ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Arsenic sequestration by mineralization in Schwertmannite	**Experiment number**: EC-470
Beamline: ID18F	**Date of experiment**: from: 18 sep 2009 to: 21 sep 2009	**Date of report**: 30 mar 2011
Shifts: 18	**Local contact(s)**: Rémi Tucoulou	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Synchrotron-based X-ray study of iron oxide transformations in terraces from the Tinto-Odiel river system: influence on arsenic mobility

Acid mine drainage (AMD) generated by sulphide oxidative dissolution is a major cause of water contamination world-wide (Olías et al., 2006). The Iberian Pyrite Belt (IPB; SW Iberian Peninsula) is the major reserve of massive pyrite deposits in the world, with more than one hundred abandoned mines (Sáez et al., 1999). Oxidation of pyrite and the lack of alkalinity-producing rocks in the region generates a huge amount of AMD, which is drained via numerous mining effluents to the Tinto and Odiel rivers. Recent studies have shown that these two rivers discharge an enormous amount of metal(loid)s into the Estuary of Huelva (e.g. 36 t y^{-1} of As; Olías et al., 2006). The contribution of pollutants by Tinto and Odiel rivers to the Atlantic Ocean represents a significant percentage of the global gross flux of dissolved metals transported by rivers into the oceans world-wide (e.g. up to 60% of Zn and 17% of Cu; Nieto et al., 2007). In mining environments in the IPB, riverbeds are covered with several centimeters (up to 10 cm) of yellowish and reddish loose and crusty Fe-rich precipitates, creating different terrace levels along the channel. These terraces frequently define structures constituted by a sequence of different associations of iron phases.

Simultaneous analysis of micro-X-ray diffraction (μ-XRD) and micro-X-ray fluorescence (μ-XRF) based on synchrotron light sources, and electron microprobe (EMP) analyses, were performed on iron terrace samples taken from Tinto-Odiel river system from the IBP. Iron terraces are formed during the oxidation and precipitation of dissolved iron along the riverbeds impacted by AMD. This work includes the study of actively-forming current terraces and fossil terraces isolated from the stream courses due to the river migration over time. The results of the study of current terrace samples from AMD-affected streams of two IPB abandoned mines (Tinto Santa Rosa and Cueva de la Mora) showed that fresh precipitates at the surface are composed primarily of metastable schwertmannite, which is gradually transformed at depth over short-time scales into goethite (Fig. 1).

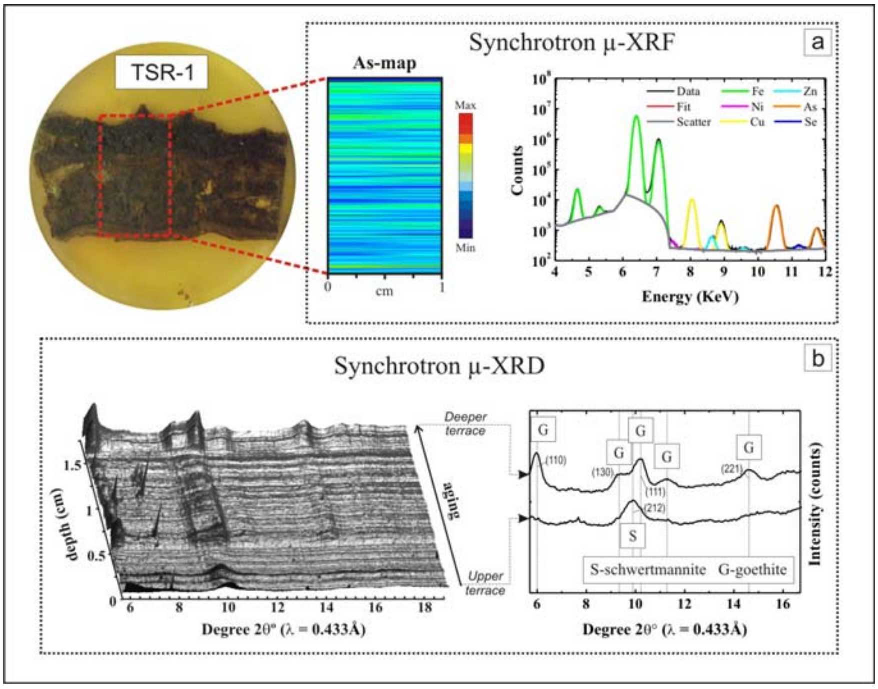

Figure 1. Micro cross-section analyzed in TSR-1 sample by synchrotron-based (a) **μ**-XRF: arsenic mapping and calibration spectrum fitted with PyMCA software, and (b) **μ**-XRD: 1D-XRD patterns of one cross-band line after integration of data with package Fit2D.

Sediments of ancient terraces are composed mainly of goethite, which most likely originated from the re-crystallization of a precursor schwertmannite. However, at century-time scale, goethite partially re-crystallizes to hematite due to diagenetic processes (Fig. 2).

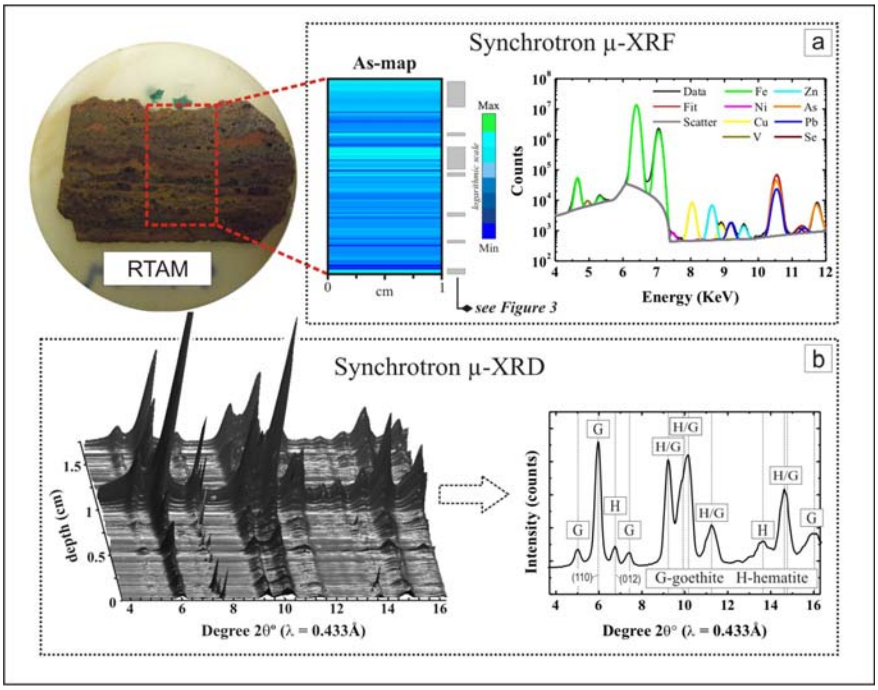

Figure 2. Micro cross-section analyzed in RTAM sample by synchrotron-based (a) **μ**-XRF: arsenic mapping and calibration spectrum fitted with PyMCA software, and (b) **μ**-XRD: 1D-XRD patterns of one cross-band line after integration of data with package Fit2D.

The transformation rate of goethite into hematite is negatively correlated with grain size and the crystallinity of goethite (Fig. 3). Moreover, this transformation is accompanied by an increase in grain size and a decrease in surface area of hematite, and a concomitant decrease in arsenic trapped in the solid.

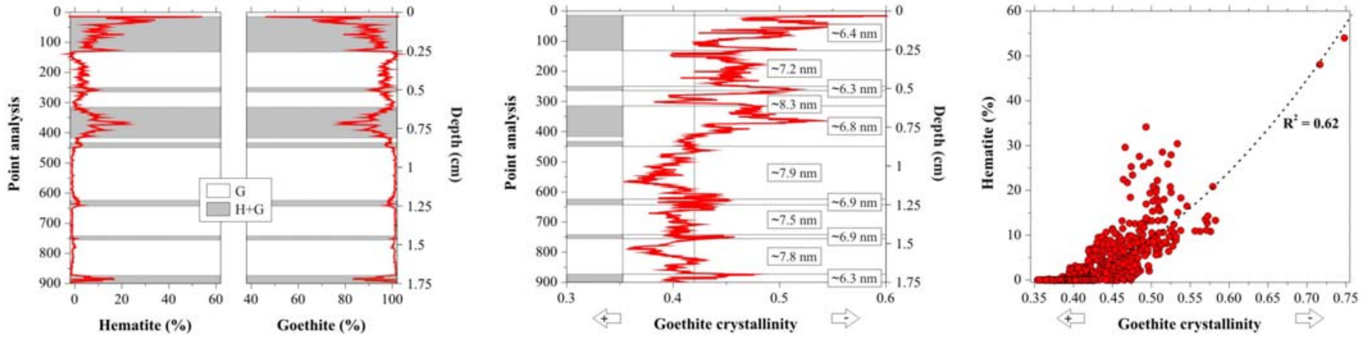

Figure 3. Variation of the percentage of hematite and goethite and of the crystallinity of goethite along the RTAM sample. Grey areas correspond to levels of goethite + hematite and white areas to levels of only goethite. Note that grey areas match levels of high arsenic concentration as shown in Figure 2. Relationship between crystallinity of goethite and percentage of hematite.

This increase in the arsenic mobility during the diagenetic maturation should be considered in the development of conceptual and analytical models describing long-term fate, transport and bioavailability of arsenic in environmental systems.

References

Nieto, J.M., Sarmiento, A.M., Olías, M., Cánovas, C.R., Riba, I., Kalman, J., Delvalls, T.A., 2007. Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, SW Spain) and bioavailability of the transported metals to the Huelva Estuary. Environment International 33, 445-455.

Olías, M., Cánovas, C.R., Nieto, J.M., Sarmiento, A.M., 2006. Evaluation of the dissolved contaminant load transported by the Tinto and Odiel rivers (South West Spain). Applied Geochemistry 21, 1733-1749.

Sáez, R., Pascual, E., Toscano, M., Almodóvar, G.R., 1999. The Iberian type of volcano-sedimentary massive sulphide deposits. Mineralium Deposita 34, 549-570.

Please: more information available at (http://dx.doi.org/10.1016/j.chemgeo.2010.11.021):

R. Pérez-López, M.P. Asta, G. Román-Ross, J.M. Nieto, C. Ayora, R. Tucoulou (2011). Synchrotron-based X-ray study of iron oxide transformations in terraces from the Tinto-Odiel river system: Influence on arsenic mobility. Chemical Geology 280, 336-343.