



	<b>Experiment title:</b> <b>Uranium redox state and binding environment in an organic- rich soil from a mining-impacted peatbog in France</b>	<b>Experiment number:</b> EC-953
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 26/10/2012 to: 29/10/2012	<b>Date of report:</b> 28/02/2013
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. André Rossberg	<i>Received at ESRF:</i>
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## Report:

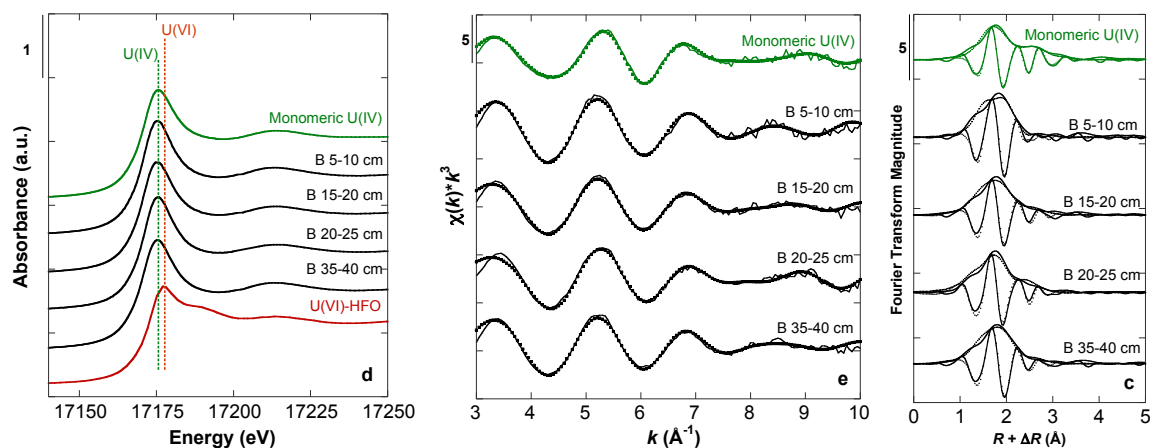
### Abstract

While the accumulation of uranium in organic-rich soils has been reported in numerous occasions (Regenspurg et al., 2010; Moulin, 2008; Owen and Otton, 1995), the precise mechanism of the accumulation remains elusive. The aims of the present uranium L<sub>3</sub>-edge XAS experiments are to shed light on the mechanism of U accumulation in a mining-impacted wetland by characterizing (a) the uranium oxidation state and (b) the uranium species predominant in the soil as a function of depth. We collected XANES and EXAFS data and the results show that U in the soil is predominantly tetravalent and sorbed onto certain substrate(s) in the soil through phosphate binding.

### Experimental details

Because of the samples sensitivity to air and their hazard, in an anaerobic jar at EPFL, the samples were mounted onto SH01B sample holders supplied by BM20, sealed in individual Mylar bag, and sealed in a metallic jar under N<sub>2</sub>-atmosphere. The samples were then taken to BM20 ESRF by the experimentalists. Upon the arrival, in the negative pressure glovebox at the beamline, the samples holders were taken out of the jar and the Mylar bag and examined under N<sub>2</sub> gas flow by the ESRF Safety Group for radiation protection reason. The samples were then stored in the N<sub>2</sub>-purged metallic jar until analysis. Upon analysis, the sample was mounted quickly onto the cryostat rod and inserted into the cryostat. XANES data showed no evidence of air-induced oxidation with this approach. We collected U L<sub>3</sub>-edge (17.166 KeV) EXAFS spectra as well as XANES data on selected samples in fluorescence mode under He-liquid temperature (~10 K) with the help of the cryostat. The multi-element solid-state Ge detector enabled the collection of acceptable quality data even for those samples with U concentrations ~500-1,000 ppm. In addition, three standards were used to help constrain data interpretation: (a) uraninite; (b) monomeric U(IV); (c) U(VI) sorbed on ferrihydrite.

## Results



XANES spectra exhibit an absorption maximum at 17,175.0 eV for all samples, suggesting that U is predominantly in its U(IV) valence state in the soil, which is consistent with the metal reducing conditions evidenced by other analyses. Unfiltered and  $k^3$ -weighted extended X-ray absorption fine structure (EXAFS) spectra show oscillations for soil samples similar to those of the monomeric U(IV) model compound (Bernier-Latmani et al., 2010), suggesting a similar atomic environment. Shell-by-shell fits of EXAFS data further confirm the absence of a U-U pair correlation typical of U(IV) minerals and the presence of U(IV) coordinated to phosphate, a monomeric-U(IV)-like species.

## Conclusions and future work

Together with electron microscopic observation results (not shown in this experimental report to ESRF), we conclude that U in the soil is predominantly tetravalent and sorbed onto certain kind of aggregates through phosphate binding. Laboratory studies have previously demonstrated that U(VI) bioreduction could yield monomeric U(IV) characterized by U(IV) association to phosphate groups in batch and column systems (Bernier-Latmani et al., 2010; Fletcher et al., 2010; Sharp et al., 2011). Additionally, abiotic U(VI) reduction via  $\text{PO}_4$ -sorbed magnetite ( $\text{Fe}_3\text{O}_4$ ) and vivianite ( $\text{Fe}_3(\text{PO}_4)_2$ ) (Veeramani et al., 2011) also produced the same product. The results of the present field study are thus consistent with those of the previous laboratory studies suggesting that U(IV) tend to bind to phosphate groups that leads to the formation of monomeric-U(IV)-like species.

A manuscript including the results above will be submitted to Nature Geoscience in April 2013.

In the framework of the present project on U speciation in a mining-impacted wetland, we will not apply for further beamtime at ESRF. However, we would like to apply for beamtime in 2014 for an upcoming project on depleted uranium mobility in environment.

## References

- Regenspurg, S. *et al.* Speciation of naturally-accumulated uranium in an organic-rich soil of an alpine region (Switzerland). *Geochimica et Cosmochimica Acta* **74**, 2082-2098 (2010).
- Moulin, J. *Comportement des radionucléides des familles de l'uranium dans les eaux superficielles du site de la Crouzille (Limousin). Implications géochimiques.* PhD thesis, Ecole Centrale Paris, (2008).
- Owen, D. E. & Otton, J. K. Mountain Wetlands - Efficient Uranium Filters - Potential Impacts. *Ecol. Eng.* **5**, 77-93 (1995).
- Bernier-Latmani, R. *et al.* Non-uraninite Products of Microbial U(VI) Reduction. *Environmental Science & Technology* **44**, 9456-9462 (2010).
- Fletcher, K. E. *et al.* U(VI) Reduction to Mononuclear U(IV) by Desulfitobacterium Species. *Environmental Science & Technology* **44**, 4705-4709 (2010).
- Sharp, J. O. *et al.* Uranium speciation and stability after reductive immobilization in aquifer sediments. *Geochimica et Cosmochimica Acta* **75**, 6497-6510 (2011).
- Veeramani, H. *et al.* Products of abiotic U(VI) reduction by biogenic magnetite and vivianite. *Geochimica Et Cosmochimica Acta* **75**, 2512-2528 (2011).