



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>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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: Retention mechanism of rare earth elements on Fe nanominerals	Experiment number: EV-438
Beamline: BM30	Date of experiment: from: 18/11/2021 to: 23/11/2021	Date of report: 02/09/2022
Shifts: 15	Local contact(s): Antonio Aguilar	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Sergio Carrero, IDAEA*, CSIC, Spain Joan Gutierrez Leon*, IDAEA, CISC, Spain Jordi Cama i Robert*, IDAEA, CSIC, Spain		

Report:

In this experiment a series of schwertmannite samples (a Fe-oxyhydroxysulfate samples, $\text{Fe}_8\text{O}_8\text{OH}_6\text{SO}_4 \cdot 5\text{H}_2\text{O}$) with different rare earth element (REE) adsorbed were studied using X-ray Absorption Fluorescence for Extended X-ray Absorption Fine Structure (EXAFS) analysis, with the aim to determinate the structural coordination of adsorbed REE on the schwertmannite surface. Previous results indicate that REE adsorbed onto schwertmannite surface from covalent bonding with Fe in a bidentate coordination. However, the uncertain of EXAFS models indicated that other possible coordination, such as monodentate, cannot be ruled out (Lozano et al., 2019). REE desorption experiments carried out in our lab show that REE desorption is highly dependent of pH (Fig 1) where light REE are easily desorbed in comparison with heavy REE. The equilibrium constants calculated for this desorption reactions indicated that heavy and light REE are released from bidentate ($n = 2$) and monodentate ($n = 1$) complexes, respectively (Fig. 1 b). The working hypothesis used for this experiment was that both adsorption coordination was present on REE adsorbed onto the schwertmannite surface where monodentate proportion increase toward light REE. This hypothesis could explain the higher desorption rate in light REE with respect to heave REE with a coordination number close to 1. To prove this hypothesis, we proposed an X-ray absorption spectroscopy (XAS) experiment at BM30 in schwertmannite samples loaded with La, Gd and Lu, before and after desorption experiments run at different pH (3.5, 4.5, 5.5 and 6.5).

The experiment was performed with an incident energy en the range of 5420 to 5880 eV for La L3-edge, 7200 eV for Gd L3-edge and 9100 to 9880 eV for Lu L3-edge. The fist day of beamtime was devoted to the beamline alignment and the acquisition of XANES in La, Gd and

Lu reference solids in order to calibrate the detector and optimize the acquisition of the emission lines analyzed in these experiments. Samples were in a He cryostat to reduce the thermal vibration.

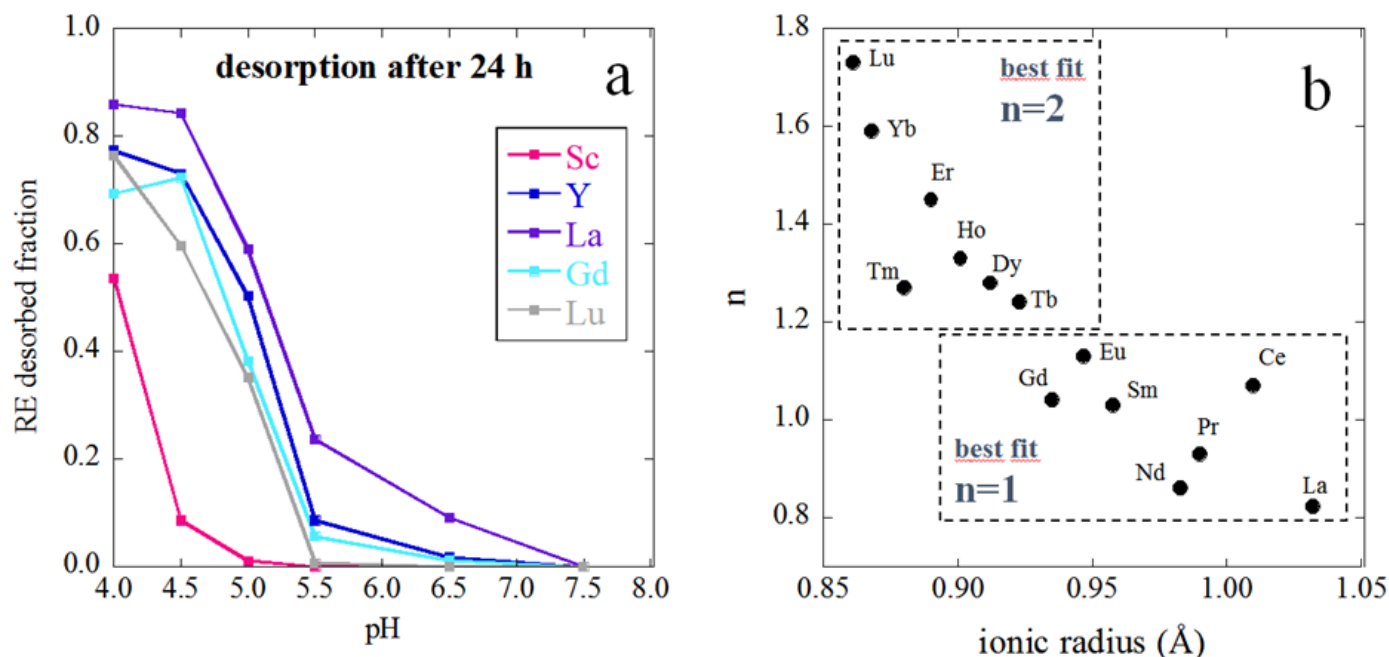


Figure 1. a) Experimental desorbed RE fraction from schwertmannite as a function of pH; b) n index of the surface complexation reaction obtained from the slope values of the linear regressions as function of the RE ionic radius (Å)

During the rest of the experiment, schwertmannite samples with La and Gd and Lu before and after desorption experiment, were measured:

Schwertmannite with La.

Figure 2 display the EXAFS obtained in the schwertmannite sample loaded with La before the desorption experiment. The La concentration in this sample was in the order of 5 g kg^{-1} and it was the most concentrate sample. However, the normalization and result interpretation of the EXAFS spectra was not possible due to poor signal. The low photon flow around 7 keV in BM30 and the low La concentration in this sample prevented the acquisition of a good EXAFS spectra, event when many scans were run. The rest of La samples were not run in this experiment due to their concentration in La was lower that the display sample in Fig. 2.

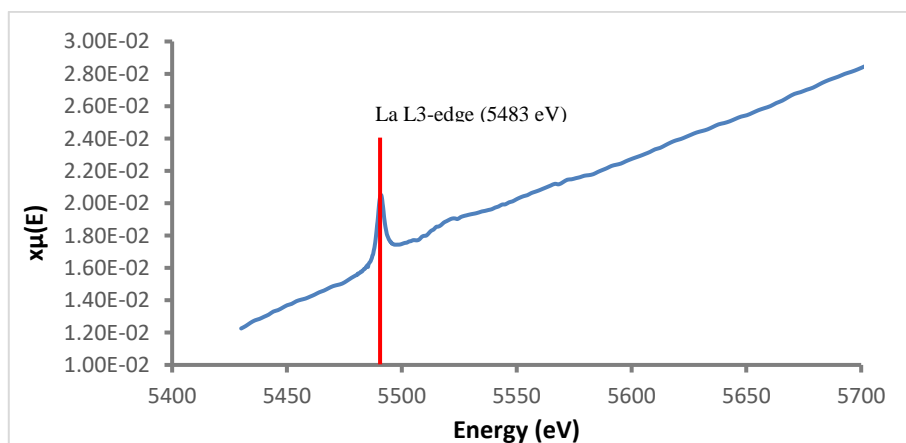


Figure 2: La L3-edge EXAFS in schwertmannite sample loaded with La. The small jump between pre and post-edge prevent a proper background subtraction for structural analysis.

Schwertmannite with Gd.

Figure 3 display the EXAFS spectra obtained in the schwertmannite sample loaded with Gd before the desorption experiment. As in the precious case, this sample contain the highest Gd concentration (around 3.5 g kg^{-1}). In this case, the Gd emission line analyzed was very close to Fe K-edge. Due to the matrix is a Fe-oxyhydroxide, the high Fe adsorption overlap the Gd signal, bringing a spectrum which could not be interpreted. Other Gd absorption lines (i.e., L1 and L2) were also tested, however the low Gd concentration brings a poor signal in those lines and, finally, we desisted to measure the schwertmannite samples loaded with Gd.

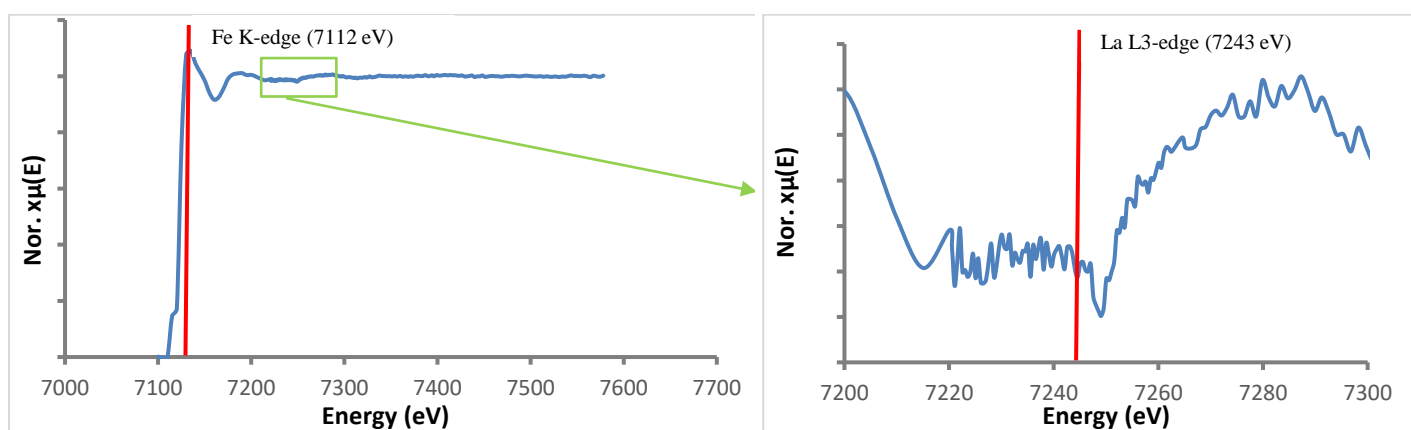


Figure 3: EXAFS in schwertmannite sample loaded with Gd around the Gd L3-edge. Fe K-edge (right) is clearly observed, and the Gd L3-edge (left) was total overlapped.

Schwertmannite with Lu.

Figure 4 display the EXAFS spectra obtained in schwertmannite sample before and after desorption experiment at pH 4.5. For this group of samples, we obtained a good signal in Lu L3-edge and background subtraction was performed.

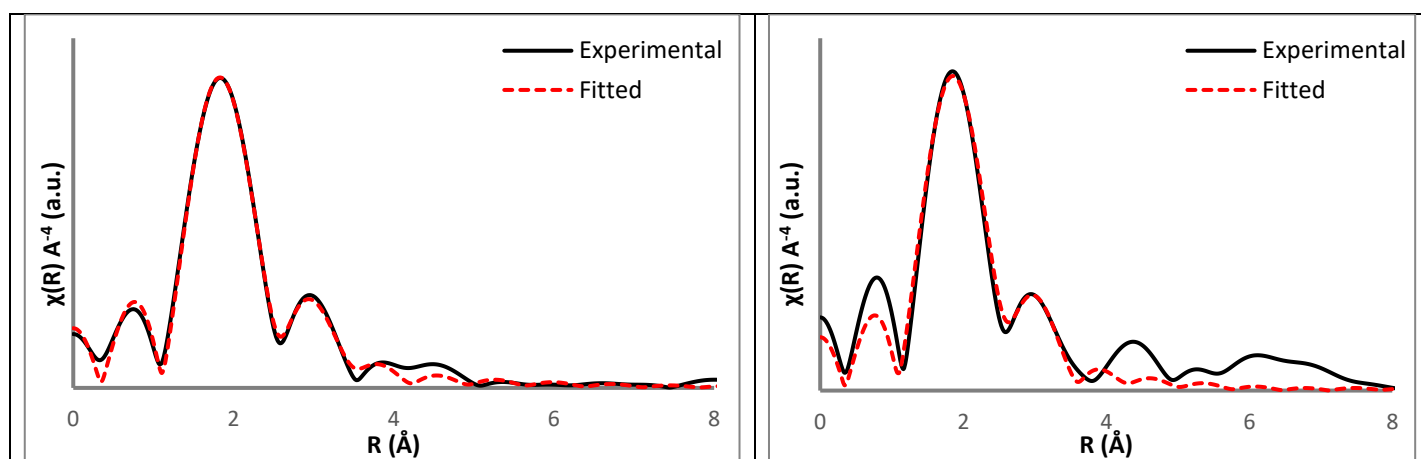


Figure 4: Fourier transform amplitude of EXAFS spectra of Lu after adsorption (left) and after desorption at pH 4.5 (right). The best fit obtained was bidentate binuclear and monodentate for Lu after adsorption and desorption experiment, respectively.

The preliminary interpretation of EXAFS data display that Lu coordination on schwertmannite after adsorption fits with a bidentate binuclear binding mechanism according to the models runs using Artemis software. This result is in agreement with previous experiments (Lozano et al., 2019). However, the samples after desorption at any pH fit with a monodentate coordination model, where Lu form just one covalent bind with schwertmannite surface (Table 1):

	Lu adsorption	Lu desorp. at 4.5	Lu desorp. at 5.5	Lu desorp. at 6.5
$\Delta\chi^2$ monodentate	78.018	10.828	36.251	59.029
$\Delta\chi^2$ Bidentate binucl.	31.338	24.404	68.328	97.590

The main propose of this experiment was the comparison of desorption mechanism between heavy, medium, and light REE elements adsorb on schwertmannite. However, the analytical problems with La and Gd prevent us to conclude the desorption reaction and the effect of pH in retention mechanism depending on the REE analyzed. Lanthanum and Gd samples should be run a beamline equipped with High-Energy Resolution Fluorescence Detected (HERFD) that can discriminate the signal from Fe K-edge and Gd L3-edge and detect elements in a very low concentration.

Lozano A., Ayora C. and Fernández-Martínez A. (2019) Sorption of rare earth elements onto basaluminite: The role of sulfate and pH. *Geochim. Cosmochim. Acta* **258**, 50–62.