluate the temporal evolution of the mineral phases. The experiment consisted of 5 mL of sample in a porcelain vessel and air drying according to the laboratory conditions. During the first 37 days the precipitation of was accompanied through visual inspection. After that period, T and RH were measured with HANNA digital Thermo-hygrometer HI9564 (probe HI 70602). Mineral phases were morphologically characterized by a binocular lens and sorted for X-ray diffraction (XRD) and scanning electron microscopy (SEM-EDX). Each sub-sample was analyzed with the diffractometer operating at 40 kV and 30 mA, while for SEM-EDX the microscopy worked at 20 keV and samples were gold-coated. To evaluate the temporal evolution of the amount of voltaite, digital image analysis was performed on the photographic record, where the method used was Pixel counting proposed by Coimbra and Olóriz (2012).

## Results and discussion

Chemical analysis reveals that water is highly acidic with 96,250 mg/L of CaCO<sub>3</sub> and pH of 1.13, and extremely sulfated with a concentration of 2,569,152 mg/L (tab. 1). This blue-greenish AMD-water was 90.31 mS/cm of EC and 356 mV of ORP at 23°C.

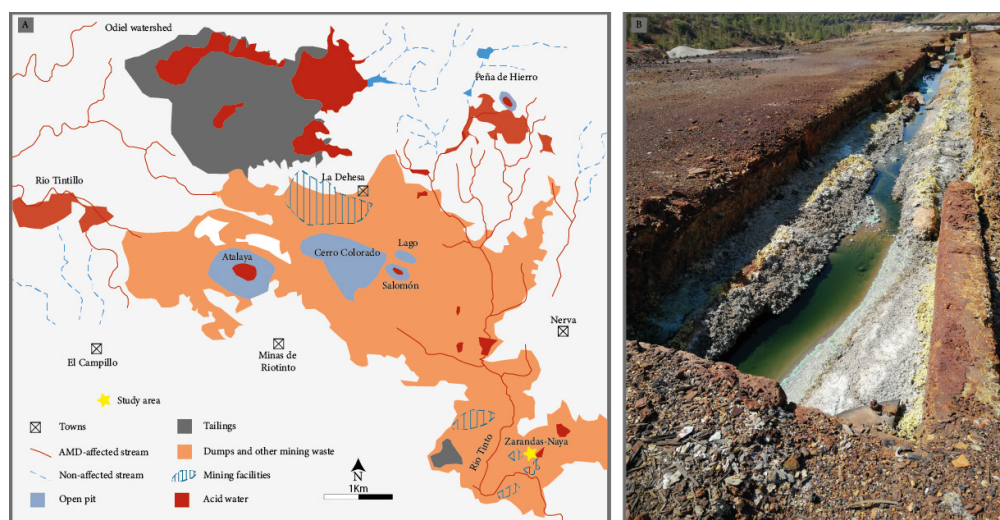
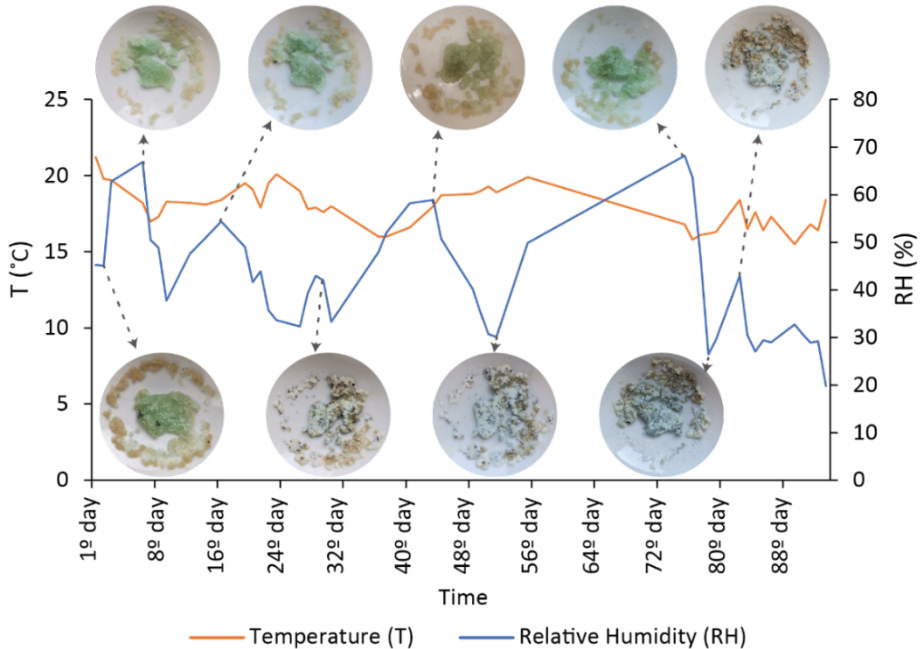


Figure 1 (A) Detailed map of Río Tinto mining district (adapted from Olías et al. 2020) and (B) sampling site in Zarandas area (Rio Tinto, Spain).

**Table 1** Chemical proprieties of the mine-influenced water collected in the Zarandas mine (Rio Tinto, Spain).

pH	EC mS/cm	ORP mV	T °C	Sulfate mg/L	Acidity mg/L of CaCO <sub>3</sub>
1.13	91.31	356	23	2,569,152	96,250



**Figure 2** Temporal variation of the RH and T and images of the neoformed minerals.

A phase with the green-emerald color of melanterite precipitated during first two days of the air dehydration experiment. Small black patches, typical of voltaite, were observed after seven days of dehydration. During the sample air drying, the T and RH range was 15 °C to 20 °C and 21% to 68%, respectively. Figure 2 shows the variation of these two parameters with sample photos captured at the minimum and maximum moments of RH points. At high RH, the sample presents highly soluble efflorescences such as melanterite and halotrichite, the first neoformed minerals crystallized (fig. 2). The voltaite appears when the RH decreases, revealing that lower humidity promotes its formation (fig. 2 and 3). In the case of melanterite, this mineral begins to dehydrate and the blue-green color change to white color, showing the switch to a less hydrated

phase. This new mineral is rozenite, a ferrous sulfate salt with a lower number of water molecules that can occur when RH is below 60% and T is between 10 to 20 °C (Chou *et al.* 2013). In addition, a less hydrated phase that appear at lower RH was szomolnokite. Behind the voltaite and rozenite-szomolnokite, the rhomboclase is another sulfate that appears when the RH decreases (fig. 2).

The temporal evolution of the amount of voltaite is represented in figure 3, which demonstrates that when RH was lower the % of voltaite was higher.

The neoformed minerals identified in the lab test are summarized in table 2. Figure 4 shows the paragenetic sequence observed, with respective XRD and SEM-EDX results. Melanterite was the first hydrated iron sulfate salt formed, with a blue-green color and a prismatic habit as shown in fig. 4a. The

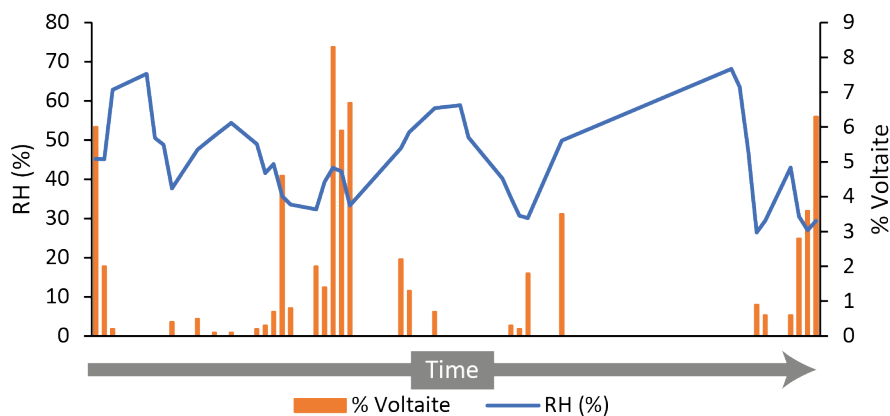


Figure 3 Temporal evolution of the % Voltaite and RH variation.

Table 2 Inventory of identified efflorescent salts.

Mineral	Abbreviation	Ideal Formula
Melanterite	Mln	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Halotrichite	Hth	$\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Rhombochase	Rbc	$\text{HFe}(\text{SO}_4)_2 \cdot 4(\text{H}_2\text{O})$
Voltaite	Vlt	$\text{K}_2\text{Fe}^{2+}5\text{Fe}^{3+}3\text{Al}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$
Rozenite	Rzn	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
Szomolnokite	Szo	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$

following mineral phases were observed: halotrichite, which is an aluminum-iron sulfate salt and rhomboclase, an iron sulfate mineral. Both minerals were white to colorless (fig.4b). However, with distinct morphologies, halotrichite showed the typical aggregates of “hair-like crystals”, while rhomboclase had prismatic habit. Voltaite has black color with a cubic to octahedral form, composed of potassium, iron, and sulfate (fig. 4c). In the highly dehydrated stage of the test lab, the XRD analysis reveals the presence of the rozenite/szomolnokite phases (fig. 4d). Rozenite and szomolnokite are both iron sulfate salts with differences in the number of waters of hydration. The first one can have a white or pale green color and a prismatic habit, while the other has pale yellow color and forms fine-grained crusts.

## Conclusions

Air dehydration experiment showed that the sequence of sulfate precipitation was mainly influenced by RH variation. In this

case, the temperature (around 15-20 °C) had no relevant impact on the precipitation of the sulfate minerals since remained relatively stable. The paragenesis sequence associated with this extremely contaminated water was: first melanterite-halotrichite; in a second stage occurs the formation of voltaite due to the decrease of humidity and rozenite starts to appear; and finally, there is the mineral assemblage rhomboclase-halotrichite-voltaite-rozenite/szomolnokite. Although there are some variations in the order of precipitation, the experiment illustrated the general sequential crystallization of the soluble metal salts earlier described by Burman (1975). The experiment also revealed that voltaite formation occurs when the RH is below 65%. Therefore, lower humidity was the main contributor to their formation. Finally, the transformation of melanterite into rozenite was observed for RH between 40 and 30%, which is in concordance with previous studies (Chou *et al.* 2013).

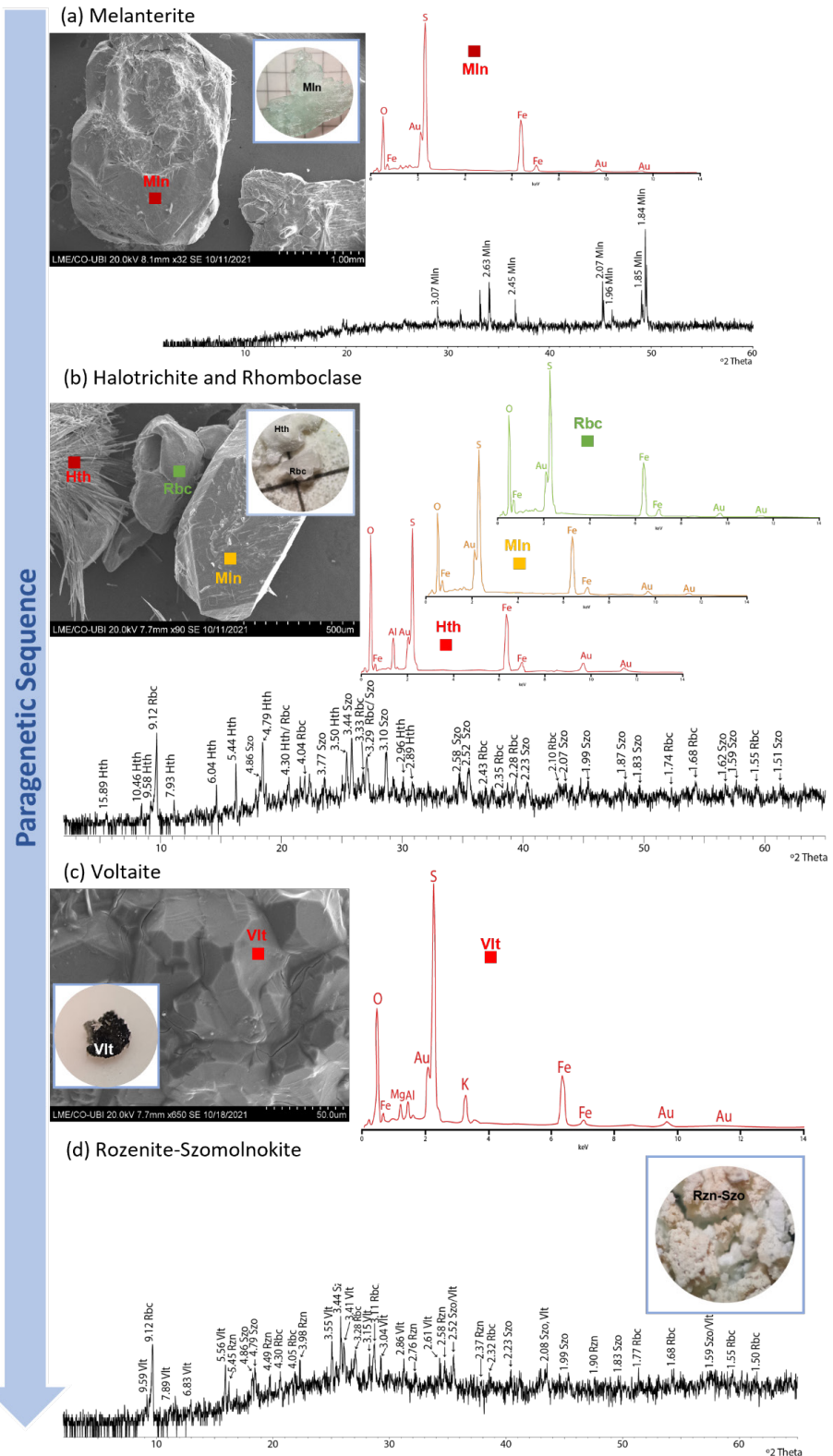


Figure 4 Paragenetic sequence of the neoformed minerals during the air dehydration experiment.



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