	Experiment title: Structural XAS analysis of uranyl-arsenic species and their sorption onto FeOOH and Montmorillonite	Experiment number: CH-3081
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Report:

The mobility of uranium(VI) in the environment is controlled by its soluble aqueous complexes and its precipitates occurring as minerals. About one-third amongst the approx. 200 known uranium minerals is represented by uranyl-phosphate and uranyl-arsenate minerals. While the existence and behavior of dissolved uranyl phosphate complexes had been subject of research by several authors, the investigation of aqueous uranyl arsenate complexes is rare. There is no report to date that investigates aqueous uranyl arsenate complexes structurally. Consequently, more detailed knowledge on uranyl arsenate complexes is still needed.

The determination of structural parameters in aqueous solution with EXAFS spectroscopy is limited by uranium concentrations of $\sim 5 \cdot 10^{-5}$ M. There is a strong tendency of uranyl-arsenates to precipitate at concentrations above $\sim 5 \cdot 10^{-6}$ M, especially at pH values beyond 2. Such precipitates occur at room temperature within one to two minutes after mixing of the starting solutions. Because the detection limit of EXAFS can not easily be lowered, the

samples must be prepared at or beyond the detection limit for uranium. Since the oversaturation leads to spontaneous precipitation we explored ways to conserve the solution species. We found that shock-freezing of the solution in liquid nitrogen immediately after mixing of the starting solutions is an appropriate approach.

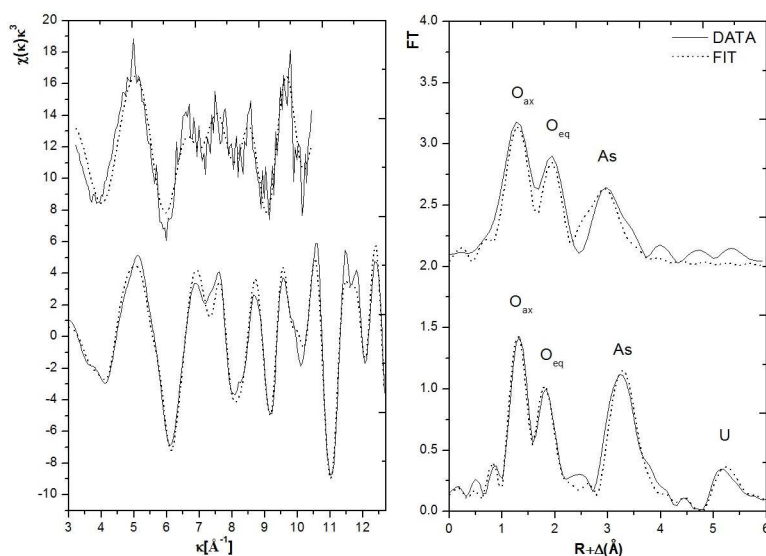


Figure 1. U L_{III}-edge k^3 -weighted EXAFS spectra (left) and the corresponding Fourier transforms (right) of a shock frozen liquid sample at 15 K with uranium to arsenic concentrations of 0.05mM to 0.5mM at pH 2 (a), and solid uranyl-arsenate precipitate $H[(UO_2)(AsO_4)] \cdot 4H_2O$ at pH 3 (b)

The k^3 -weighted EXAFS spectra of the solid precipitate $H[(UO_2)(AsO_4)] \cdot 4H_2O$ is shown in Figure 1 together with the frozen liquid sample. The EXAFS of $H[(UO_2)(AsO_4)] \cdot 4H_2O$ exhibits the characteristic short U- O_{eq} bond length of 2.28 Å. The monodentate bound arsenate shows a U-As distance of 3.69 Å and the next uranium atoms in a U-U distance of 5.38 Å. The coordination of the shock-frozen solution species differ clearly from the precipitate. The only structurally unchanged feature is the trans-dioxo cation of 2 axial oxygen atoms at a U- O_{ax} distance of 1.78 Å. The second peak in the EXAFS spectrum, which corresponds to the equatorial oxygen atoms, shows U- O_{eq} bond length of 2.39 Å with a coordination number of 4.8 – 5.1. In the liquid samples, the calculated U-As bond distance of 3.39 Å is shorter than that observed in solid $H[(UO_2)(AsO_4)] \cdot 4H_2O$. This short bond length indicates most likely a bidentate coordination between the central uranium atom and the arsenate ligand, instead of the monodentate one in the precipitate. Higher shells were not observed, indicating that the aqueous species is a monomer.