

## 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> <b>Speciation of U and Th in silicate glasses at highly reducing conditions relevant to Earth's core formation</b>		<b>Experiment number:</b> 16-01-800
<b>Beamline:</b> BM16	<b>Date of experiment:</b> from: 12.11.2020 to: 22.11.2020 from: 08.12.2020 to: 13.12.2020	<b>Date of report:</b> 5/01/2021
<b>Shifts:</b> 18	<b>Local contact(s):</b> Elena Bazarkina	<i>Received at ESRF:</i> <b>5/01/2021</b>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>ROSA Angelika Dorothea<sup>1*</sup>, Mohamed Ali Bouhifd<sup>2</sup></b> <sup>1</sup> European Synchrotron Radiation Facility, Grenoble, France <sup>2</sup> Laboratoire Magmas et Volcans, Clermont-Ferrand, France		

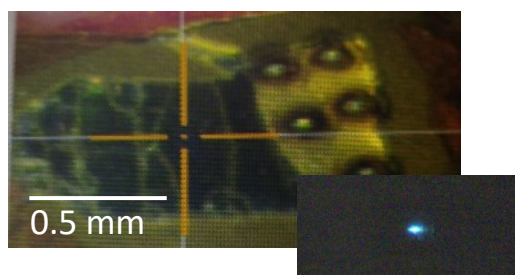
## Report:

### Objectives and expected results:

The main objective of this study was to determine the valence of Uranium and Thorium contained in silicate glasses as tracers (600-6000 ppm) synthesized previously at highly reducing conditions relevant to those that prevailed in the Early Earth's interior. This knowledge is crucial to interpret their experimentally observed distribution behaviours between a silicate melt and a metal melt [1] and to deduce their abundances in the Earth's mantle and core [2,3]. In order to investigate if the valence state changes of U and Th are at the origin of the observed distribution behaviour we performed HERFD-XANES measurements complemented with PFY measurements at their L<sub>3</sub>-edges.

### Results and the conclusion of the study:

For U L<sub>3</sub> HERFD-XANES measurements (incoming energy ~17.1 keV) the beamline FAME-UHD (BM16) was operating using a Si(220) double-crystal monochromator combined with a set of two Rh coated harmonic rejection mirrors inclined to 3 mrad. The beam was focused in vertical and horizontal to a size of 150\*200 μm<sup>2</sup>, which was necessary to probe only the signal from the silicate glass parts, which have typical dimensions of 0.5\*0.5 mm<sup>2</sup>. A crystal analyser spectrometer (CAS) with a Roland radius of 1 m was employed. Samples were placed with an angle of 45° to the incoming beam. The CAS was equipped with six Ge(777) crystals aligned to a Bragg's angle of 77.4° degree allowing a high energy resolution (~3 eV) at the emission energy of U L<sub>α1</sub> 13.615 keV. A digital camera equipped with a microfocus objective was employed to identify the position of the beam on the samples.

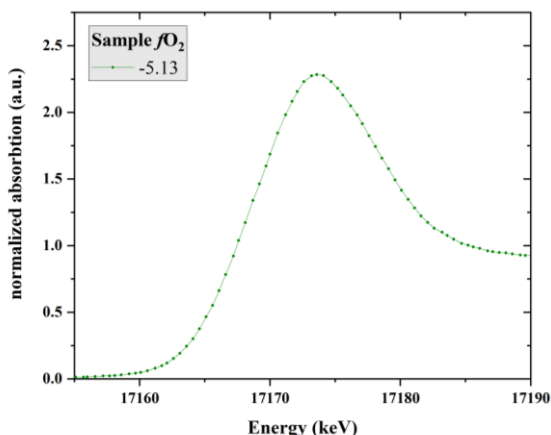


**Fig. 1.** Photograph of a polished sample aligned onto the X-ray beam (in the cross hair). Note the two distinct parts of the sample (silicon glass, green) and the metal (gold with holes due to LA-ICP-MS measurements). Note the slight blueish fluorescence on the sample induced by the X-ray beam (dark insert).

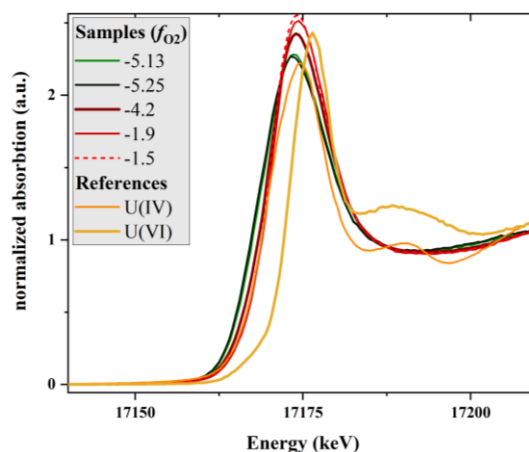
We performed U L<sub>3</sub>-edge HERFD-XANES measurements on 10 glass samples synthesised at different oxygen fugacities ( $f_{O_2} = -5.25, -5.13, -4.32, -4.13, -1.9, -1.67, -1.61, -1.54, -1.46, -1.05$ ) but equivalent ( $P/T$ ) conditions (1 GPa and 1773 K). For each sample at least 4 and up to 8 spectra were acquired between 17.0 to 17.5 keV (requiring each 30 minutes). A reference spectra of Y at its K-edge in transmission mode was regularly acquired in order to account for small energy drifts of the monochromator. An additional spectrum of a standard solution containing 2000 ppm of uranyl (U<sub>IV</sub>) was acquired to ensure a tight calibration of the white line and first XANES peak maximum to the valence of U. Finally, for

the sample with the highest content of Uranium (6000 ppm) test EXAFS spectra were acquired up to a k-range of  $8 \text{ \AA}^{-1}$ . No HERFD data were obtained for Th due to time-consuming CAS changes required and because the priority was given to U as a sensitive to  $f_{O_2}$  (see below).

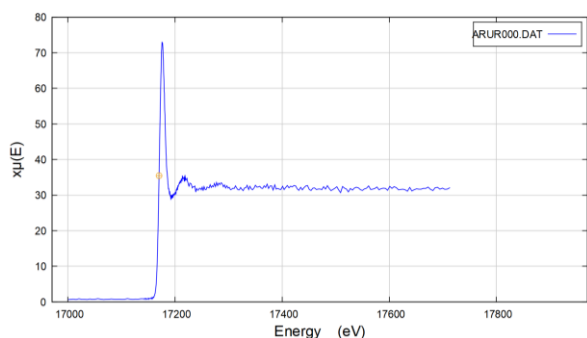
The acquired HERFD-XANES spectra were of very high quality in terms of signal to noise ratio and suppressions of the background signal (flat pre-edge line) (**Fig2. a,b**). The EXAFS signal was however affected by a high-noise signal already after a k-range of  $6 \text{ \AA}^{-1}$  (Fig.3a,b)



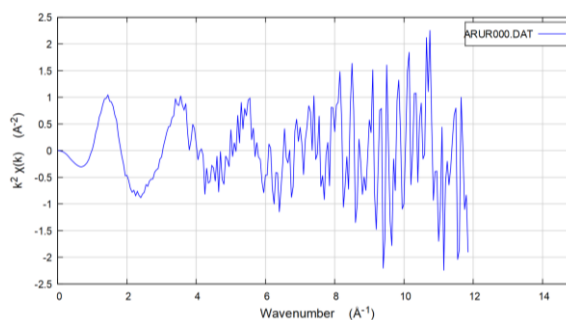
**Fig. 2a.** Typical U  $L_3$ -edge HERFD-XANES spectra acquired on the sample.



**Fig. 2b.** Compilation of U  $L_3$ -edge HERFD-XANES spectra acquired on the samples and references.



**Fig. 3a.** Typical U  $L_3$ -edge HERFD spectra for EXAFS analysis.

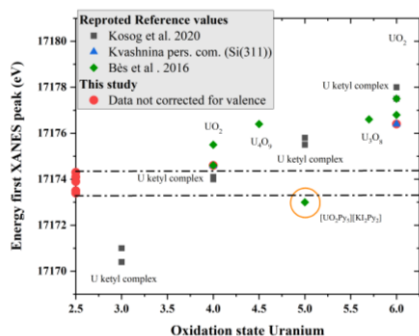


**Fig. 3b.** EXAFS part of the U  $L_3$ -edge HERFD EXANES spectra 3a in k-space.

The acquired U  $L_3$  edge HERFD-XANES data from the samples showed a clear variation of the edge and first XANES peak maximum energy position (FXPM) as a function of  $f_{O_2}$ . The total energy shift of the FXPM with varying  $f_{O_2}$  was found to equal  $\Delta E_{FXPM} = 2.1 \text{ eV}$ . This observation is in line with the experimentally observed change in partitioning behaviour and expected changes in U valence state.

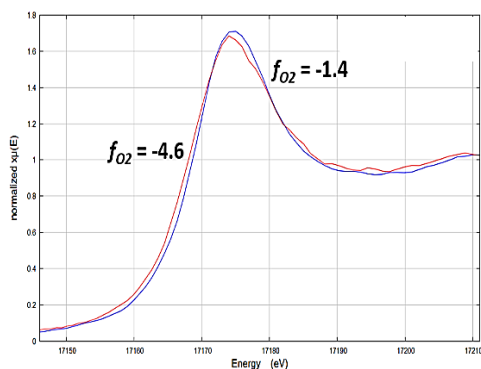
However, previous studies on the FXPM variation of the U  $L_3$ -edge with its valence revealed that the FXPM does not vary linearly with the valence if ligands are differing (**Fig. 4**).  $L_3$ -edge measurements are indeed highly affected by the nature and sort of ligand [4,5].

Our glass compositions are very simply in terms of chemistry ( $\text{SiO}_2$ , 50.37 wt.%,  $\text{MgO}$  34.86 wt.%,  $\text{Al}_2\text{O}_3$  2.60 wt.%,  $\text{FeO}$  7.50 wt.%,  $\text{CaO}$  2.88 wt.%,  $\text{K}_2\text{O}$  0.30 wt.%) and it would be unlikely that another ligand than oxygen would coordinate U. We therefore believe that our acquired data can be aligned to our reference values of Uranium oxygen compounds (red dots). This would indicate a shift from  $\text{U}^{4+}$  at high  $f_{O_2}$  towards  $\text{U}^{3+}$  at low  $f_{O_2}$ . **However, the results are still ambiguous in terms of mix-valence states, which are difficult to assess from the present measurements alone.** FDMNES calculations are currently in progress in order to extract information on the structural environment (ligands, bond length) from the experimental HERFD-XANES data and to confirm the hypothesis of valence change.

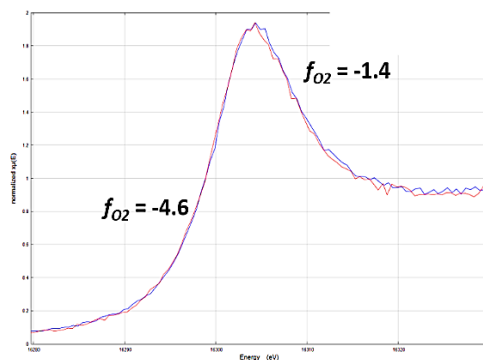


**Fig. 4.** Compilation of First XANES peak maxima (FXPM) energy position as a function of U valence reported in previous studies (black, blue, green symbols) and acquired in the present experiment (red dots). Note that the range of FXPM of the samples are shown on the left qualitatively at a valence of 2.5 for presentation purposes.

The present HERFD-XANES data were complemented with partial fluorescence yield measurements at U and Th  $L_3$ -edges at the beamline BM23 through inhouse research in order to investigate qualitatively if Th valence is affected by  $f_{O_2}$  variation. For these measurements the beamline was operating with a Si(111) monochromator combined with a KB-system comprised of two Pt coated mirrors inclined to 3 mrad for harmonic rejection and beam focusing to  $3 \times 3 \mu\text{m}^2$ . These measurements revealed that Th valence state is unaffected by  $f_{O_2}$  variations as there was no detectable shift of the spectra with  $f_{O_2}$  (**Fig. 5b**). In the U XANES data (PFY) acquired in the same samples, we could detect a shift to lower energy values of the FXPM similar to observations in the  $L_3$  U HERFD-XANES data from FAME-UHD (**Fig. 5a**).



**Fig. 5a** U  $L_3$  edge PFY XANES



**Fig. 5b.** Th  $L_3$  edge PFY XANES

#### Justification and comments about the use of beam time:

The beamtime has been fully exploited and high-quality HERFD-XANES measurements have been performed on highly diluted and sub-millimetric samples. Data have been analysed in terms of U valence state variation, indicating a reduction. **A clear distinction of mixed U valence states and the valence of Th requires additional  $M_4$ -edge measurements [4,5].**

#### Publication(s):

A publication is in progress, **but requires additional  $M_4$ -edge measurements to identify unambiguously mixed valence states in U and the valence of Th [4,5]. Beamtime proposals have been sent for this purposes in this spring call 2021.**

#### Acknowledgements

We want to thank the ESRF for allocating beamtime to this experiment and especially the staff of the beamline BM16 for their assistance.

#### References:

[1] Faure, P. et al., (2020) *Geochim. Cosmochim. A.*, 275, 83. [2] Rubie D. et al. (2015) *Icarus* 248, 89-108. [3] Bouhifd M.A., et al. (2013) *Geochim. Cosmochim. A.* 114, 13-28. [4] Bès, R. et al., *Inorg. Chem.* (2016), 55, 4260. [5] Chevreux, P., et al., (2021), *J. Nuc. Mat.*, 544, 152666.