

## 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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can 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.

**Experiment title:**

Anion speciation in soils by XAS spectroscopy

**Experiment****number:**

25-01-772

<b>Beamline:</b> BM25A	<b>Date of experiment:</b> from: 2/16/11 to: 2/19/11	<b>Date of report:</b> 9/1/11
<b>Shifts:</b> 9	<b>Local contact(s):</b> Germán R. Castro	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

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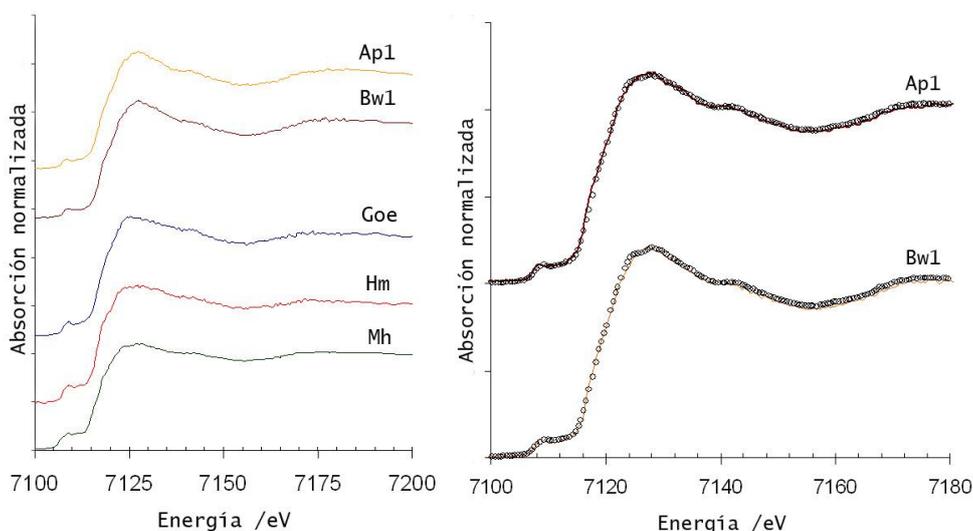
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Ana Gutierrez Leon, ESRF, Grenoble, France

Juan Rubio Zuazo, ESRF, Grenoble, France

**Report:**

The reactivity of various elements in two horizons of an oxisol was analyzed. In a first experiment Fe speciation was studied by means of the Fe K-edge XANES spectra from reference compounds and soil samples (Figure 1).



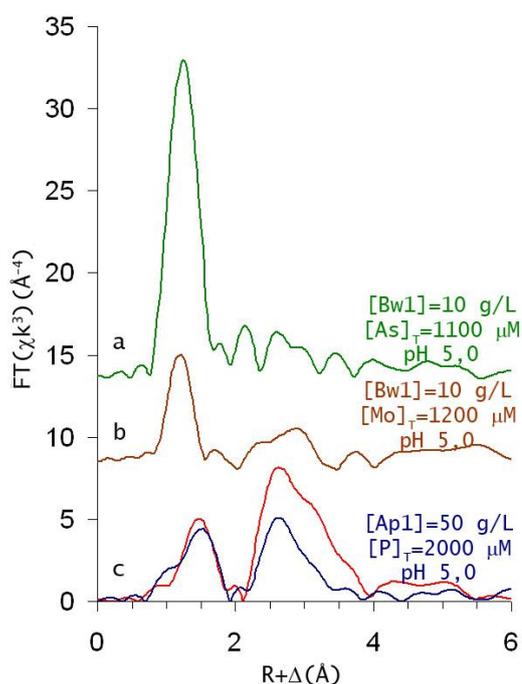
**Figure 1** Left, Fe K-edge XANES spectra of oxisol samples (Ap1, Bw1) and reference oxide minerals (Goe=goethite, Hm=hematite, Mh=maghemite). Right, linear combination fitting (LCF) of the reference compounds; solid lines are the experimental data and open circles represent the theoretical fit.

The results from LCF confirmed the presence of reference iron oxides in the oxisol samples, pointing out a greater content of hematite (Table 1).

**Table 1** Ratio of reference mineral compounds calculated by Linear Combination Fitting using the entire Fe K-edge XANES spectra

	Goethite (%)	Hematite (%)	Maghemite (%)
Ap1	31.3 ± 1.6	61.7 ± 2.4	7.0 ± 2.9
Bw1	20.7 ± 1.7	73.2 ± 2.6	6.1 ± 3.1

EXAFS spectra were analyzed in order to assess the speciation of anions such as arsenate and molybdate, which were previously adsorbed in the soil samples. The radial distribution functions obtained by Fourier-transformation of the Fe K-edge EXAFS spectra from pure hematite (red color) and the topsoil horizon, Ap1 (blue color), with adsorbed phosphate, are shown in Figure 2c. Both spectra were controlled by backscattering from an O first shell at 1.8 Å, with additional contributions from two shells at 2 to 4 Å. The spectrum for the hematite reference sample agrees with the results reported previously in the literature (O'Day et al. 2004) with two Fe-Fe distances at 2.8 and 3.3 Å corresponding to edge sharing and corner sharing distances, respectively. A lower second-shell peak of the Fourier-transformed EXAFS spectrum was observed in the soil sample Ap1, confirming that phosphate result in a structural change (Voegelin et al. 2010).



**Figure 2** Fourier-transformed (FT)  $k^3$ -weighted: (a) As K-edge EXAFS spectra; (b) Mo K-edge EXAFS spectra; and (c) Fe K-edge EXAFS spectra of selected samples. In red, hematite FT Fe K-edge EXAFS spectrum, for comparison. Ap1=topsoil horizon; Bw1=subsoil horizon.

The Fourier-transformed  $k^3$ -weighted As(V) K-edge EXAFS spectrum is shown in Figure 2a. The As-O distance of 1.6 Å is typical for adsorbed As(V) compounds. The shell at 3.5 Å for As-Fe is characteristic of corner sharing tetrahedra-octahedra, resulting from a monodentate surface complex. The As-Fe distances at 2.8 and 3.2 Å result from an edge sharing of the oxyanion tetrahedra and the iron octahedra, and a corner sharing bidentate binuclear complex, respectively (Fendorf et al. 1997).

The Fourier-transformed Mo(VI) EXAFS spectrum is shown in Figure 2b. The spectrum is dominated by backscattering from an O first shell at 1.6 Å, as well as Mo-Fe distances at 2 to 3.5 Å, probably due to edge sharing bidentate mononuclear and corner-sharing bidentate binuclear (Arai 2010).

The treatment of the data derived from the measurements carried out at the ESRF is still in progress as a part of a doctoral thesis and eventually, a complete analysis of the experiments (fitting of the EXAFS and analysis of the XAFS features) will be published.

- Arai, Y., 2010. X-ray absorption spectroscopic investigation of molybdenum multinuclear sorption mechanism at the goethite-water interface. *Environ. Sci. Technol.* 44, 8491-8496.
- Fendorf, S., Eick, M. J., Grossl, P., Sparks, D. L., 1997. Arsenate and chromate retention mechanisms on goethite. 1. Surface structure. *Environ. Sci. Technol.* 31, 315-320.
- O'Day, P. A., Rivera Jr, N., Root, R., Carroll, S. A., 2004. X-ray absorption spectroscopic study of Fe reference compounds for the analysis of natural sediments. *Am. Miner.* 89, 572-585.
- Voegelin, A., Kaegi, R., Frommer, J., Vantelon, D., Hug, S. J., 2010. Effect of phosphate, silicate, and Ca on Fe(III)-precipitates formed in aerated Fe(II)- and As(III)-containing water studied by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* 74, 164-186.