Names and affiliations of applicants (* indicates experimentalists):

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Report:

The proposal aimed at understanding the mechanisms responsible for uranium remobilization from contaminated sediments exposed to reducing conditions or re-oxidizing conditions similar to surface storage conditions. The proposal requested beamtime on BM16 for HERFD-XANES and on BM30B FAME for EXAFS.

BM16 – FAME UHD

A first beamtime was allocated on BM16, which was the second user-beamtime for this new beamline. The monochromator was equipped with Si220 crystals with sagittal focusing of the second crystal and we used a set of four Ge777 crystal analyzers to record High-Energy Resolution Fluorescence Detection (HERFD) X-ray Absorption Near Edge Structure (XANES) spectroscopy at the U L_{III}-edge. Data were recorded at 10K in a liq He Cryo.

We recorded high-quality HERDF-XANES data on U-contaminated samples (1000 – 3000 ppm U; Fig. 2) and on synthetic (1 wt% U) and natural (40 wt% U) model compounds (Fig. 1). The most diluted sediment samples with U concentrations of 200 ppm could be analyzed in HERDF mode but recording XANES data required a minimum of 12 hours per sample (Fig. 3). Data fitting using Linear Combination of model compound spectra is ongoing and yield accurate determination of the U oxidation state (Figs. 2 &3).

BM30B - FAME

A second beamtime was allocated on BM30B to perform U L_{III}-edge EXAFS analyses on the same series of samples, in fluorescence detection mode using the 30 elements array detector. Very good quality EXAFS data were recorded to a k of 12 Å^{-1}, merging 8-12 EXAFS scan for environmental samples (1000 – 3000 ppm U; Fig. 4), and merging 4-6 scans for model compounds (~1 wt% U; Fig. 5). Interpretation of these data is ongoing in order to identify the molecular environment of uranium in our environmental samples after the re-oxidation experiments, thus revealing which phases are the most resistant to uranium oxidation.

Fig. 1. BM16 - U(VI) and U(IV) model compounds (Ge 777 analyzer, maximum of the L-alpha emission line)

a

b
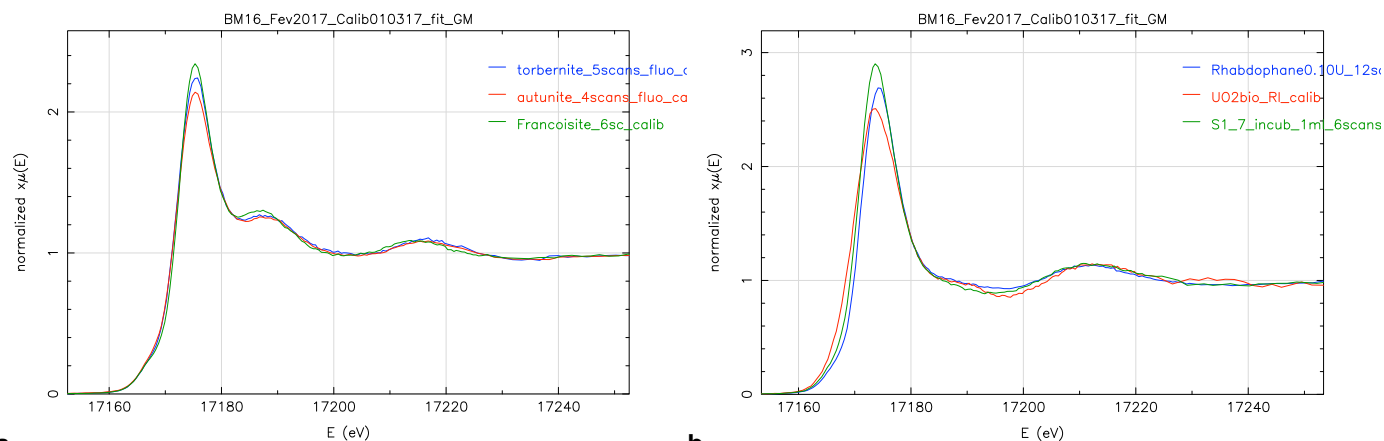
Figure 1a. HERFD U L$_{III}$ XANES spectra of U(VI) natural model compounds: torbernite (Cu)(UO$_2$)$_2$(PO$_4$)$_2$·12 H$_2$O ; autunite Ca(UO$_2$)(PO$_4$)$_2$·12 H$_2$O ; francoisite (Nd,Y,Sm,Ce)(UO$_2$)$_3$(PO$_4$)$_2$O(OH)•6(H$_2$O)

Figure 1b. HERFD U L$_{III}$-edge XANES spectra of U(IV) synthetic and biogenic model compounds: synthetic U(IV)-doped La-rabdophane (La$_{0.9}$U$_{0.1}$Ca$_{0.1}$)PO$_4$•(H$_2$O) ; biogenic uraninite UO$_2$; biotic U(IV)-humic sample.

Fig. 2. BM16 - Linear Combination Fitting of XANES spectra for U(IV) and U(IV)-rich samples (1500 ppm U)
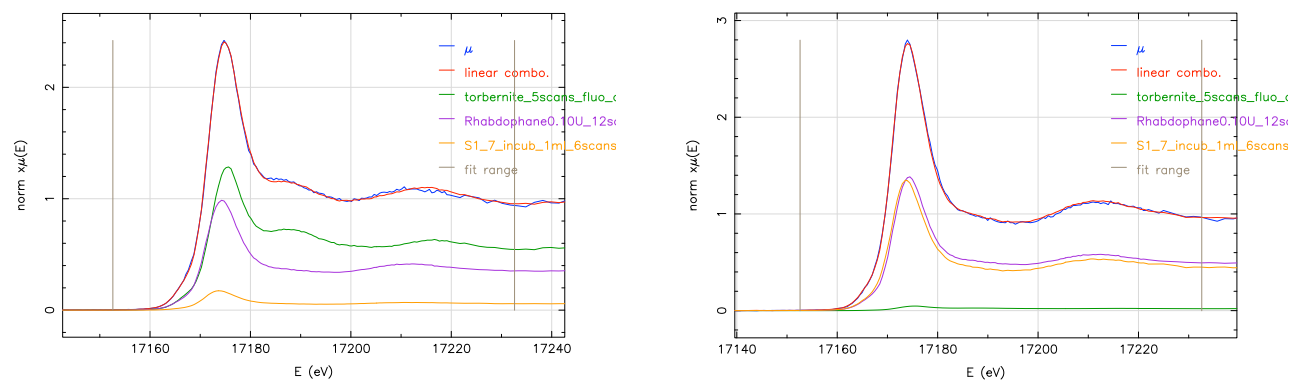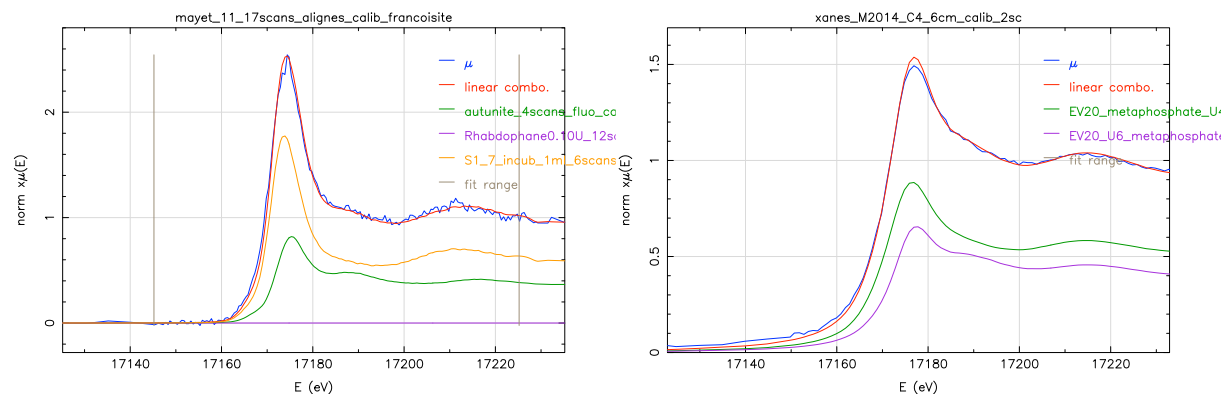

Fig. 3 BM16 - Linear Combination Fitting of XANES spectra for dilute sediment samples

200 ppm U sediment (BM16 – Ge 777 analyzer)
17 scans of 50 mn = 14 hours

50 ppm U (BM30B – Ge 30 elts)
2 scans of 20 mn = 0.7 hours
Data from former proposal #30-02 1076 Jan 2015

Fig. 4. BM30B – Typical XANES and EXAFS data collected in fluorescence mode (Ge 30 elements array detector) on environmental samples (U ~ 1000 ppm wt), showing distinct local structures around U in U(VI) and U(IV)-rich samples (samples 2/3 and 1, respectively).
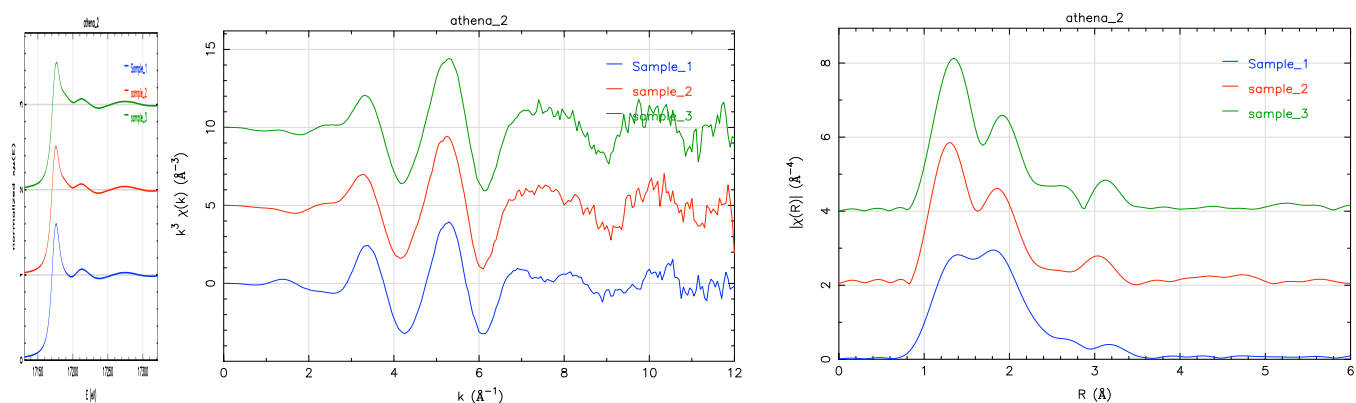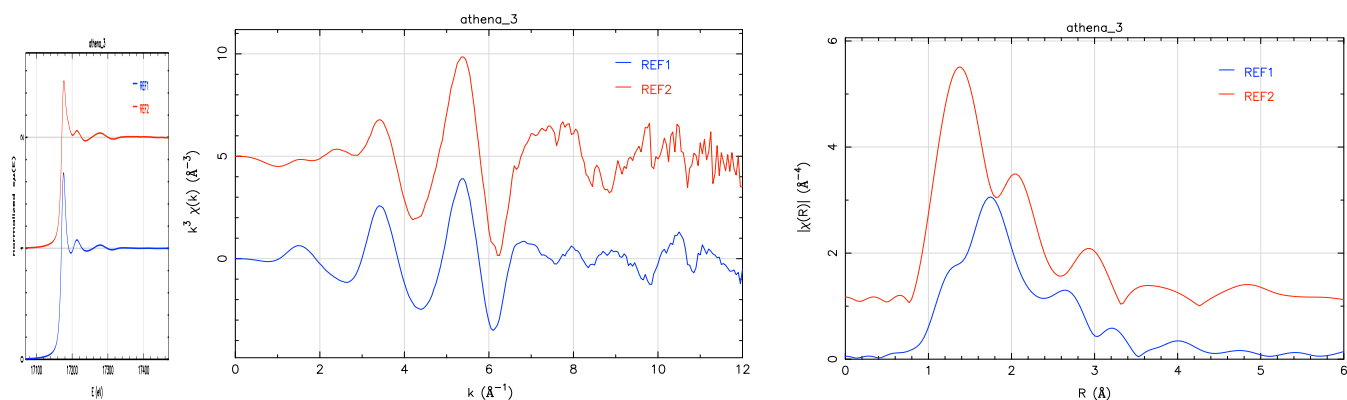

Fig. 4. Typical XANES and EXAFS data collected in fluorescence mode (Ge 30 elements array detector) on U(VI) and U(IV)-rich model compounds (U ~ 1 wt %).

Publications :

Stetten L., Mangeret A, Brest J., Seder-Colomina M., Le Pape P., Ikogou M., Zeyen N., Thouvenot A., Julien A., Alcalde G., Reyss J.L., Bombled B., Rabouille C., Olivi L., Proux O., Cazala C., Morin G. (2017) Geochemical control on the reduction of U(VI) to mononuclear U(IV) species in lacustrine sediments. *Geochimica et Cosmochimica Acta* (accepted).