



## 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

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> 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.



	<b>Experiment title:</b> Uranium paleo-speciation in lake sediments as analogues for long-term near-surface repository sites	<b>Experiment number:</b> EV-411
<b>Beamline:</b>	<b>Date of experiment:</b> from: 16/06/21 to: 21/06/21	<b>Date of report:</b> <i>March 9, 2023</i>
<b>Shifts:</b>	<b>Local contact(s):</b> Olivier Mathon	<i>Received at ESRF:</i> <i>March 9, 2023</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> *Guillaume Morin (IMPMC, UMR7590, Paris, France) *Pierre Lefebvre (IMPMC, UMR7590, Paris, France) Pierre Le Pape (IMPMC, UMR7590, Paris, France) Jessica Brest (IMPMC, UMR7590, Paris, France)		

#### Report:

The proposal aimed at directly determining the evolution of uranium (U) speciation during the last 10 000 yrs in a naturally U-rich (up to 5000 mg/kg) lake catchment in the French Alps. Major issues concerned the mechanisms of long-term U accumulation in the wetland upstream from the lake and the evolution of U speciation over time. This goal can only be achieved by using XAS spectroscopy at the U L<sub>III</sub>-edge, that is combined in our project with isotopic measurements, dating methods, and mineralogy. Measuring such paleo-speciation of U will yield unique information on the long-term fate of U(IV) in anoxic conditions representative of near/sub-surface contaminated media and repository sites.

The experiment at the 2-pole wiggler beamline BM23 was thus dedicated to U speciation analysis in wetland soils core samples. The beamtime was splitted into two parts, the first one being dedicated to  $\mu$ XRF mapping in order to localize U at the micro-scale in the soil and  $\mu$ XANES spectra were collected to determine U redox state in representative microstructures, including biological remains. As detailed in the publication issued from to this beamtime (Lefebvre et al. 2022), data were collected at room temperature and the X-ray beam was focused with two mirrors in Kirkpatrick-Baez (KB) geometry to a  $3 \times 3 \mu\text{m}^2$  full width at half maximum at sample position. An optical microscope focused on sample position was placed right above the beam for proper tracking of the analyzed spot. The sample was embedded in epoxy resin as for SEM observations but within a N<sub>2</sub>-filled glove bag to prevent exposure to air, covered with Kapton tape to limit oxidation during the experiment and placed perpendicular to the X-ray beam. A continuous N<sub>2</sub> flow was applied on the sample surface to prevent oxidation by air over the course of the experiment. The Si-drift fluorescence detector was placed at a 45° angle between the beam and the sample plane. The incident beam energy was selected using a Si(1 1 1) double-crystal monochromator and was set to 17.5 keV for  $\mu$ -XRF mapping. The emission spectrum energy was calibrated using the Cu K $\alpha$  and K $\beta$  emission lines from Cu tape. The XRF spectra were converted to element-specific fluorescence intensity maps with the PyMca software through batch curve fitting of emission lines of elements of interest (including U L $\alpha$  and Fe K $\alpha$ ). We acquired  $2 \times 2 \text{ mm}^2$   $\mu$ -XRF maps with horizontal 5  $\mu\text{m}$  steps and vertical 10  $\mu\text{m}$  steps, with a counting time of 0.2 s per point. After  $\mu$ -XRF mapping, U-rich areas of interest were analyzed for their U oxidation state by  $\mu$ -XANES at the U L<sub>3</sub>-edge. For this purpose,  $\mu$ -XAS spectra (1000 points, 50 ms/point) were measured from 17.050 to 17.550 keV (17.400 keV for the first spectra), for a total duration of 66 s.

Room-temperature beam-damage kinetics (U(VI) photo-reduction) was estimated by acquiring 7 to 10 successive scans on the same spot, at four different locations (see Fig. 7, points a to d). Each scan was LC fitted to determine the evolution of U(VI) and U(IV) proportions over time (Figs. S2 and S3 in Lefebvre et al. 2022). At all spots, the U(IV) proportion significantly increased over time, ultimately exceeding U(VI) at two spots after 4 to 6 min. These kinetic measurements showed that every second scan acquired on the same position was significantly impacted by beam exposure, while the first scan (66 s acquisition time) was always affected by <10 % of relative U(VI) reduction. Proper U redox could thus be determined by LCF of I-XANES spectra obtained by merging individual first scans acquired on pristine spots of a same U-bearing area through successive displacements of > 10  $\mu\text{m}$  between each scan acquisition. To do so, additional I-XRF maps were acquired on selected areas where necessary, with horizontal and vertical 2.5  $\mu\text{m}$  steps to obtain more detailed chemical maps.

The second part of the beamtime was dedicated to EXAFS spectroscopy at the U L<sub>III</sub>-edge in order to determine the molecular environment of U in bulk wetland soil core samples. This EXAFS approach is necessary to complement the  $\mu$ XAS approach because

it yields a molecular-level description of U speciation and a quantification of the respective U species. Particular focus was given to the sorption process of U to organic matter and the identification of the functional groups involved in U binding, this by comparison with relevant synthetic organo-U model compounds, using a Linear combination fitting approach as well as a detailed shell-by-shell analysis. As detailed in (Lefebvre et al. 2022), EXAFS data were collected at high  $k$ -range for bulk wetland soil samples. In addition, solid residues obtained after 1 M bicarbonate extraction of together with the Lake sediment bulk sample were also analyzed for XANES data. The energy was selected with a Si(1 1 1) double-crystal monochromator and the samples were placed in a liquid He cryostat maintained at a temperature of 10 K. XAS measurements were performed in transmission detection mode for the two U-rich soil samples and in fluorescence detection mode with a Vortex silicon-drift energy-dispersive fluorescence detector for the other samples. Between 40 and 121 scans were collected on each sample, in continuous mode at a speed of 6.8 eV/s using a 50 ms sampling time (0.34 eV steps). Variable energy ranges within the XANES to EXAFS region were chosen depending on the samples, which resulted in 2- to 4-min long XAS scans. No beam-damage was observed for any sample under these data collection conditions.

All bulk XAS spectra at the U  $L_{III}$ -edge were merged, normalized and background-subtracted using the Athena software (Ravel and Newville, 2005). The incident beam energy was calibrated by setting to 17,038.0 eV the first inflection point of the yttrium (Y) K-edge transmission spectrum acquired on an Y foil using a double-transmission setup. The EXAFS spectra were binned to a  $0.04 \text{ \AA}^{-1}$   $k$ -step and deglitched when necessary, and the  $E_0$  value was set to 17173.4 eV, which corresponds to the inflexion point of the U(VI)  $L_{III}$ -edge. Least-square linear combination fitting (LCF) of XANES spectra at the U  $L_3$ -edge was performed using a Fortran 90 custom-built software based on a Levenberg-Marquardt minimization algorithm, similar to the software used in previous studies from our group as detailed in (Lefebvre et al. 2022). Prior to LCF analysis of EXAFS data, a Principal Component Analysis (PCA) of the  $k^3$ -weighted U  $L_{III}$ -edge EXAFS spectra dataset of our wetland samples was performed over the  $2\text{--}12 \text{ \AA}^{-1}$   $k$ -range using the SIXpack program (Webb, 2005). The PCA was followed by a Target Transform (TT) analysis of our model compound spectra database in order to select the most relevant components to perform LCF analysis of the wetland samples EXAFS data. Error analysis and goodness of fit estimators are detailed in Lefebvre et al. (2022). Least-square LCF of EXAFS spectra was then performed using a Fortran 90 custom-built software based on a Levenberg-Marquardt minimization algorithm, similar to the software used in previous studies, as detailed in Lefebvre et al. (2022). The unfiltered experimental  $k^3\chi(k)$  functions were fit in  $k$ -space over the  $2\text{--}12$  or  $2\text{--}10 \text{ \AA}^{-1}$   $k$ -range. Fit quality and error analysis is detailed in Lefebvre et al. (2022).

Shell-by-shell fitting of the unfiltered U  $L_{III}$ -edge  $k^3$ -weighted EXAFS spectra was performed using a Fortran 90 custom-built least-squares fitting software based on a Levenberg-Marquardt minimizing algorithm, similar to the code used in previous studies as detailed in Lefebvre et al. (2022). Continuous Cauchy Wavelet Transforms (CCWT) of the experimental and fitted EXAFS spectra were calculated using the MATLAB script by Muñoz et al. (2003, 2005). In order to decipher between close fitting solutions, fit quality of the second neighbor contributions were examined in R space by a reduced chi-square parameter and comparisons of fit solutions were done according to F-tests at 95 or 90 % confidence.

Our main spectroscopic results indicate that, at the particle scale, U is associated to a variety of organic constituents of the soil matrix with a homogenous oxidation state. Bulk EXAFS spectroscopy at the U  $L_{III}$ -edge shows that U is mostly mononuclear, with dominant monodentate binding to organic moieties (C neighbors at  $3.45 \text{ \AA}$ ). An additional minor fraction of U under polymeric forms is inferred from wavelet (CCWT) analysis of the EXAFS data. These observations are reinforced by 1 M bicarbonate extractions that result in the dissolution of 82–96 % of total U, including putative polymeric species. Combining these spectroscopic results with isotopic information, our study by Lefebvre et al (2022) shows that, partial U(VI) reduction to U(IV) occurs as a second step, after sorption onto organic matter. Moreover, the wetland acts as an active reactor where U has been massively accumulating for up to 14500 years, especially as U(VI) forms associated to organic matter, and is further partly exported to the lake through soil erosion.

#### Publication issued from the beamtime

Lefebvre P., Le Pape P., Mangeret A., Gourgiotis A., Sabatier P., Louvat P., Diez O., Mathon O., Hunault M.O.J.Y., Baya C., Darricau L., Cazala C., Bargar J.R., Gaillardet J., Morin G. (2022) Uranium sorption to organic matter and long-term accumulation in a pristine alpine wetland. *Geochimica et Cosmochimica Acta* 338, 322-346. <https://doi.org/10.1016/j.gca.2022.10.018>

#### Cited References

Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* 12, 537–541.

Webb, S.M., 2005. SIXpack: a graphical user interface for XAS analysis using IFEFFIT. *Phys. Scr.* 2005, 1011.

Muñoz, M., Argoul, P., Farges, F., 2003. Continuous Cauchy wavelet transform analyses of EXAFS spectra: A qualitative approach. *Am. Mineral.* 88, 694–700.

Muñoz, M., Farges, F., Argoul, P., 2005. Continuous Cauchy wavelet transform of XAFS spectra. *Phys. Scr.* 2005, 221.

