

## 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.



**Experiment title:** Speciation of uranium in alluvium aquifer sediments of Punjab, India: implication for high uranium enrichment in groundwater

**Experiment number:** A20-1-845

<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 08 June 2022 to: 13 June 2022	<b>Date of report:</b> 14 October 2022
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. Damien Prieur	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Ashis Biswas*</b> <i>Department of Earth and Environmental Sciences, Indian Institute of Science Education and Research (IISER) Bhopal, Bhopal Bypass Road, Bhauri 462066, Bhopal, Madhya Pradesh, India</i>		

### Report:

**Background of the experiment:** Occurrences of elevated concentrations ( $>30 \mu\text{g/L}$ , WHO provisional drinking water guideline) of uranium (U) in groundwater of shallow alluvium aquifers (depth:  $<60 \text{ m}$ ) are a severe drinking water quality problem in the southwestern part of Punjab, India. The goal of the experiment at the BM20 (ROBL) Beamline at ESRF was to characterize the speciation and mineral host phases of U in aquifer sediments of the U-contaminated area by U  $L_3$ -edge XANES analysis for explaining the geochemistry of U mobilization and transport in the aquifer. As detailed in the experiment proposal, a borehole was drilled to a depth of  $\sim 40 \text{ m}$  at a highly U-contaminated village to determine the shallow aquifer-aquitard framework of the area and collect sediment for geochemical analysis in every 1.5 m interval in general and more frequently whenever a change in the lithology was observed. Sixteen sediment samples from different lithologic units were selected for U speciation study at the BM20 beamline at ESRF.

**Experiment at the beamline:** All samples were scanned to collect U  $L_3$ -edge XANES data. However, due to the low U concentration ( $\leq 6.4 \text{ mg/kg}$ ), the U fluorescence signal in thirteen samples was insignificant; therefore, XANES data could not be collected for these samples. Only in three samples we could see the U  $L_3$ -edge, and these samples were analyzed over 8 shifts to collect 37 to 47 spectra for each sample to improve the signal-to-noise ratio. Although it was not proposed in the experiment proposal, to utilize the remaining beamtime (7 shifts), we attempted to characterize the speciation and mineral host phases of arsenic (As) in aquifer sediments of West Bengal, India, an area known for the largest mass poisoning in human history due to the drinking of As-contaminated groundwater. With the remaining beamtime, we could collect As K-edge XANES data for fourteen samples and references. The analyzed references represent sorbed arsenate and arsenite to different mineral phases, which are likely to be present in the aquifer sediments of the study area.

**Data processing and results obtained so far:** The energy calibrated, merged, and normalized U  $L_3$ -edge XANES spectra of three samples are displayed in Fig. 1. Despite merging a large number of spectra for individual samples, the merged sample spectra are still noisy. The overall inspection of the sample spectra suggests that U is present in multiple oxidation states (+IV and +VI) in the aquifer sediments of the investigated area. We are currently trying to estimate the distribution of U in different oxidation states by linear combination fitting (LCF) of the sample spectra. However, this estimation is likely to have high uncertainty due to the poor quality of the sample spectra.

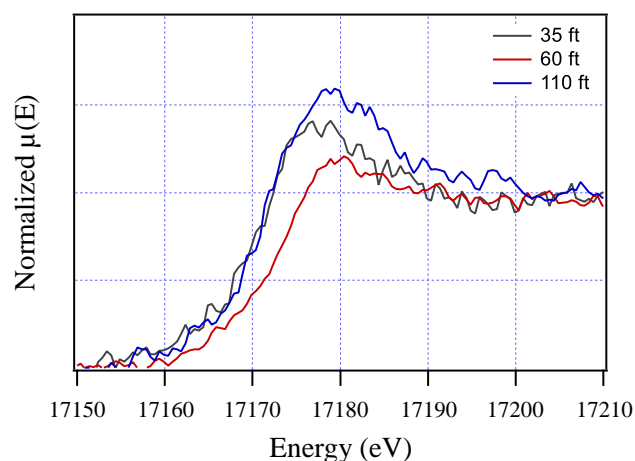


Fig. 1: U  $L_3$ -edge XANES spectra of aquifer sediments collected from different depths of a U-contaminated area

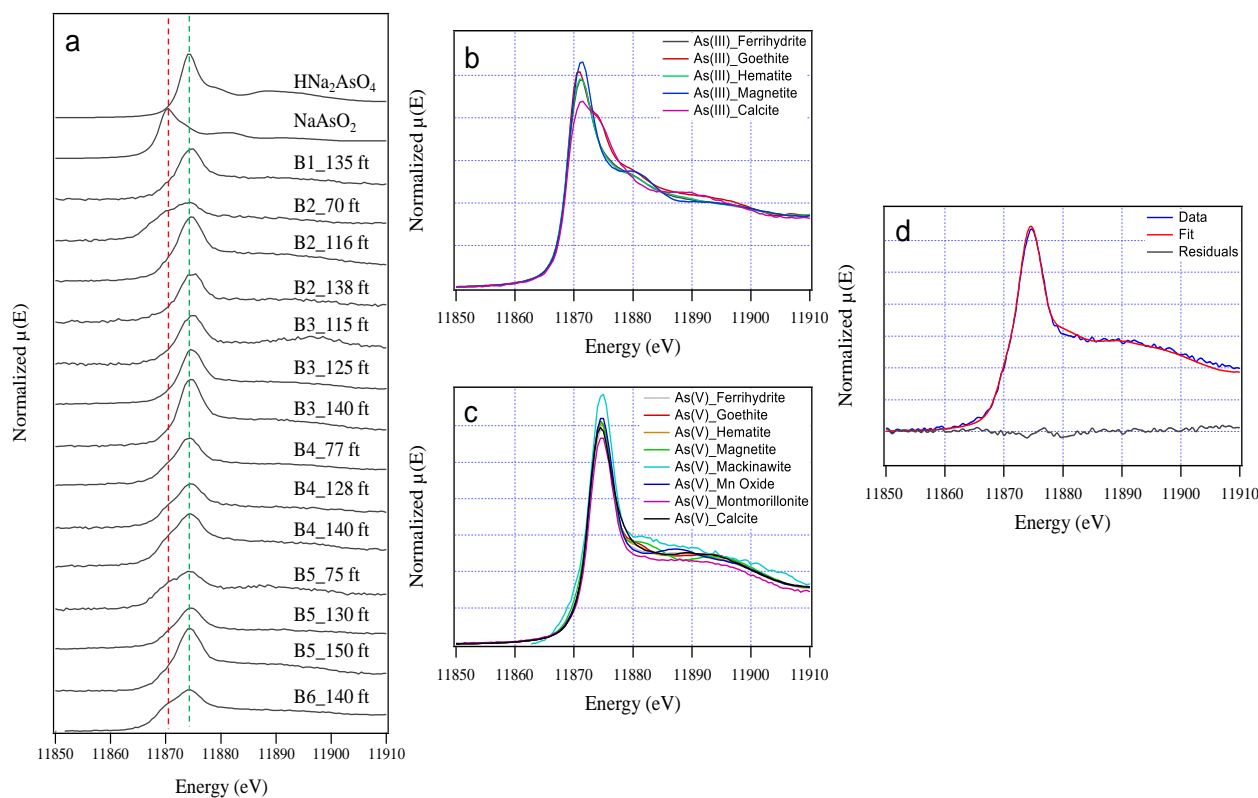


Fig. 2: As K-edge XANES spectra of a) aquifer sediments collected from different depths of six boreholes, b) As(III) references, c) As(V) references, and d) LCF of a representative sample with two components

The energy calibrated, merged, and normalized As K-edge XANES spectra of samples are presented in Fig. 2a. Spectra are dominated by a large peak at the energy position of arsenate (~11872.5 eV) and a weak shoulder at the energy position of arsenite (~11869 eV), suggesting that As is present in these samples as the mixture of arsenate and arsenite. The principal component analysis (PCA) of the sample spectra revealed that two components are required to explain the spectral variability in the analyzed samples; two components cumulatively account for 99.2% of the variability. The target transform (TT) analysis with these two components provided an excellent SPOIL value ( $\leq 1.5$ ) for all analyzed references. A close inspection of the reference spectra revealed that differences in the XANES spectra of sorbed arsenite (Fig. 2b) and arsenate to different mineral phases (Fig. 2c) are often insignificant, at the most at the level of noise associated with the sample spectra. Therefore, it is concluded that with the obtained data for the sample, we can determine the speciation of As in the sediment as the sorbed arsenate and arsenite only; further specifying the mineral phase to which arsenate and arsenite are sorbed would be an overinterpretation of the data. For arsenate and arsenite, the lowest SPOIL and R values in the TT analysis were obtained for their sorption onto hematite. Therefore, the spectra of arsenate and arsenite sorbed onto hematite were selected for the LCF analysis of the sample spectra to determine the distribution of sorbed arsenate and arsenite in the analyzed samples (Fig. 2d).

Results suggest that, on average, 65% ( $\pm 21\%$ ) and 31% ( $\pm 19\%$ ) of As is present as sorbed arsenate and arsenite, respectively, in the aquifer sediment of the study area. Aquifer sediment color has a strong influence on the distribution of As species. Arsenic speciation is dominated by the sorbed arsenate in the brown color aquifer sediment, while the percentage of sorbed arsenite increases, sometimes even predominating the As speciation in the gray color sediment. These results support our earlier findings that redox condition is more reducing in the Holocene aquifers of gray color sand than in the Pleistocene brown color sand. The findings of this experiment will be combined with other sediment geochemistry and hydrogeochemical data to develop a water-sediment interaction model for explaining the transport of As at the interface of Holocene and Pleistocene aquifers and, therefore, to assess the long-term sustainability of the Pleistocene aquifer for providing As-safe water.