



Experiment title: EXAFS investigation of U(IV) precipitates		Experiment number: CH-2972
Beamline: BM 20	Date of experiment: from: 5.10.2009 to: 7.10.2009 (6 shifts) from: 27.2.2010 to: 29.2.2010 (6 shifts) from: 14.3.2010 to: 15.3.2010 (3 shifts)	Date of report: 18.3.2010
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Report:

Defined amounts of 0.02 M U(IV) stock solution (1 M NaHCO₃, pH 8.6) were added to freshly prepared and equilibrated solutions of silicic acid (pH ~7). Two samples with equal uranium concentration and different silicic acid content were prepared. The starting suspensions consisted of 1 x 10⁻³ M U and 1 x 10⁻³ M Si (sample **B**) and of 1 x 10⁻³ M U and 3 x 10⁻³ M Si (sample **C**). The colloids were precipitated from the suspensions through decreasing the pH to 4 by adding HClO₄. The decreased pH results in a loss of the repulsive forces between the particles due to neutralization of the surface charge. The precipitates were centrifuged and stored in wet state in air-tight double-sealed cuvettes. The molar Si/U ratio after centrifugation was 0.83 for sample **B** and 1.68 for sample **C**. The samples were measured at room temperature.

Furthermore, a sample of amorphous U(IV) oxyhydroxide was used as a reference sample (sample **A**). It was prepared by electrolysis of 0.05 M U(VI) in an aqueous solution of 0.1 M HClO₄ at -0.3 V (vs. Ag/AgCl) according to a procedure described previously (Ikeda et al., 2009). This sample was measured as a colloidal suspension in aqueous solution (pH <2) at room temperature. Coffinite served as a second reference sample (sample **D**). The sample was prepared by hydrothermal synthesis according to the procedure described by Fuchs and Hoekstra (1959) and measured as a dry powder at 15 K.

U(IV) forms stable colloidal suspensions at low pH values and in the absence of complexing media. The chemical composition of these colloids, which depends on preparation method, pH, temperature and alteration, can be described as amorphous U(IV) oxyhydroxide. The observation that silicic acid stabilizes such colloid suspensions at neutral pH values raises the question how the structure and surface of such colloids might be modified by the silicate. U L₃ edge EXAFS spectroscopy was applied to gain information on the next-neighbor arrangement of uranium. In the reference sample of U(IV) oxyhydroxide, uranium is coordinated by oxygen atoms from bound aquo ions, oxo and hydroxo groups. This leads to a variety of U-O scattering contributions approximated in the shell fit by a total of ~6 oxygen atoms with U-O distances of 2.34 and 2.52 Å. The next strong peak indicates an U-U distance of 3.85 Å. Whereas crystalline UO₂ has 12 uranium next neighbors, there is only an average value of 5.1 uranium next neighbors in the U(IV)

oxyhydroxide of sample **A**. The reduced coordination number is a result of a strong structural disorder.

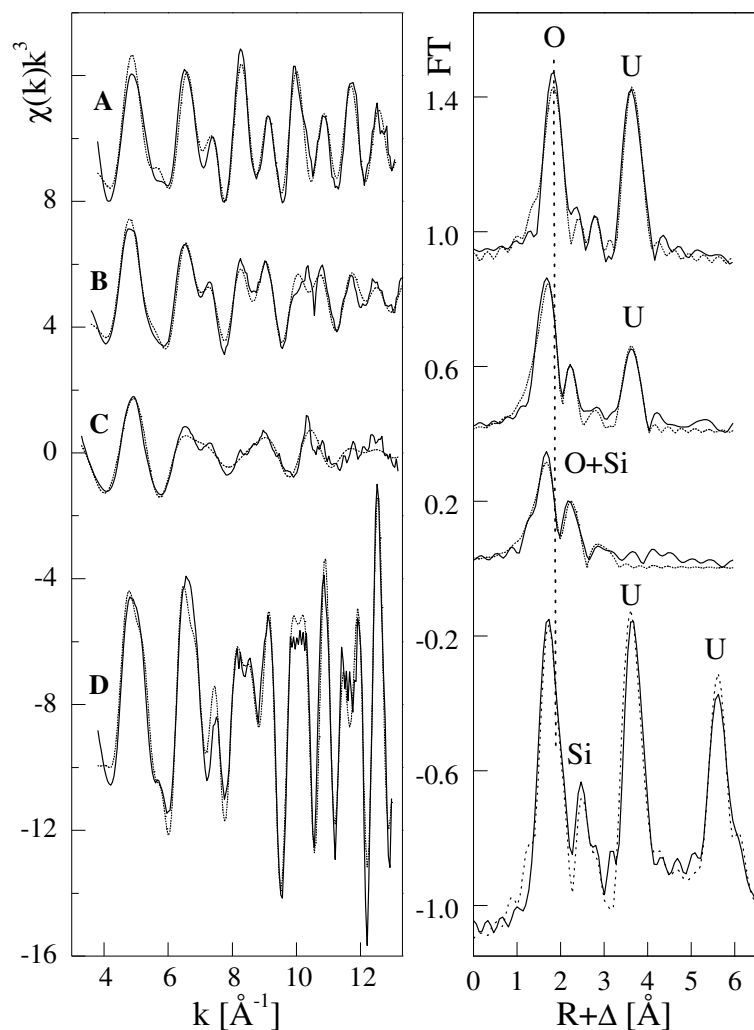


Fig. 1. Uranium L_3 edge EXAFS (left) and their corresponding Fourier transform (right) of $\text{UO}_n(\text{OH})_{4-2n} \cdot m\text{H}_2\text{O}$ colloid (sample **A**), colloid samples with initial molar Si:U ratios of 0.83 (sample **B**) and 1.68 (sample **C**), and synthetic coffinite (sample **D**); the spectrum of sample **D** was collected at 15 K, the measurement of the other samples was performed at room temperature.

In the presence of silica there is a clear change in the first coordination sphere. The next neighbors around uranium of the silica containing samples **B** and **C** could be fitted with two contributions of oxygen at U-O distances of ~ 2.23 to 2.83 \AA . It is obvious that the majority of the oxygen atoms is located at a distance of ~ 2.23 \AA in the silica containing samples. This distance is significantly shorter than the main U-O distance of 2.34 \AA observed in the U(IV) oxyhydroxide and indicates clear structural differences. It should be mentioned that carbonate does not play a major role because the U-O distance in U(IV) carbonate, $[\text{U}(\text{CO}_3)_5]^{6-}$, is 2.45 \AA , i.e. it is significantly longer. The next longer distance can be fit with a U-O distance of 2.83 \AA , but this value is too long to be physically reasonable for an oxygen coordination. The scattering contribution of this shell is assumed to be influenced by a superposition with a contribution from silicon. A short U-Si distance of 3.1 \AA is for instance known from coffinite (sample **D**), USiO_4 , where the shortest U-Si distance results from a SiO_4 polyhedron coordinated in a bidentate, edge-sharing fashion. However, there is no indication of an individual Si backscattering peak in the EXAFS Fourier transform. Furthermore, there is a significant weakening of the U-U backscattering signal with increasing silica content. An interaction of both ions obviously results in the formation of a polymeric structure. Once silica enters the structure, the characteristic U-O-U bonds of U(IV) oxyhydroxide are replaced by U-O-Si bonds. That there exists chemical affinity between uranium(IV) and silicate can be deduced from the existence of the mineral coffinite. However, the structure of the uranium/silica polymers is much more disordered than that of crystalline coffinite.