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 via the User Portal:

https://wwws.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.

ESRF	**Experiment title:** Uranium speciation in sediments from uranium contaminated lake (France)	**Experiment number**: EV 20
Beamline: BM23	**Date of experiment**: from: 26 Jun 2013 to: 02 Jul 2013	**Date of report**: Sep 2, 2013
Shifts: 18	**Local contact(s)**: Olivier Mathon	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The proposed study aims at determining uranium speciation in bottom-lake sediments downstream of a former U-mining site in Northern Massif Central, France. EXAFS and XANES spectroscopy are used to identify the nature of the deposited U-bearing phases
and to follow the possible changes in uranium speciation after deposition in relation with redox cycling at and below the water sediment interface. These issues are addressed thanks to the study of bottom lake sediment cores carefully collected and preserved from oxidation.

The knowledge of uranium speciation in such contaminated lake sediments is critical to our evaluation of the efficiency of U sequestration in these sediments over the last decades and these information are of key importance to improve the management of such lakes.

XANES data were recorded at the U $L\text{-}_{III}$ edge on a large series of sediment samples with U concentrations ranging between 50 and 300 mg/kg U, in fluorescence detection mode using a 13 elements Ge array detector **(Figure 1)**. These data indicate significant changes in U oxidation state with depth in the sediment, which could be quantified by linear decomposition of the XANES data using appropriate model compounds data prepared for this experiement and that were analyzed during the same beamtime. **(Figure 2)**

Due to high Fe fluorescence background in the samples studied, EXAFS data could only be collected on the most concentrated sample **(Figure 3)**. The analysis of uranium speciation in these samples is under progress. Data will be fit using linear combinations of U(IV) and U(VI) model compound spectra collected during this beamtime and which are relevant of U speciation in sediments.

Complementary analyzes, including spatially resolved U spectroscopy might be necessary to fully determine U speciation in these complex natural samples.

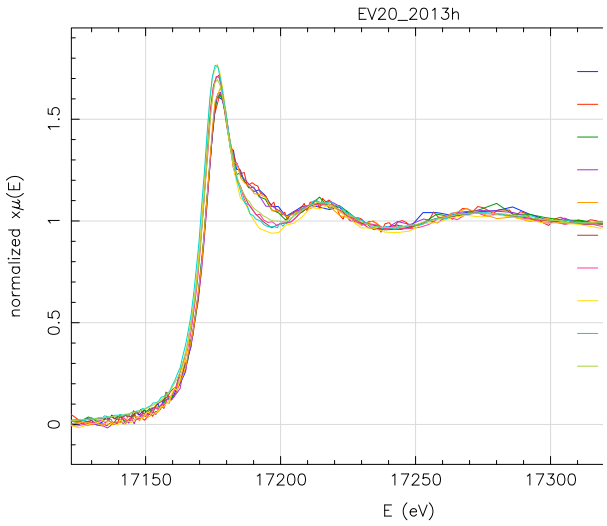
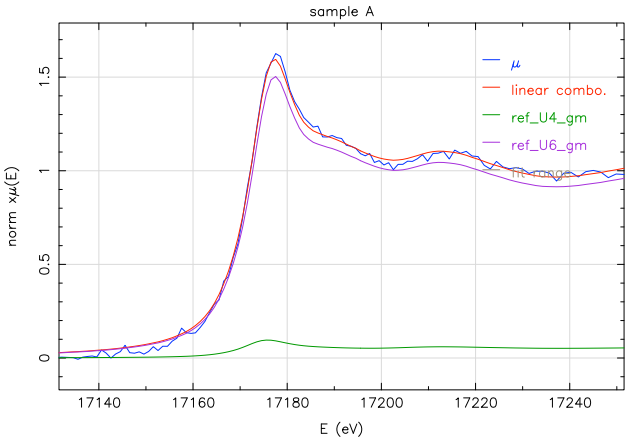
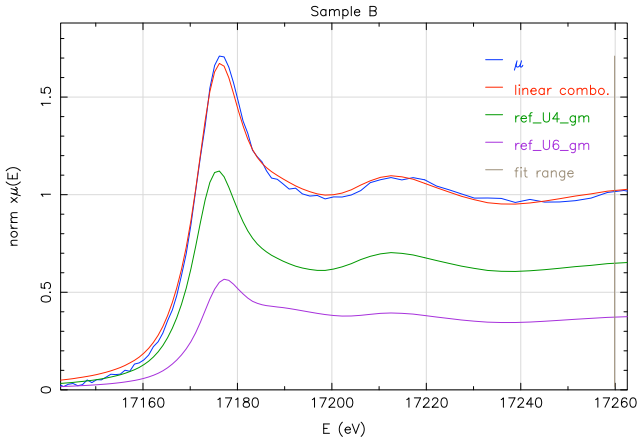


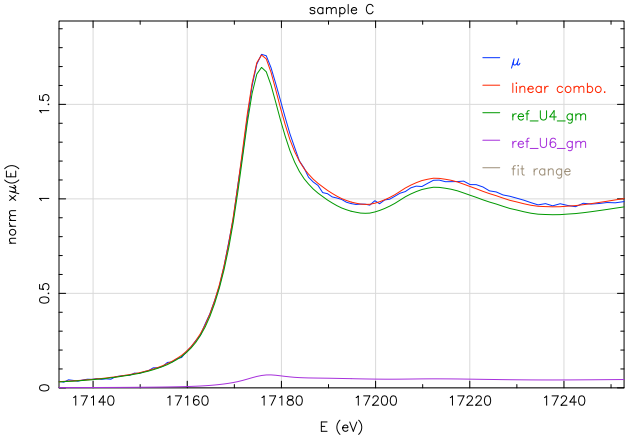
Figure 1: XANES spectra at the U LIII-edge collected on a series of natural sediment samples collected at different depth within a sediment core. The change in the energy position of the absorption edge and in the shape of the XANES structure indicates changes in the U oxidation state with depth. The shoulder at 17190 eV is especially indicative of the multiple scattering within the axial $[O=U=O]^{2+}$ uranyl molecule, the most common form of U(VI).



5% U(IV) 95% U(VI)



64% U(IV) 36% U(VI)



95% U(IV) 5% U(VI)

Figure 2: Linear combination fit of XANES spectra at the U LIII-edge for selected natural sediment samples collected at different depth within a sediment core. The fitting components correspond to synthetic pure U(IV) and U(VI) model compounds, analyzed during this experiment.

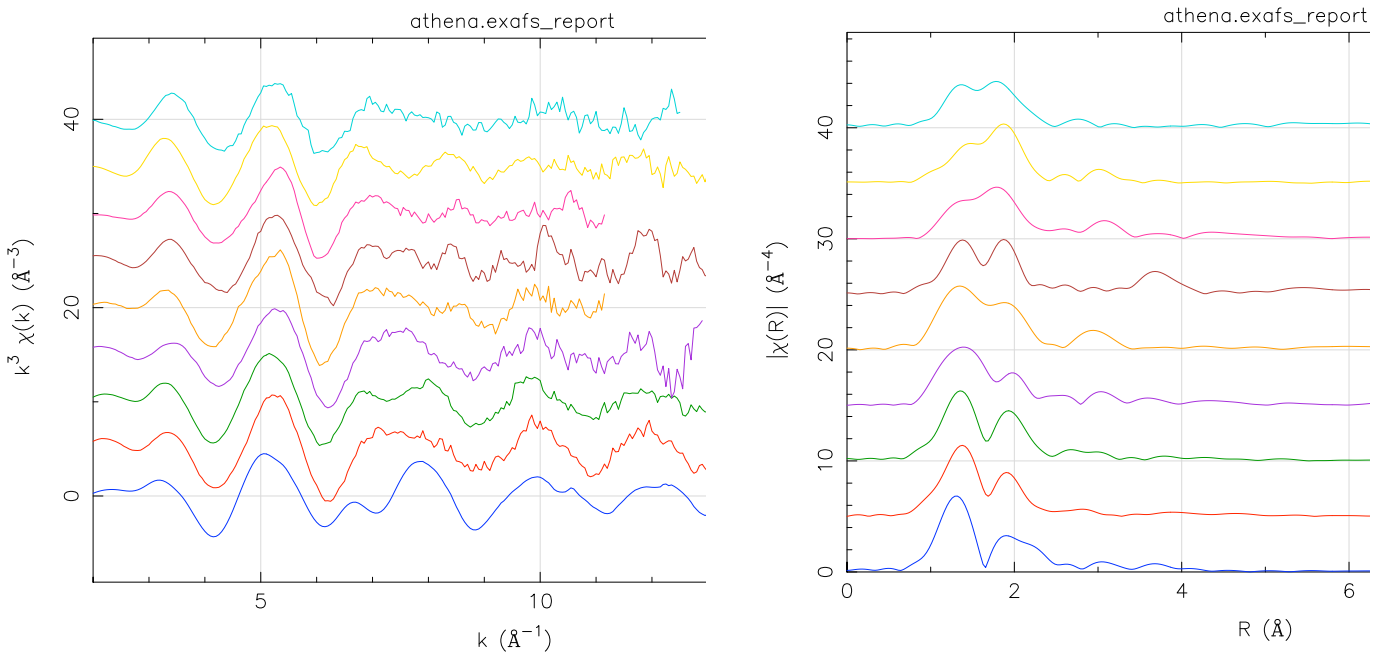


Figure 3. EXAFS spectrum of a sediment sample (320 ppm U) compared to EXAFS spectra of model compound samples including diluted sorption samples recorded in fluorescence detection mode at 15 K under He atmosphere. The bottom spectrum correspond to crystalline uranyl nitrate recorded in transmission mode. Amplitudes of the Fourier Transform are given on the right side.

Publications :

Seder-Colomina M., Morin G., Brest J., Ona-Nguema G., Gordien N., Pernelle J.J., Banerjee D., Mathon, O., Esposito G., Van Hullebusch E. (2015) Uranium(VI) scavenging by amorphous iron phosphate encrusting Sphaerotilus natans filaments. Environmental Science and Technology 49, 14065–14075. DOI: 10.1021/acs.est.5b03148

G. Morin, A. Mangeret, G. Othmane, L. Stetten, M. Seder-Colomina, J. Brest, G. Ona-Nguema, S. Bassot, C. Courbet, J. Guillevic, A. Thouvenot, O. Mathon, O. Proux, J.R. Bargar (2016) Mononuclear U(IV) complexes and ningyoite as major uranium species in lake sediments. Geochemical Perspectives Letters 2, 95-105.