EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

# 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.

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|---|---|---|
| ESRF | **Experiment title:**<br>Role of natural colloids as environmental nanovectors of As in contaminated soils: a case study in Madrid (Spain) province | **Experiment number**:<br>CRG 25-01 817 |
| **Beamline**:<br>BM25A | **Date of experiment**:<br>from: 2/10/2011 at 08:00 to 5/10/2011 at 08:00 | **Date of report**:<br><br>*Received at ESRF:* |
| **Shifts:**<br>9 | **Local contact(s)**:<br>Dr Miquel Lluis CORRO MOYA<br>Dr. Jon Ander GALLASTEGUI | |

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## Report:

Elevated metal concentrations in groundwater supplies in the Madrid (Spain) tertiary detrital aquifer have recently been recognised (Rocio-Vazquez et al., 2011). Although most of the As contamination processes are originated by natural inorganic sources, As and other metals present in groundwater may be the result of leaching of mine tailings, dissolution of arsenic-rich smelter deposition of particulates, and subsequent infiltration and dissolution of arsenic-bearing minerals naturally present in the catchment's area. Knowledge on the sources of this element, the mechanisms controlling its release and mobility, and its natural attenuation processes are crucial to minimize the risk and consequences of metal contamination as well as to implement specific remediation strategies. Not much information is available on the role that other processes such as the association of As on soil colloids and their mobilisation as nanovectors of contaminants may play on the distribution of As and other metals in soils affected by acid mine drainage (AMD). As a fundamental step within the research project CGL2010-17434 financed by the Spanish National Research Plan, our experiment aimed to study the molecular-scale speciation of As in selected natural coloids samples obtained from metal(loid)s contaminated soil samples aiming to assess the role of soil natural colloidal particles as nanovectores of toxic elements in the contamination process of the soil-water system.

### Experimental methods

Samples were collected from an abandoned smelting factory located in Guadalix de la Sierra (Community of Madrid, Spain), in which arsenopyrite encapsulated in quartz was processed for wolfram extraction during the Second World War. Four different samples were collected for this study: (1) waste rocks from the mine pile (WP), (2) sediments from the riverbed (RB) (0-10 cm) of a small stream that seasonally collects surface runoff from the arsenic-bearing waste pile, (3) soils from the subsoil (SS) (10-40 cm) under the riverbed layer, and (4) sediments (0-15 cm) from a natural pond (SP) collecting all runoff.

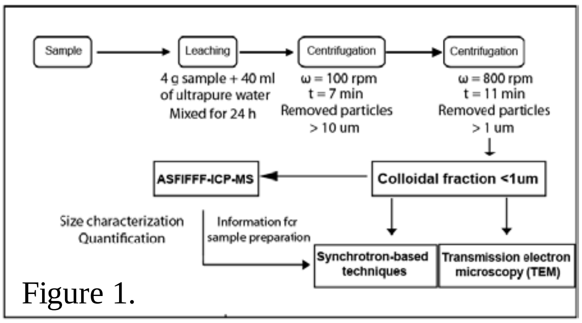

Figure 1.

Colloid samples were isolated on the basis of a centrifugation protocol aiming to separate particle size fractions larger than the target size (< 1µm) (Figure 1). A volume of the suspension was injected directly to the AsFlFFF (Asymmetric-Flow Field-Flow Fractionation) coupled to an ICP-mass spectrometer. Further, ultrafiltration membranes were removed from the holders and colloids measured by XAS. Colloidal suspensions were also placed on Ni grids for subsequent Transmission Electron Microscopy (TEM) observations.

During our experiment, As and Fe k-edge XAS spectra were measured on bending-magnet BM25A beamline (SpLine) (6 GeV, 100 mA, Si(111) monochromator crystals) in fluorescence mode using a 13-element Si(Li) solid state detector with the sample at room temperature. All spectra (approx. 25 scans per sample) have been analized using the computer packages Sixpack and EXAFSPAK (SSRL), together with *ab initio* reference phase shift and amplitude functions for EXAFS calculated with the program FEFF and calibrated against experimental reference compound data. Arsenic and Fe spectra were analyzed using the programs Athena (Ravel and Newville, 2005) for linear combination fits. Background was subtracted using a linear fit through the pre-edge region and the Autobak routine in Athena for the spline fit through the EXAFS region. Arsenic XANES spectra were fit by linear least-squares combination fits of reference compounds to verify the As oxidation state.

## Results

Analysis of As XAS spectra of the colloidal fractions let us identify scorodite as the main As component in the WP. In addition, As adsorption on ferrihydrite was the main As-colloid retention mechanism in RB, SS and SP colloid samples (Figures 2). Results obtained from shell-by-shell fits of As K- EXAFS spectra were consistent with inner sphere complexation of As on Fe oxihydroxides through bidentate binuclear bridging complexes. Results of the analysis of Fe XAS spectra indicated that scorodite was the dominant component in the WP. A mixture of smectite and Fe(III)-oxide was shown as the main components in the RB, SS, and SP samples (Figures 3).

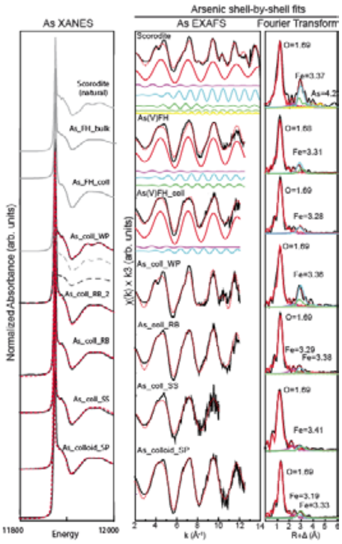

Figure 2.

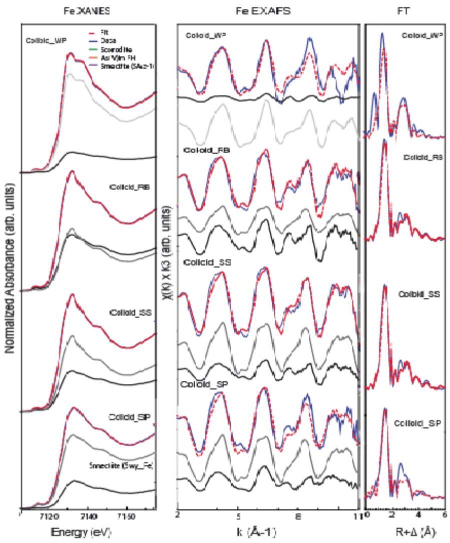

Figure 3.

## Conclusions

XAS analysis of the colloid fraction could be performed after isolation of the colloids on utrafiltration membranes. Arsenic is present mostly as scorodite in the colloidal fraction of WP, but it is adsorbed in ferrihydrite in RB, SS and SP. XAS results indicated that the colloid particles have local structure similar to crystalline minerals even at nanometer particle sizes and were dominated by mineral compounds. No organic fraction was detected. Our results show the potential role of Fe-oxyhydroxides phases and, to a lesser extent scorodite, as nanovectors of As in contaminated soils. Further studies will investigate stability and transport processes of colloidal particles within the project CGL2010-17434 supported by the Spanish National Research Plan.

Preliminary results have been presented as:

> Garrido, F., Laborda, F., Bolea, E., Helmhart, M., O'Day P.A., and Serrano S. Colloidal arsenic distribution and speciation in mine soils. *Mineralogical Magazine*, Vol. 75 (3), 895 (2011).

Total results are in preparation as:

> Serrano, S., O'Day, P., Gómez-González, MA., Laborda, F., Bolea, E., Helmhart, M., and Garrido, F. Colloidal arsenic distribution and speciation in mine soils. *In preparation*