

# THE STABILITY OF SCHWERTMANNITE AND ITS INFLUENCE ON THE CHEMISTRY OF ACID ROCK DRAINAGE IN THE IBERIAN PYRITE BELT

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The behavior of trace elements in Acid Rock Drainage (ARD) is controlled by several factors, such as mineralogy of the primary ores and enclosing rocks, weathering conditions and hydrological variability. Moreover, precipitates newly formed from ARD, such as jarosite, schwertmannite and goethite may play a key role in the removal of trace elements from solution. In particular, schwertmannite is a ubiquitous mineral formed from ARD in the Iberian Pyrite Belt, SW Spain, and plays a major role in controlling the water chemistry of many streams. It has been reported, however, that schwertmannite is metastable and transforms into goethite in months (Bigham *et al.*, 1996). The influence of this transformation in the retention of trapped contaminants is a process that is not sufficiently understood.

The stability of schwertmannite was investigated in the acid discharge of the Monte Romero abandoned mine, Iberian Pyrite Belt, SW Spain. The mineral precipitates from supersaturated solutions mainly caused by the oxidation of Fe(II) to Fe(III), and forms the characteristic terraces (Figure 1). During the transit of the water along the schwertmannite terraces (around 4 hours of residence time), only As and V showed a systematic decrease in concentration, which is in agreement with earlier studies. The remaining contaminants, such as Zn, Al, Cu, Pb, Cd, Ni and Co do not experience any significant variation downstream. This is attributed to the fact that, at acidic pH, only As and V form anions as predominant species in solution, and are expected to be electrostatically attached to the positively charged schwertmannite surface (zero charge pH= 7.2).

Samples of precipitates were taken from the surface and from some depths down to 20 cm deep from the terraces (Figure 1). Surface samples consisted of a yellow-orange powder and a highly porous and unconsolidated brown solid. The samples gained consistency and turned dark brown with depth. Examination of powdered solid samples with XRD revealed that all the surface fresh precipitates corresponded to monomineralic schwertmannite, whereas goethite was the most abundant phase detected in the precipitates underneath. Unlike previous reports, jarosite was always found together with goethite. The inspection of the samples under SEM showed different crystal morphology depending on whether they were from the surface or collected at depth. The typical aggregates of spheres with pin-cushion morphology were observed in the surface

fresh precipitates, whereas the deeper samples showed similar spherulitic aggregates but made up of elongated and planar crystals (Fig. 2).

In the laboratory, natural schwertmannite was kept in contact with its coexisting acid water in a flask with a solidliquid mass ratio of 1:5 for 353 days. During this time, the pH of the solution dropped from 3.07 to 1.74 whereas the concentrations of SO<sub>4</sub>, Fe increased, and schwertmannite transformed into goethite plus H<sub>3</sub>O-jarosite during the first five months, and then into only goethite. This evolution is qualitatively similar to the results presented by Bigham *et al.* (1996). Nevertheless, the evolution observed in our experiments is faster than that described by these authors. The fact that in our experiments the transformation was almost complete after only 323 days (vs. 543 days in the work by Bigham *et al.*, 1996) can be due to the use in our study of a lower

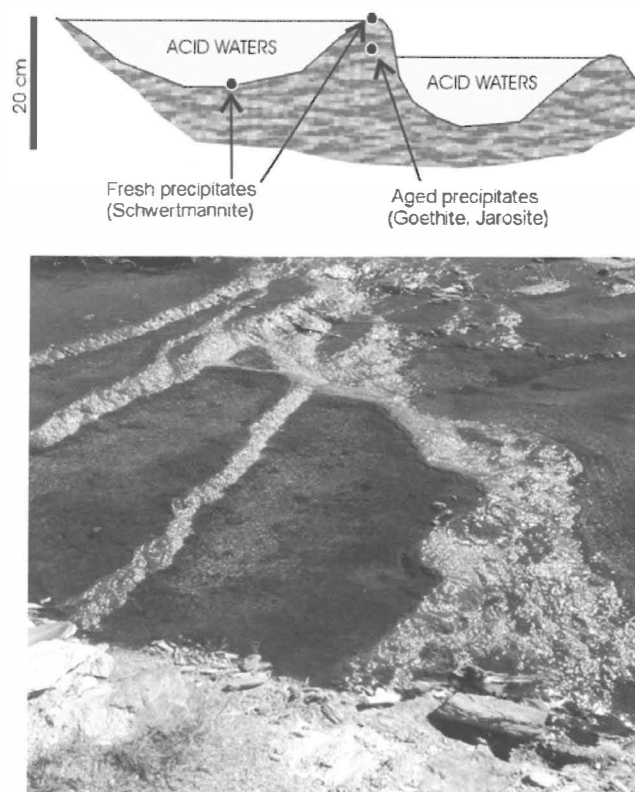


Figure 1: Terraces of precipitates from the acid stream of Monte Romero mine, and sketch of the sampling points.

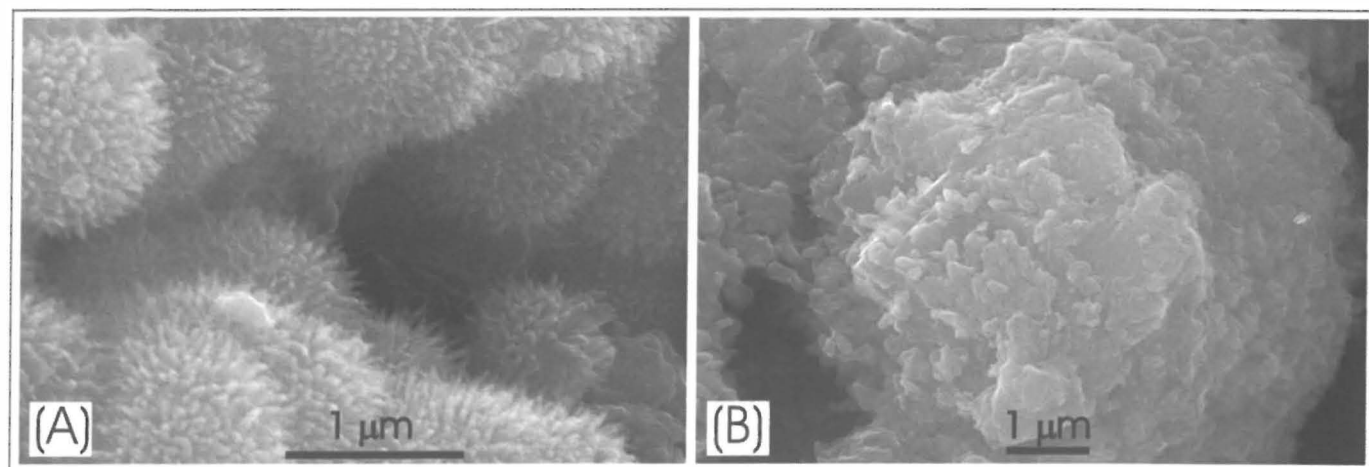


Figure 2: Field Emission Scanning Electron Microscope images of schwertmannite: (A) fresh precipitates, and (B) aged precipitates from Monte Romero (Iberian Pyrite Belt, SW Spain).

initial pH and a higher solid:solution ratio. Another interesting difference is that, whereas in the experiment of Bigham *et al.* (1996) all the schwertmannite transformed into goethite, the presence of jarosite has been unambiguously detected in our experiments. This difference can be attributed to the much higher sulfate concentration in our experiments (always >30 mmol/L vs. a maximum of 2 mmol/L in Bigham *et al.*, 1996).

As in the case of Zn, the concentrations of trace cations such as Ni, Co, and Cd did not show any significant change throughout the aging process, suggesting that they were not incorporated in the goethite or jarosite structures. Under our experimental conditions all these elements form an uncharged aqueous complex species with sulfate,  $\text{MSO}_4(\text{aq})$ , which must have also avoided their adsorption on the positively charged surfaces of the Fe-S-O phases.

However, Al underwent an interesting evolution, first decreasing from 133 to 7 and then increasing to 199 mg L<sup>-1</sup>, the minimum concentration coinciding with the first sampling in which the goethite peaks became evident in the XRD patterns of the solid sample. It is difficult to attribute the evolution of Al concentration to sorption/desorption processes on the surface of the Fe-phases, since the aqueous speciation of Al does not significantly change within the measured pH range, being  $\text{AlSO}_4^+$ ,  $\text{Al}(\text{SO}_4)_2^-$  and  $\text{Al}^{3+}$  the predominant species. The evolution of Al concentrations may be attributed to the precipitation of jurbanite ( $\text{AlOH}_2\text{SO}_4$ ) during the first part of the experiment and the latter dissolution of this mineral. This hypothesis is supported by the calculated saturation states of the solution with respect to jurbanite. Alternatively, the Al decrease coincides with the formation of  $\text{H}_3\text{O}$ -jarosite indicating that Al could be co-precipitated with this mineral. Indeed, Al currently replaces Fe(III) in the jarosite structure, giving rise to the jarosite-alunite series (Dutrizac and Jambor, 2000). The later increase in Al concentration could be attributed to the lack of jarosite precipitation but with part of the schwertmannite still dissolving. Although present in lower concentrations, the evolution of dissolved Cu is the same as described for Al. Cu has also been reported to

incorporate in minor amounts in minerals of the jarosite group (Scott, 1987).

In the case of Pb, its concentration initially increased sharply from 90 to 210  $\mu\text{g L}^{-1}$  and then dropped progressively to values close to 10  $\mu\text{g L}^{-1}$ . The initial increase may be related to desorption due to the decrease of pH during that part of the experiment and the subsequent decrease in the Pb concentrations may be attributed to adsorption on goethite surface and co-precipitation in the jarosite structure. The most significant decrease in Pb concentration, however, took place during the first part of the aging experiment together with the formation of  $\text{H}_3\text{O}$ -jarosite, suggesting a major role of  $\text{H}_3\text{O}$ -jarosite in Pb retention.

In the literature, the relative ability of jarosite and goethite to retain As remains unclear. Whereas some earlier studies claim that As can remain immobilized in jarosite by replacing sulfur in sulfate tetrahedral, other works show that As is retained preferentially in goethite over jarosite. In our experiment, the most relevant evolution is shown by As, which decreased from 350  $\mu\text{g L}^{-1}$  to below the detection limit, and then increased again to 600  $\mu\text{g L}^{-1}$  towards the end of the experiment. The As removal coincides with schwertmannite presence (first 34 days) and  $\text{H}_3\text{O}$ -jarosite formation (first 164 days). By contrast, As increased in solution when goethite was the only solid to form (after day 164), suggesting that goethite is a less efficient As sink than schwertmannite and jarosite.

Despite the significant variation in their concentrations in solution, about 80% of the total Al and Cu inventories and more than 99% As and Pb remained in the solid phase throughout the entire aging process, and confirm that, regardless aging transformations, the Fe(III) hydroxy-sulfates are relevant in natural attenuation of contaminants from ARD.

## REFERENCES

- Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L. and Wolf, M. (1996). *Geochim. Cosmochim. Acta*, 60: 2111-2121.