



## 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 speciation in natural carbonates – implications for Earth's oxygenation history	<b>Experiment number:</b> ES-970
<b>Beamline:</b>	<b>Date of experiment:</b> from: 7 April 2021 to: 12 April 2021	<b>Date of report:</b> Sep 12, 2022
<b>Shifts:</b>	<b>Local contact(s):</b> Prof. Kristina Kvashnina	<i>Received at ESRF:</i>

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

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**Report:**

The chemical behavior of redox sensitive metals in nature is strongly tied to the oxidation state of the metal and its ligands. Yet, direct observations of rare metals are challenged by the low abundance in the environment. In this experiment, we demonstrated the use of High Energy Resolution Fluorescence Detection X-Ray Absorption Near Edge Spectroscopy (HERFD-XANES) to study uranium in geological samples at the U L<sub>3</sub> and M<sub>4</sub> edges (Table 1). Well-constrained XANES spectra were derived for environmental samples (sediments) with  $\geq 1.6$  ppm U and  $\geq 80$  ppm U at the two edges, respectively.

**Table 1. In ES-970, U L<sub>3</sub> and U M<sub>4</sub> HERFD-XANES spectra were collected for the following samples:**

Sample list (synthetic and natural)	U (ppm)	U L <sub>3</sub>	U M <sub>4</sub>
E1* Pure aragonite from Scleratinian Coral (Coco-1)	3.4	√	<DL
E2* Modern limestone (C1_30_32; MJ30), 40% aragonite, 30% calcite	4.3	√	<DL
E3 Modern limestone (C1_38_40), 40% aragonite, 30% calcite	4.7	√	<DL
E4* Ancient marine limestone (KPO19061), >99% calcite	1.6	√	<DL
E5 Ancient argillaceous limestone (WH1-16), calcite with clay	4.3	√	<DL
E6 Modern limestone (C3_20_22), 40% aragonite, 30% calcite	4.0	√	<DL
E7* Ancient marine limestone (KPO19048), >99% calcite	0.7	Poor	<DL
E8 Modern limestone (C2_0_2), 40% aragonite, 30% calcite	2.0	√	<DL
E9* Modern limestone (C1_0_2; MJ1), 40% aragonite, 30% calcite	1.9	√	<DL
E10 Alum shale (C9E6_1650), ancient organic-rich mudrock	110	√	√
E11 Alum shale (C9E6_1800), ancient organic-rich mudrock	110	√	√
E12 Alum shale (C1E5E6_m115), ancient organic-rich mudrock	80	√	√

\* Planned experiments according to the original proposal. We were also able to analyse samples at the U L<sub>3</sub> edge, and even record good XANES spectra at the M<sub>4</sub> edge for U-rich samples with  $\geq 80$  ppm U. Below detection level: <DL.

Linear combination fitting to a wide range of U reference materials (Kvashnina, unpublished), including uraninite  $U(IV)O_2$  and various penta- and hexavalent U compounds showed that most of the sedimentary samples (except surface sediments) could be fitted with a mixture of oxidized sediment and uraninite (fig. 2). Still, there is no pure synthetic reference material that adequately fit the the hexavalent U phase(s) present in the samples.

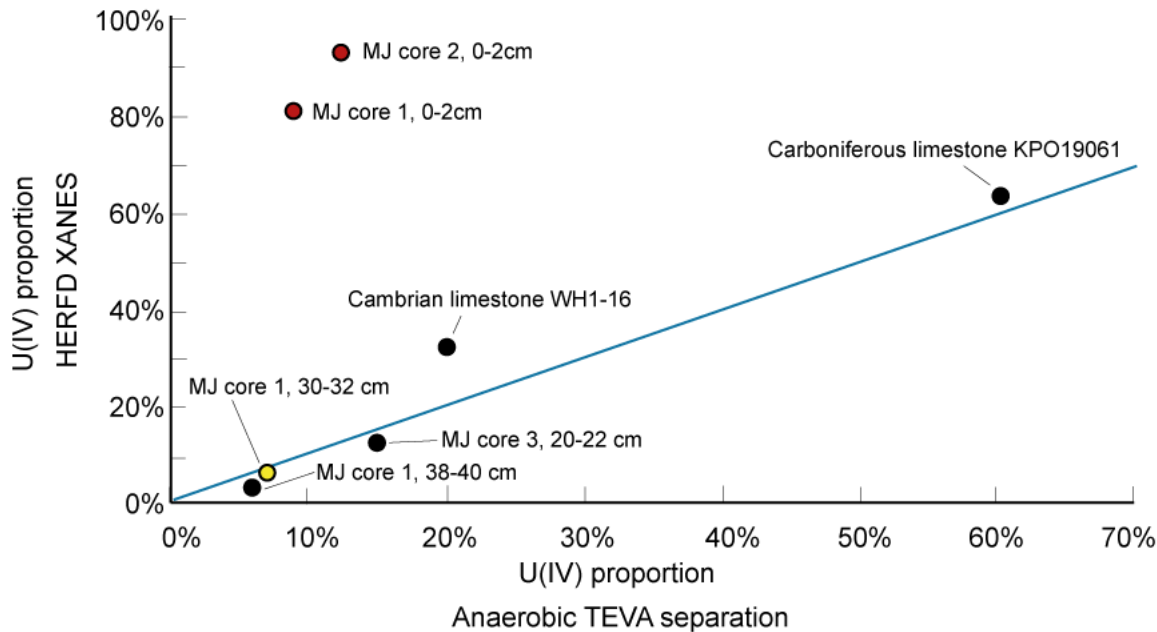


Figure 1. Comparison of the estimated average U oxidation state in marine carbonate sediment samples based on data from our newly calibrated anaerobic U(IV)-U(VI) extraction method and linear combination fitting of the HERFD-XANES results. The linear combination assumes samples are best described as binary mixtures of an oxidized sediment sample (MJ1 with 92% U(VI) and 8% U(IV); yellow circle) and tetravalent uraninite ( $UO_2$ ).

## Discussion of main results

### 1) Expected hexavalent U and discovered mixed oxidation states

Thermodynamic considerations predict that uranium resides as tetravalent species in marine sediments. We found that both hexavalent and tetravalent U species are present in carbonate samples. We are currently writing a manuscript on this topic (Olesen et al., in prep).

The HERFD-XANES data consolidates that U resides as hexavalent U in most of the studied sediment samples – even in samples that have been deposited under strictly anoxic and sulfidic conditions (discussed further below). There was no sign of oxidation at the beamline, and follow-up experiments in our laboratory using various protocols for our newly established anaerobic extraction technique shows that U resides in a form that is either air-sensitive and/or sensitive to oxidizing fluids; i.e. U sensitive to ferric iron present in the pore fluid before extraction. This problem only seem to occur for modern/wet sediments and not for ancient/geological rock powders. We have found a procedure to minimize oxidation of wet sediment samples. Still, future work should aim to analyse samples anoxically and/or at ultra-low temperature and to characterize the unknown tetravalent U phases.

### 2) Confirmed hexavalent U with multiple methods in even the most extreme anoxic environment

We also found a near perfect match between the U oxidation state estimates obtained by HERFD-XANES analyses the  $U L_3$  and  $U M_4$  edge. This measurement was only possible for the U-rich organic-rich mudrock samples. It came as a real surprise that all of the uranium resides in hexavalent U species, so we have come up with various explanations for this. In combination with oxidation-sensitivity experiments, we consider U as

hosted in the form of nanocrystalline  $\text{UO}_2$  in these samples – perhaps in association with organic/biological material. Given that U reduction occurs via microbial reduction in both marine carbonates underlying oxic bottom waters and in marine organic-rich mudrocks underlying anoxic waters, we consider it likely that both types of sediments host the same form of tetravalent U phases. Yet, this still needs experimental verification.

The discovery of U(VI) in these samples has important environmental implications because oxidized/hexavalent U is thought to be easily mobilized in nature. Hence, oxidative fluids percolating the Alum shale and other organic-rich mudrocks t should be is of real concern in terms of ground water pollution.