

Arsenic Attenuation in Acid Mine Drainage: Atomic Reasons for Field Space and Time Variations

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INTRODUCTION.

Acid mine drainage (AMD), generated by sulphide oxidative dissolution, leads to high concentrations of dissolved metals and arsenic and it is a major cause of water contamination world-wide. The Iberian Pyrite Belt (IPB) is the major reserve of massive pyrite deposits in the world, with more than one hundred abandoned mines. Oxidation of pyrite and the lack of alkalinity source rocks in the region generates a huge amount of AMD, collected by the Tinto and Odiel rivers, which transport an enormous amount of metal(loid)s into the Ria de Huelva and Gulf of Cadiz (eg. 36 tons per year of As, Ollás et al., 2006).

Schwertmannite, a Fe (III) hydroxysulphate plays a major role in controlling the water chemistry of AMD from IPB. Schwertmannite precipitates from supersaturated solutions mainly owing to the microbial oxidation of Fe(II) to Fe(III). In a few hours, schwertmannite precipitation along the streams removed more than half of the arsenic load from solution, whereas the concentration of divalent trace metals remains almost unchanged.

RESULTS AND DISCUSSION.

Schwertmannite, which is metastable, recrystallises into goethite and jarosite in a time scale of few months. The study of the bed stream sediments of an AMD impacted stream (Tinto Santa Rosa, Odiel basin) allowed us to observe that while schwertmannite was the dominant phase in upper stream sediments, its relative proportion fell further downstream, accompanied by an increase in the content of goethite and jarosite. Results from water and solid phase chemistry modeling, and X-Ray Absorption Spectroscopy (XAS) showed that (1) upper stream sedimentary arsenic was sorbed onto

schwertmannite, whereas downstream it appeared mainly associated with goethite and jarosite; and (2) arsenic speciation changed with depth in the consolidated terrace sediments, as its chief mineralogical host shifted from schwertmannite in the surface sediments to goethite at depth. Although all these iron precipitates have been shown to be efficient at sequestering arsenic from solution, differences in the concentration of arsenic associated with the solids were observed. The highest arsenic concentrations were associated with sediments composed primarily of schwertmannite (Asta et al, 2009). Indeed, the examination of a laboratory ageing experiment and the XANES speciation data of the solids shows that arsenic increases in solution first due to schwertmannite dissolution and then to desorption from jarosite, surface sorption on goethite being the main As scavenging process. Arsenic desorption reactions from jarosite in the second stage are likely influenced by presence of high concentrations of competing sulphates. However, the competitive effect of sulphate on the As(V) sorption capacity of goethite must be much lower than that of jarosite (Román-Ross et al., in review)

To understand the behaviour at atomic scale, the structure for schwertmannite has been resolved by means of Pair Distribution Function (PDF) data, X-ray Diffraction (XRD) analyses and Density Functional Theory (DFT) calculations. It consists of a highly defective network of edge and corner sharing iron octahedra with a deformed hollandite-structure and sulfate ions occupying the positions inside the channels. Arsenic replaces sulphate, and our XAS data show a trend to the formation of inner-sphere bidentate complexes when the arsenate is co-precipitated with schwertmannite, and of inner-sphere monodentate

complexes when the arsenate is adsorbed onto previously precipitated schwertmannite (Fernández-Martínez et al., in press).

Acidic river system from IPB is even older than the beginning of mining activity, which dates back to the Third Millennium B.C. Along the Tinto river there are old iron terraces occupying different elevations above the present river and corresponding to a natural and not to an industrially contaminated environment. The oldest of these iron terraces, so-called as Alto de la Mesa, lies 60 m above the current river level and may be as old as 6 My. Stratigraphically, this formation is defined as a typical fluvial point-bar sequence showing the alternation of coarse and fine sediments. Sediments of ancient terraces are composed mainly of goethite, which most likely originated from the re-crystallization of a precursor schwertmannite as observed in current terraces. According to synchrotron-based X-ray analyses (μ -XRF and μ -XRD), it is observed that goethite again re-crystallizes with time due to diagenetic processes. The levels of coarse-sized goethite increase the crystallinity without transforming into other iron phases; while the levels of fine-sized goethite are becoming less stable and partially re-crystallize to hematite. At goethite-hematite levels, the grain size of goethite is directly proportional to the crystallinity and inversely proportional to the transformation rate of hematite. In addition, transformation of goethite is accompanied by an increase of grain size and hence a decrease in specific surface area of hematite that decreases the arsenic concentration trapped in the solid. This increase in the mobility of arsenic during the diagenetic maturation should be considered during development of conceptual and

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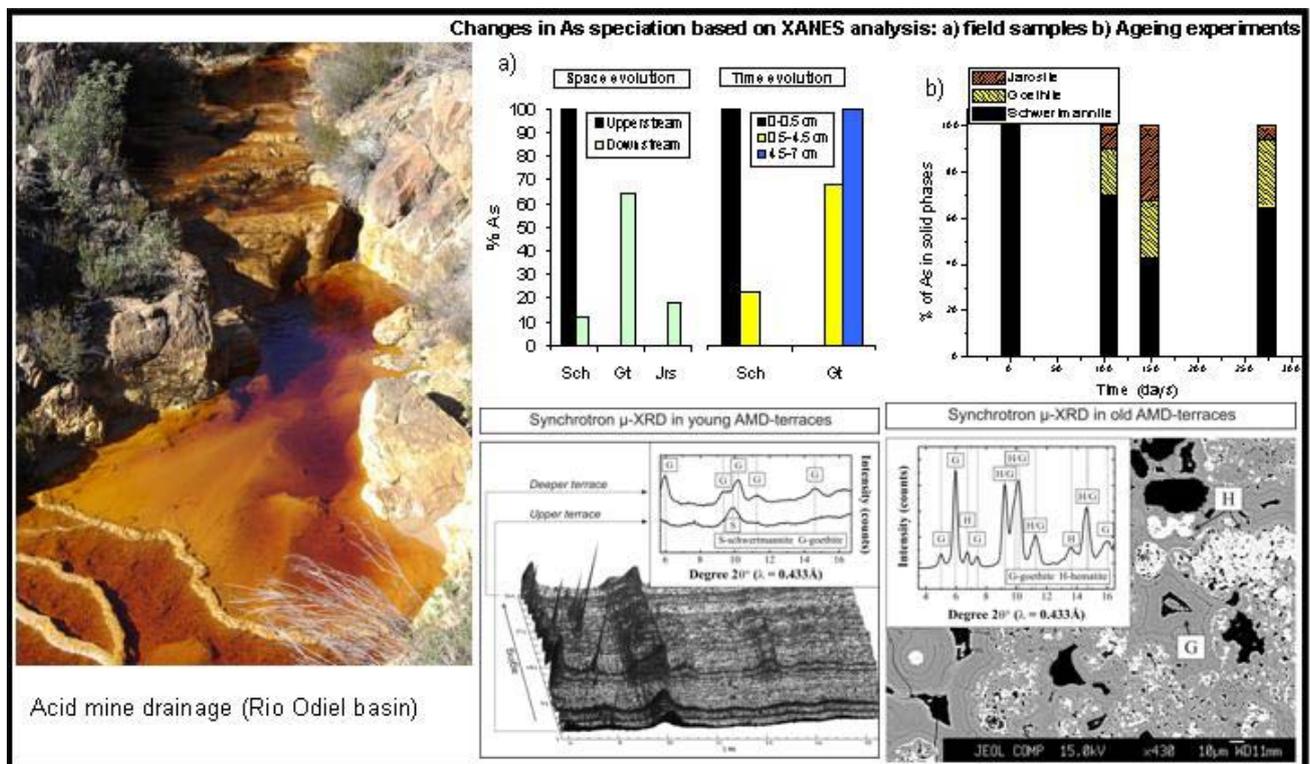


fig 1. Arsenic behaviour during Schwertmannite transformation in AMD in the Odiel basin, Spain.

analytical models describing long-term fate, transport and bio-availability of arsenic in IPB Systems (Pérez-López et al, in review).

CONCLUSIONS.

According to our results the understanding of the geochemical processes controlling arsenic mobility cannot be achieved unless the mineralogical/chemical composition of the arsenic sources at molecular scale is known. The speciation of arsenic in these precipitates is critical for the determination of its environmental fate and for the development of effective management strategy for AMD.

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