 ROBL-CRG	<b>Experiment title:</b> <b>Uranyl sorption to clay minerals and analogues</b>	<b>Experiment number:</b>  <b>20-01-653</b> <b>(20-01-641)</b>
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> 07.09.-10.09.05;      30.10.-03.11.05; 06.05.-09.05.06;      26.11.-28.11.06	<b>Date of report:</b> 11.01.07
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## Report:

After more than one decade of studying uranyl sorption complexes onto surfaces of environmental relevance like clay minerals, Fe or Mn oxyhydroxides, the structure of the surface complexes is often yet not resolved. Open questions include the existence and structure of ternary surface complexes (i.e. with carbonate or silicate monomers), the possible formation of hydrogen bonds between the double-bond oxygen atom of the uranyl moiety and ligand oxygens, and the transition from sorbed uranyl monomers to sorbed uranyl polymers to uranyl surface precipitates. Here we present first results of uranyl sorption to gibbsite, the surface groups representative for a wide range of Al-containing natural minerals relevant for limiting U migration. Experiments were conducted in the pH-range 5 – 8.5, at an ionic strength of 0.01 M NaClO<sub>4</sub>, [UO<sub>2</sub><sup>2+</sup>] = 5×10<sup>-6</sup> M, a solid to solution ratio of 0.5 g/40 mL, and a contact time of 2 days in the overhead shaker in equilibrium with the atmosphere (speciation as shown in Fig. 2). Two samples at the highest pH of 7.5 and 8.5 were additionally prepared in a carbonate-free inert gas glovebox.

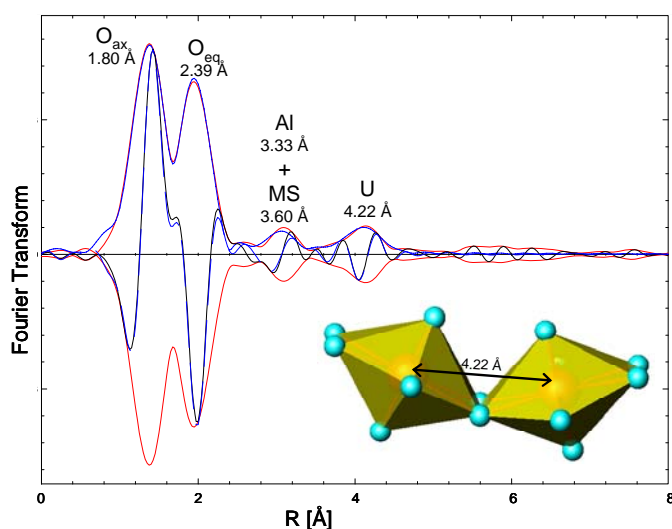
With the exception of the spectrum at pH 8.5 in equilibrium with open atmosphere, all spectra were statistically identical as shown by PCA (example shown in Fig. 1). The Fourier transform peak at 3.1 Å (not corrected for phase shift) was largely (but not completely) fitted by the 4-legged multiple scattering path U-Oax1-U-Oax2, using the constraints as suggested by (1) (CN 2, distance 2x U-Oax, Debye-Waller 2xU-Oax). For all samples except of U6-27, inclusion of an U-Al path slightly improved the total fit result. The distance of this U-Al path varied between 3.33 and 3.34 Å. Note that the contribution of this path to the total fit was always small (3-6 %), and especially coordination numbers, but probably even distances may be subject to substantial error. The distance is in line with a bidentate inner-sphere sorption complex to Al(O,OH)<sub>6</sub> octahedra, e.g. that on imogolite with 3.3 to 3.35 Å (2), but slightly shorter than the 3.40 to 3.44 Å found for montmorillonite (3).

Furthermore, for all but sample U6-27, inclusion of a U-U backscattering shell greatly improved the fit. Coordination numbers varied between 0.8 and 1.1, and distances between 4.21 and 4.22 Å. The coordination numbers of approximately one suggest formation of dimeric sorption species. Such

oligomeric sorption complexes have been suggested earlier by (4), (5, 6). However, the distance of 4.22 Å does not agree with 3.9 Å for multimeric uranyl carbonato complexes on hematite at pH > 6.5 (5), with 4.01 Å for polynuclear sorption complex on alumina at pH 6.5 (4), with quantum-chemical distances of 3.94 to 4.09 Å for uranyl dimers (7), with 3.78 to 3.86 Å for polymeric uranyl hydrolysis complexes (8, 9). The fitted distance does also not agree with that of schoepite and meta-schoepite (nearest U-U 3.8-3.9 Å) and other precipitates, which may have formed in this system due to local supersaturation (average conditions exclude supersaturation with respect to known likely solids). It agrees well, however, with several uranyl hydroxide structures like beta-hydroxide (4.22 Å) and gamma hydroxide (4.23 Å) and the peroxide mineral studtite (4.21 Å) (10).

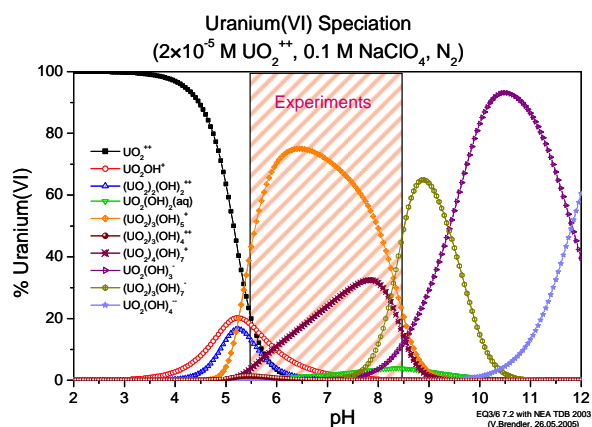
The possible structure of such uranyl dimers may be derived from simplified geometric considerations, assuming only one distance of Oeq as justified by the comparatively small Debye-Waller factor of 0.006 to 0.008 Å<sup>2</sup>, and assuming an equal distribution of Oeq in the equatorial plane of the uranyl unit. It follows, that an edge-sharing complex of two pentagonal uranyl units (coordination number of Oeq ≈ 5) with the fitted U-Oeq distance of 2.4 Å would result in a maximum U-U distance of 3.88 Å.

The fitted coordination numbers of Oeq=6 suggest, however, hexagonal uranyl units. In this case, the maximum U-U distance for an edge-sharing arrangement is 4.16 Å, hence only slightly smaller than the experimental value of 4.2 Å. Therefore, formation of edge-sharing, hexagonal uranyl dimers is the most likely arrangement. The small size mismatch of 0.04 Å is at the limit of the EXAFS precision for such a distance. Furthermore, small variations of the Oeq-U-Oeq angles from the average value of 60° can easily account for the observed mismatch, as for instance in studtite (10).



**Fig. 1.**

Fit of uranyl-gibbsite spectra of sample U6-24. Experimental Fourier magnitude (red) and imaginary part (black) along with fit (blue). The peak at about 3 Å (uncorrected for phase shift) is dominated by multiple scattering (MS) from the axial oxygen atoms (15 % of the total area), while the Al path contributes only 5 %. Inset: Proposed dimer structure consisting of two edge-sharing hexagonal uranyl units.



**Fig. 2.**

Aqueous uranyl speciation in equilibrium with CO<sub>2</sub>-free N<sub>2</sub>-atmosphere calculated for the experimental conditions. In the relevant pH-range from 5.5 to 8.5, the trimeric 3-5 hydroxo complex is predicted to prevail.

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