Arsenic mobilization in iron precipitates from Acid Mine Drainages at different time-scales

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INTRODUCTION

Arsenic (As) is considered one of the most toxic elements worldwide. It is commonly associated with pyrite in sulfide deposits. The weathering of the huge sulfide deposits located in the Iberian Pyrite Belt (IPB; SW Iberian Peninsula) provides a significant percentage of trace metals to the Atlantic Ocean through the Tinto and Odiel rivers. The outcropping sulfide deposits tend to weather under meteoric conditions giving rise to oxidative dissolution of the ore forming minerals, producing a strong acidity in the river-media and loading them with very high concentrations of metals and metalloids.

Schwertmannite ($Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$) is a poorly-crystalline phase that precipitates commonly on the riverbeds affected by acid mine drainage (AMD). Due to its rapid nucleation and growth, it can serve as an effective sink for As and other trace elements. This metastable phase recrystallizes into crystalline phases such as goethite (FeOOH) and jarosite ($KFe_3(SO_4)_2(OH)_6$) over a time-scale of weeks. Due to diagenetic processes goethite may recrystallize into other more stable phases such as hematite (Fe_2O_3) at century time-scale.

In watercourses affected by AMD these ferric phases often form terraces that exhibit distinct transitions from recently -formed sediments to ancient sediments formed in paleo-riverbeds.

In this study, several samples were taken along the Tinto river basin. Complementary, laboratory experiments were carried out with synthetic schwertmannite. The overall goal of this work is to describe the aging process of schwertmannite to more crystalline phases at field and at the laboratory, as well as to study the As behavior during the recrystallization process.

METHODOLOGY

In the field, terraces of three different ages were sampled: (1) the oldest terraces (6 Ma; "Alto de la Mesa" area) are located 60 m above the present Tinto river stream, (2) intermediate terraces (2 Ma; "Nerva" area) are 15 m above the river level, and (3) currently forming terraces composed by fresh precipitates that are along the stream-bed affected by active AMD.

In the laboratory, the terrace samples were dried at room temperature in order to avoid mineralogical transformation. Then, two different procedures were followed; an aliquot was ground using an agate mortar and analyzed by powder X-ray diffraction (XRD), and another one was used to prepare 50 µm thin sections for examination by optical microscopy, micro-Raman spectroscopy, and synchrotron-based micro X-Ray Fluorescence (µXRF) mapping based on synchrotron light sources.

Synchrotron-based µXRF analysis was performed at the GeoSoilEnviroCARS beamline 13-BM-D at Argonne National Laboratory (Argonne, IL, USA). The storage ring was operated in continuous top-up mode at a current of approximately 102 mA during data collection. The mapping was performed at 16 keV using a focused beam, which provided a spatial resolution of ~10 µm.

Additionally, laboratory experiments were conducted to evaluate the influence of As(V) on schwertmannite formation and transformations. Synthetic schwertmannite was prepared according to the protocol described by Loan et al. (2004). The samples were synthesized in the presence of varying As(V) concentrations in solution (0, 0.25 and 1.0 mM). These suspensions were heated in an oven at 85ºC for a maximum of 21 days to accelerate the transformation process. The mineralogy was characterized by powder XRD and the supernatant solutions were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

RESULTS AND DISCUSSION

Figures 1 and 2 show the mineralogical composition of the terraces based on XRD and Raman spectroscopy data, respectively. Surfaces of newly-formed terraces were mainly composed of schwertmannite; however, goethite was present in deeper levels (Fig. 1A and 2A). Jarosite was also in some of these current terraces. The mineralogical composition of the ancient terraces was
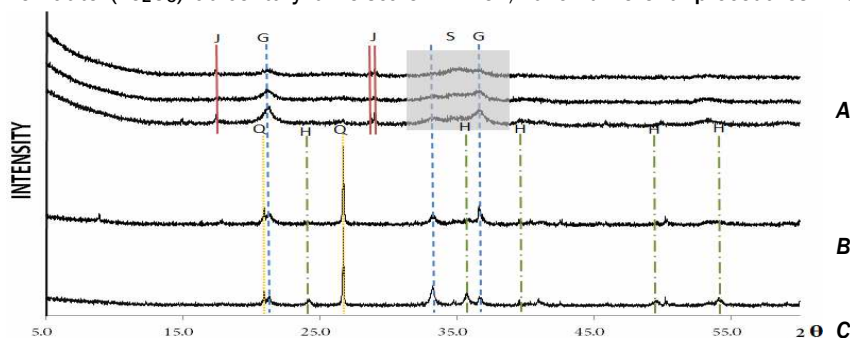

Fig.1: XRD results illustrating the mineralogical changes during the aging process in the terraces. A: all XRD patterns belong to the same newly-formed terrace (from top to bottom in order of increasing depth). B: Nerva terrace. C: "Alto de la Mesa" terrace. Mineralogy: J = Jarosite, G = Goethite, S = Schwertmannite, Q = Quartz, H = Hematite.

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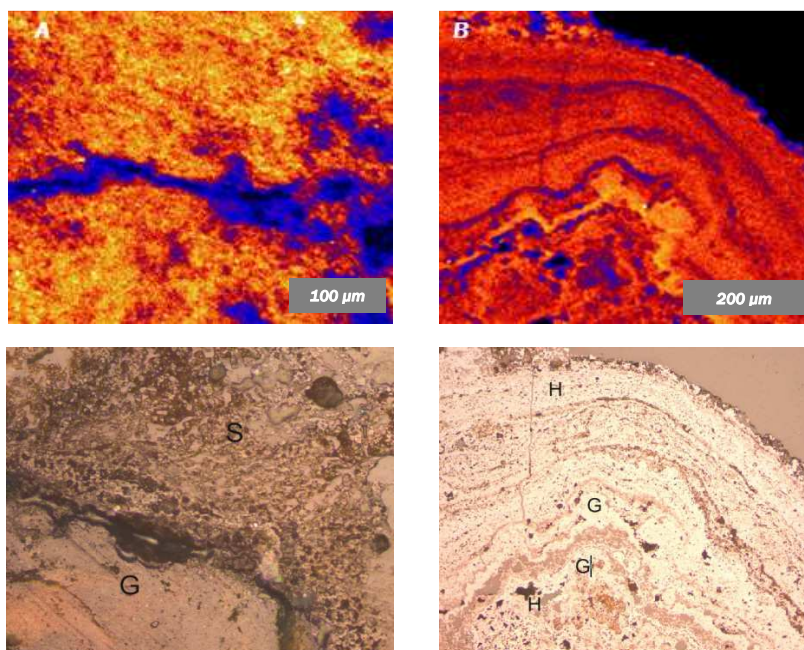* corresponding author: aparviainen@ugr.es

Fig. 2: *Terraces samples. Figures A: Actual terrace. Figures B: "Alto de la Mesa" terrace (the oldest terrace). On top, the samples are viewed with a µXRF scan for relative As concentrations. The clearer colors determine the highest As concentration, and darkest colors show the lowest As concentrations. On the bottom, the same samples are viewed with an optical microscope. The mineralogy was determined with micro-Raman spectroscopy. H = Hematite, G = Goethite, S = Schwertmannite.*

principally comprised of goethite and hematite (Fig. 1B,C and Fig. 2B). These observations are consistent with the diagenesis of poorly crystalline phases as previously described. Schwertmannite transforms to goethite over a time-scale of weeks in the fluvial sediments. In contrast, the presence of hematite in ancient sediments results from long-term diagenetic transformation of goethite (Asta et al., 2010; Pérez-López et al., 2011).

This transformation process was also observed in the laboratory experiments. Schwertmannite precipitated rapidly during the first hours of the experiment carried out without any As(V) in solution. Goethite appeared after 24 hours, whereas hematite was detected only after 550 hours (Fig. 3A).

Adding As(V) to the solution had two different implications. Firstly, the mineralogical transformation was considerably delayed. Transformation rates for schwertmannite to goethite and goethite to hematite decreased within increasing As concentration (Fig. 3B and C). In fact, in the experiment with 1mM As schwertmannite was not detected in the onset, being the precipitated Fe(III) phase completely amorphous. Minor peaks for goethite appeared in XRD patterns collected after 100 hours, but hematite was not detected during this experiment. Secondly, the As evolution was closely related to the mineralogical changes.

The majority of As remained sorbed to the initial schwertmannite. However, transformation of schwertmannite to more crystalline phases was linked to As release at the end of the experiments (Fig. 3B and C).

The As release was also detected in the µXRF maps obtained on the newly-formed and ancient terraces (Fig. 2). In the recently-formed terraces, As intensity in schwertmannite was almost as high as in the short-term formed goethite (Fig. 2A). Nonetheless, in the older samples the As intensity was higher in goethite levels, whereas decreased in the hematite layers (Fig. 2B). These data therefore confirm the observations made in the laboratory experiments.
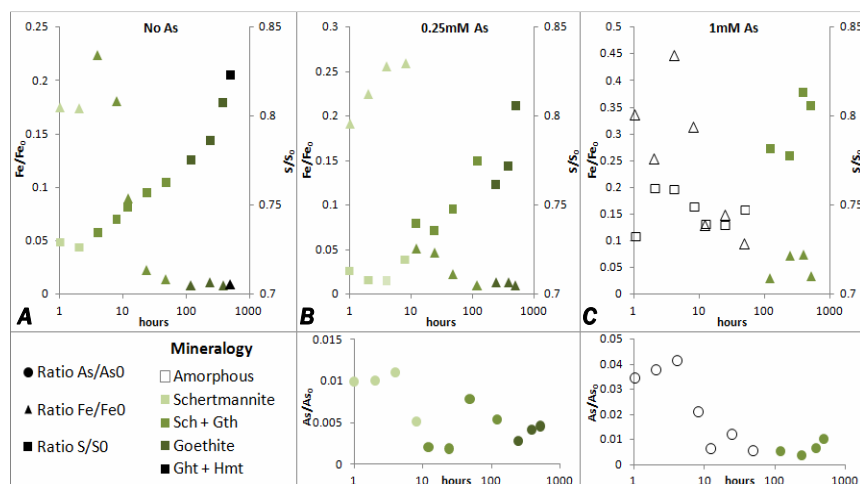
CONCLUSIONS

The aging of terrace sediments affected by AMD (schwertmannite, jarosite and goethite) and their transformation by diagenetic processes to more crystalline phases (goethite and hematite) involves increasing mobility of As, which was previously retained by the precursor schwertmannite. This mechanism of As mobilization should be considered in the development of conceptual and analytical models describing the long-term fate, transport and bioavailability of As in environmental systems from the IPB. The search for stability in this type of poorly crystalline iron oxy-hydroxysulphate could determine the flow of arsenic with time, and what is now considered a sink could become a long-term source of contamination.

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Fig. 3: *ICP-AES and XRD results from aging experiments in laboratory (supernatant water and precipitates respectively). Values are represented as ratio of the concentration in every time and the initial concentration.*