 ROBL-CRG	<b>Experiment title:</b> <b>Oxidation state and local structure of uranium in soils and sediments</b>	<b>Experiment number:</b>  20-01-626
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> 12.03.-15.03.05; 10.07.-12.07.05; 05.11.-07.11.05; 25.11.-26.11.05 15.09.-19.09.06; 17.06.-19.06.06 19.07.-20.07.06	<b>Date of report:</b> 11.01.07
<b>Shifts:</b> 50	<b>Local contact(s):</b> <b>A. Scheinost, H. Funke</b>	<i>Received at ROBL:</i> 11.01.07
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## Report:

Scheinost, A. C., Hennig, C., Somogyi, A., Martinez-Criado, G., and Knappik, R. (2006). Uranium speciation in two Freital mine tailing samples: EXAFS, micro-XRD, and micro-XRF results. *In* "Uranium in the Environment: Mining Impact and Consequences" (B. J. Merkel and A. Hasche-Berger, eds.), pp. 117-126. Springer Verlag, Berlin.

## Abstract

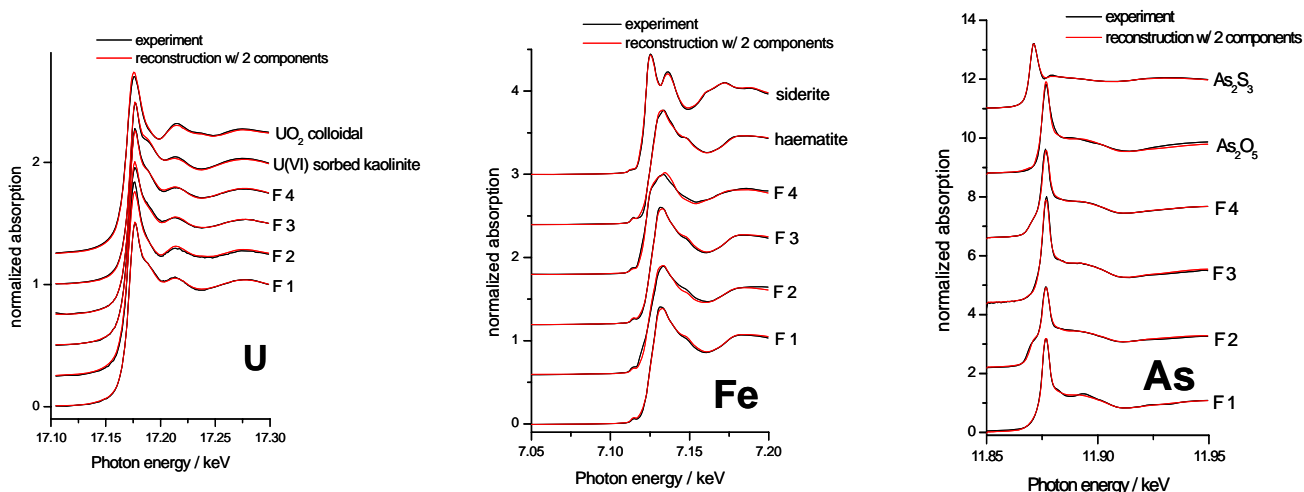
Risk assessments of actinide-contaminated soils and sediments require detailed knowledge of actinide speciation and its long-term kinetics. Former Saxonian mine tailings, which have been covered but else left undisturbed, are ideally suited to study changes in uranium speciation over timescales of decades. We investigated the major uranium species in two samples from buried mine tailings using a combination of Synchrotron-based microfocus-techniques ( $\mu$ -XRF,  $\mu$ -XRD with micrometer resolution), bulk EXAFS spectroscopy, and chemical extractions.

In sample F1 (5 m depth, oxic, pH 8, U=440 mg/kg, high Ca, S, Pb, Cu, Zn concentrations), uranium is diffusely distributed among aggregates of layer silicates (muscovite, illite and kaolinite). The chemical extractions and EXAFS results confirm that uranium is sorbed to these minerals, but is not incorporated into their crystal structure. Sorption is also in line with the high pH and low carbonate concentrations in pore water. In sample F3 (12 m depth, oxic, pH 4, U=430 mg/kg), the combination of  $\mu$ -XRF and  $\mu$ -XRD enabled us to identify several U(IV) and U(VI) containing minerals like coffinite, uraninite, uranyl hydroxide, and vanuralite. Only a minor part of U is sorbed to layer silicates as confirmed by chemical extractions and EXAFS spectroscopy.

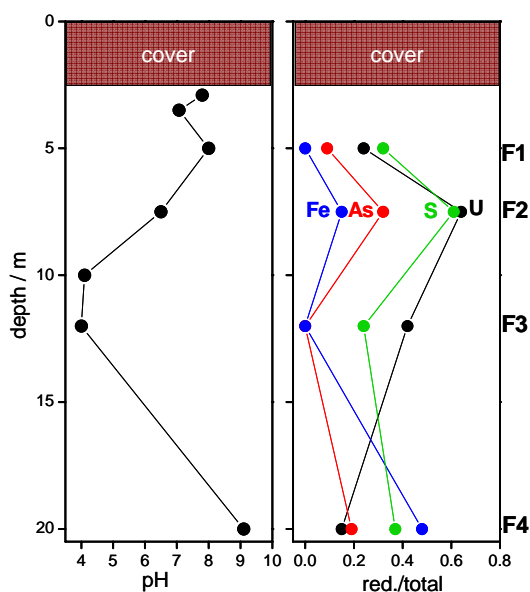
At smaller depth (F1, 5 m), sulfuric acid from the ore extraction procedure was completely neutralized by the construction waste used as cover material, resulting in precipitation of jarosite and gypsum.

Even 30 years after the ore extraction, uranium remains highly soluble. At greater depth (F3, 12 m), the low pH from ore extraction was conserved. The presence of U(IV) minerals suggest either precipitation of secondary (IV) minerals due to microbial redox activity, or incomplete dissolution of primary (IV) minerals due to ore processing inefficiency of these older sediments. The U(IV) minerals were recalcitrant during chemical extractions, suggesting low uranium solubility even at oxic redox conditions. The results demonstrate a very high variability of uranium speciation and hence potential mobility, which seems to depend on geochemical parameters and site history, but shows little influence of time.

Another task addressed during the most recent runs was to determine the redox situation along a depth profile of the tailings. For this, the oxidation states of U was compared with that of associated elements, i.e. Fe and As, by Iterative Transformation Factor Analysis (ITFA) of XANES spectra (Fig. 1). These results were further complimented by S oxidation mapping using the STXM at ID-21 (CH-1779). All investigated redox-sensitive elements suggest a maximum of reducing conditions at 7 m depth, while both the shallower and the deeper samples are more oxic (Fig. 2). The first 3 samples suggest a closer association of U with S than with Fe and As.



**Fig. 1.** U-L<sub>3</sub>, Fe-K and As-K edge XANES spectra along the tailings depth profile (F1 to F4) (black lines). The reconstruction by 2 principal components of the tailings samples and of selected references is shown in red.



**Fig. 2.** pH and redox profile of the Freital uranium tailings. The ratios of U(IV)/U(VI), Fe(II)/Fe(III), and As(III)/As(V) have been derived from the sets of spectra (Fig. 1) by ITT using the ITFA program package {Rossberg, 2003 #4}. The ratio of Se(-II)/S(VI) has been determined by experiment CH 1779 (see there).