

 ROBL-CRG	Experiment title: Uranium sorption onto natural iron colloids in mine waters	Experiment number: 20-01-632
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Shifts: 12	Local contact(s): A. Rossberg	<i>Received at ROBL:</i>
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Report:

Previous EXAFS work has shown that U(VI) adsorbs to the surfaces of Fe (hydr)oxides by forming a bidentate, edge sharing complex [1-5]. However, a spectral contribution at 2.4 Å in the Fourier transform (FT) was not explained by this binary complex. Depending on the preparation (ambient air [1,2,5], CO₂-free atmosphere [3,4], 0.1 M NaCl [4]) the FT peak is controversially discussed as contribution from C, O or Cl atoms, hence involving a ternary complex structure. We employ Monte Carlo Target Transformation Factor Analysis (MCTFA) [6] to find a fitting 3-D structural model.

Ferrihydrite samples were prepared at ambient atmosphere (#A) and by using CO₂-free reagents in a N₂-flushed glovebox (#B) to prevent any interaction with carbon. Using NaOH we titrated solutions of 1 mM Fe(NO₃)₃·9H₂O and 12 μM UO₂(NO₃)₂·6H₂O to pH 5.5 to initiate aggregation of ferrihydrite (96 mg/L) and adsorption/ coprecipitation of UO₂²⁺. The concentrated wet pastes were frozen in liquid N₂ before recording fluorescence U L_{III}-edge EXAFS spectra with a 13-element germanium detector at 30 K.

Results:

The difference spectrum between the EXAFS of sample A and B shows no significant spectral contributions (Fig. 1a). Hence inorganic carbon has no influence on the local atomic environment of U(VI) at pH 5.5. Shell fitting identified two axial O-atoms (O_{ax}) at ~1.80 Å (FT peak 1), three equatorial O-atoms (O_{eq}) at ~2.40 Å and two O_{eq} at 2.30 Å (peak 2), one Fe-atom at 3.39 Å (peak 4). Accord-

ing to the experimental conditions, a contribution of bidentately coordinated carbonate ligands to the peak at 2.4 Å can be excluded in spectrum B. Hence the only possible alternative is an O-atom at a radial distance of 2.86 Å, which improves the fit significantly. Using spectrum B, the Debye-Waller factors from the shell fit, and an Fe octahedron of hematite, we performed MCTFA in order to derive a 3-D model accounting for all shells. The MCTFA fit reproduces the spectrum B up to 4.7 Å (Fig. 1b). It is evident from Fig. 1c that the tilted orientation of the pentagonal bipyramid relative to the edge-shared octahedron is in line with a radial distance of 2.84 Å between the U-atom and the near apical O-atom (O_{ap1}), explaining the FT peak at 2.4 Å, and coincides with a radial distance of 4.30 Å to the remote apical O-atom (O_{ap2}) and with a U-O distance of 4.70 Å to the two remaining O-atoms of the octahedron. Doubts arise about the very short distance of 1.77 Å between O_{ax1} and O_{ap1} , requiring repulsion or other interaction. For instance, distortion of the U(VI) polyhedron would enable a longer distances between O_{ax1} and O_{ap1} and thus the formation of a H-bond. This is subject to further research.

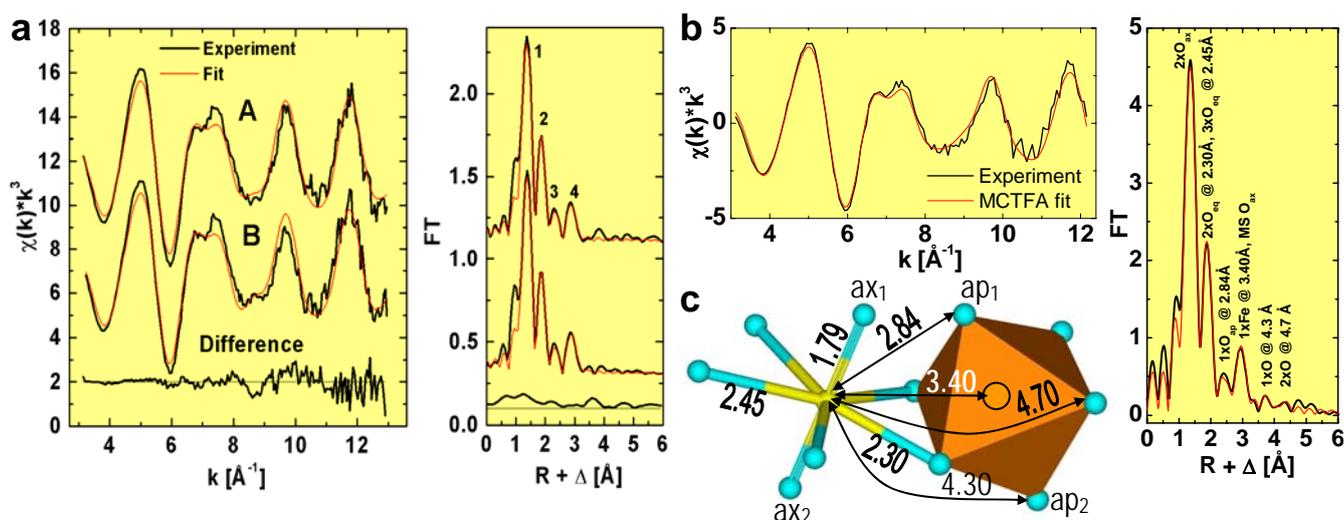


Fig. 1a. EXAFS spectra of samples A and B, their difference spectrum (A-B) and FT's. **b.** EXAFS spectrum and FT of sample B, fitted by MCTFA (MS: multiple scattering). **c.** Structure of the U(VI)-FeO₆ sorption complex found by MCTFA. Numbers give radial distances in Å, balls in yellow, blue and orange represent atoms of U, O and Fe, respectively.

References

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