

## 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>

### ***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.

**Experiment title:**

Formation and stability of U(V) during biological and abiotic reduction of uranium

**Experiment number:**

EV-192

<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 20/04/2016 to: 25/04/2016	<b>Date of report:</b> 06/01/2017
<b>Shifts:</b> 15	<b>Local contact(s):</b> Sara Lafuerza	<i>Received at ESRF:</i>

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

**Dr. Pieter Bots\*** – Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow, G1 1XJ, UK

**Dr. Sam Shaw** – School of Earth and Environmental Sciences, The University of Manchester, Manchester, M13 9PL, UK

**Prof. Melissa Denecke** – School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK

**Dr. Gareth Law\*** – School of Chemistry, The University of Manchester, Manchester, M13 9PL, UK

**Prof. Katherine Morris\*** – School of Earth and Environmental Sciences, The University of Manchester, Manchester, M13 9PL, UK

**Hannah Roberts\*** – School of Earth and Environmental Sciences, The University of Manchester, Manchester, M13 9PL, UK

**Thomas Neill\*** – School of Earth and Environmental Sciences, The University of Manchester, Manchester, M13 9PL, UK

**Report:****Abstract**

Recent studies have shown that HERFD-XANES has the potential to be used to study uranium speciation in complex environmental systems. The environmental chemistry of U is complex: the traditional view is that relatively soluble U(VI) is dominant in oxic environments, and poorly soluble U(IV) e.g. uraninite (UO<sub>2</sub>), dominates in reducing environments. However, recent work has indicated that U(V) may be significant in some key biological and inorganic systems. In this study we utilized HERFD-XANES to investigate U oxidation state and speciation in key abiotic and microbial biogeochemical processes, including U interaction with iron oxide minerals, and single culture microbial U reduction. The results demonstrate that HERFD-XANES is an excellent technique for defining U oxidation state in complex environmental samples and e that U(V) is present in select environmentally relevant experimental systems.

**Experimental details**

During the beamtime we analysed the HERFD-XANES of the U M<sub>4</sub>-edge and the Fe K-edge (where applicable) of 5 sets of samples:

1. *U(IV) and U(VI) standards*

Several samples intended as redox reference standards were analysed for their U M<sub>4</sub>-edge XANES. These samples included minerals from the University of Manchester museum collection (e.g. uranophane (U(VI)) and uraninite (U(IV))), experimental uranium precipitates (e.g. uranium adsorbed to ferrihydrite, clarkeite (NaU(VI)O<sub>2</sub>O(OH):H<sub>2</sub>O) and ninyoite CaU(IV)(PO<sub>4</sub>)H<sub>2</sub>O).

2. *Microbial reduction of U(VI) to U(IV) (Downie et al.)*

Experiments targeting microbial reduction of uranium were performed to explore the suitability of HERFD-XANES for analysis of U oxidation state in biological materials. A timeseries of samples indicated mixed

oxidation states for U over the experiment and we are considering further experiments to define the mechanisms of reduction in these biological systems.

### 3. Redox speciation of U coprecipitated with magnetite (Roberts et al.)

Magnetite ( $\text{Fe}_3\text{O}_4$ ) was crystallized in the presence of U(VI) using a direct precipitation method.

### 4. Oxidation state of uranium in organic rich sediments (Fuller et al.)

Sediment samples were collected from an area with naturally occurring uranium. Samples analysed at ESRF were all from the same sample core and at different depths (10, 20, 25, 30 and 35 cm).

### 5. U speciation following the microbial breakdown of isosaccharinic acid (Kuippers et al.)

For this purpose this study microbial enrichment cultures were investigated, these microbial communities were grown on ISA as the sole carbon source which was complexed to uranium.

## Results

1. A range of standards were measured, U(VI) standards do show different HERDF-XANES spectra, likely due to differences in the local coordination environment. Furthermore all U(IV) data from samples we measured seemed to show mixed uranium oxidation states. Future work will aim to determine if these are inherently mixed oxidation phases or oxidation occurred during analyses or sample preparation.

2. For pure culture bioreduction iterative target transformation factor analysis (ITTFA) using U(IV) and a U(VI) standards as end members was performed (Figure 2). These data suggested the presence of U(V) in these samples and these high quality U(VI), U(V) and U(IV) data are now informing further experiments.

3. HERDF-XANES analyses in the magnetite experiments confirmed U(V) was abundant in magnetite samples. Furthermore, we have found that HERDF-XANES analyses were essential in informing the interpretation and fitting procedure of our EXAFS analyses for these samples.

4. The HERDF-XANES analyses confirm that uranium is present principally as U(VI) with some reduction to U(IV) at 30cm. The HERDF-XANES results have informed EXAFS fits on parallel samples which confirm the adsorbed nature of U(VI) in these samples.

5. The HERFD-XANES analyses showed that uranium was removed from solution either as U(IV) or U(VI) dependent on the microbial community. These data have already informed complementary EXAFS data analyses and further experiments.

## Conclusions

We successfully confirmed the presence of U(V) in two of the experimental sample sets and the HERFD-XANES data has been instrumental in informing fitting procedures of complementary EXAFS data and in the design of further experiments. U(V) appears to be a significant intermediate oxidation state during the microbial reduction of U(VI) to U(IV). And U(V) appeared stabilized when present during the crystallization of magnetite.

## Publications resulting from the experimental work

Downie et al. draft in early stages of preparation

Roberts et al. draft in final stages of preparation for *Proceeding of the National Academy of Sciences*.

Fuller et al. draft in early stages of preparation

Kuippers et al. draft in early stages of preparation

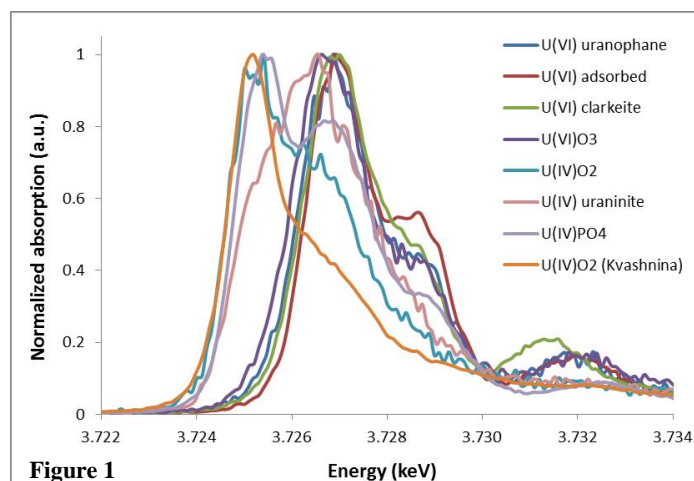


Figure 1

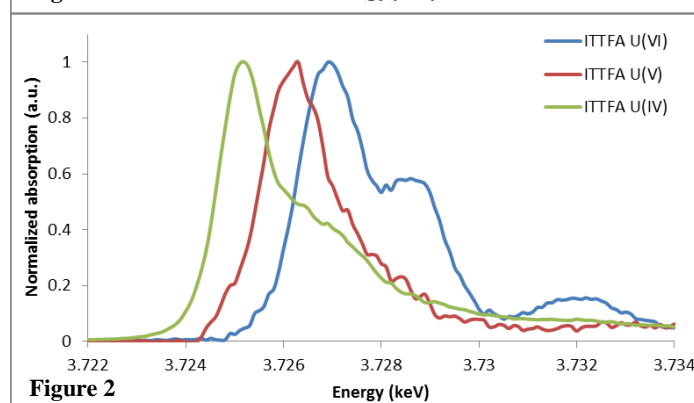


Figure 2