

Comparison of U and Np uptake on biogenic and abiotic ferrihydrite by XAFS

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XAS spectra of U and Np sorption biogenic ferrihydrite samples were compared to abiotic samples. The k^3 -weighted χ -spectrum and its Fourier-transform of the studied biogenic ferrihydrite sample bears close resemblance to the bidentate edge-sharing innersphere sorption ^1E complex, which is the main sorption species on abiotic ferrihydrite. Based on the shell fit analysis, the distances of the coordination shells $\text{U}-\text{O}_{\text{eq}}$, $\text{U}-\text{O}_{\text{ax}}$, and $\text{U}-\text{Fe}$ are similar to those determined for abiotic ferrihydrite samples.

EXPERIMENTAL. The strain of the stalk-forming, autotrophic and iron-oxidizing bacterium *Gallionella ferruginea* used in this study was isolated from a drinking-water well by MICANS (Sweden) and cultivated in our laboratory. A mineral salt solution (MSS) was prepared as described in detail.^[1] The MSS medium was autoclaved, chilled to 5 °C and infused with sterile filtered CO_2 to pH 4.6–4.8. After the CO_2 -infusion, tubes used as culture vessels, were filled with 10 mL MSS. Ferrous sulfide was prepared as already described and inserted to the bottom of the tube.^[2] The tubes were immediately inoculated with *G. ferruginea* culture. Ferric iron was precipitating quickly and formed biogenic ferrihydrite, which was removed from the tubes. Under anaerobic conditions the biogenic ferrihydrite samples were mixed with 50 mL sterile tap water, where $\text{UO}_2(\text{ClO}_4)_2$ or NpO_2ClO_4 were added until a final U or Np concentration of 0.08 mM was obtained. At the end of the sorption experiments, the samples were ultra-centrifuged for 1 h at $187.000\times g$. The formed pellets were prepared for X-ray absorption fine structure spectroscopy (XAFS) at the uranium and neptunium L_{III} -edge, which were carried out at the Rossendorf Beamline (Grenoble). The XAFS spectra were analyzed according to standard procedures.

RESULTS. The XAFS spectrum of the U sorption biogenic ferrihydrite sample is compared to those of selected references, e. g., of the bidentate edge-sharing uranyl sorption ^1E complex, described earlier^[3] and of the aqueous tris-carbonato complex $\text{UO}_2(\text{CO}_3)_3^{4-}$. The k^3 -weighted χ -spectrum and its Fourier transform of the studied biogenic ferrihydrite sample shows close resemblance to the bidentate edge-sharing inner-sphere sorption ^1E complex (s. Fig. 1), which is the most prominent surface species in the absence of carbonate and the main sorption species on abiotic ferrihydrite.^[3] As a second species, a smaller portion of the aqueous type-B ternary uranyl-carbonato complex was determined as a result of the addition of a carbon source during the cultivation of the *G. ferruginea* strain. By iterative target test factor analysis (ITFA), using the spectra of the two endmember species, we found that the ^1E complex is predominant (95 %), while the ternary uranyl-carbonato complex is present only to 5 %. Based on the shell fit analysis, the distances of the coordination shells $\text{U}-\text{O}_{\text{eq}} \sim 2.34 \text{ \AA}$, $\text{U}-\text{O}_{\text{ax}} \sim 1.79 \text{ \AA}$, and $\text{U}-\text{Fe} \sim 3.44 \text{ \AA}$ are similar to those determined of abiotic ferrihydrite samples.^[4] The data of the biogenic Np ferrihydrite sample were compared to Np interaction with a hematite surface and showed similar distances of the coordination shells, also indicating a bidentate edge-sharing coordination.^[5, 6] The structural parameters based on shell fit analysis of the EXAFS data

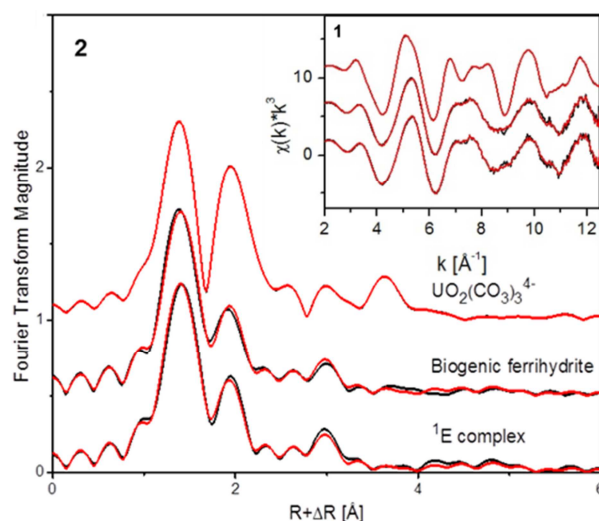


Fig. 1: U L_{III} -edge k^3 -weighted XAFS spectra (1, black) and corresponding Fourier transforms (2, black) of U sorption on biogenic ferrihydrite sample, together with the bidentate edge-sharing uranyl sorption complex (^1E) and the aqueous tris-carbonato complex ($\text{UO}_2(\text{CO}_3)_3^{4-}$); shell fits (red).

showed average distances of the coordination shells $\text{Np}-\text{O}_{\text{eq}} \sim 2.44 \text{ \AA}$, $\text{Np}-\text{O}_{\text{ax}} \sim 1.86 \text{ \AA}$, and $\text{Np}-\text{Fe} \sim 3.39 \text{ \AA}$. The complimentary information about the electronic structure and the oxidation state of the U and Np atom at the U L_{III} - and Np L_{III} -edge, respectively, were detected by using X-ray absorption near edge structure (XANES) and the high energy resolution fluorescence detection (HERFD) mode. The position and especially its fine structure are indicative of the hexavalent uranyl and pentavalent neptunyl moiety. The “yl-shoulders” are fully expressed at about 17,175 keV and 17,630 keV, respectively, and are clearly different from the U(IV) and Np(IV) reference spectra. Hence, the spectrum gives no indication for a reduction of U(VI) and Np(V).

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