Uranium(IV) surface complexes form by U(VI) reduction at the mineral-water interface

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The use of uranium as a fuel for energy and nuclear weapons has resulted in significant environmental challenges both in remediating U contaminated sediments and groundwaters, as well as in selecting geological disposal facilities to house spent radionuclide waste. The geochemistry of uranium is often dominated by its oxidation state, with U(VI) (uranyl) species recognized as more mobile and soluble than reduced U(IV) species such as uraninite (UO_2). However, recent advances highlight that the geochemstry of U(IV) is more diverse than previously recognized. Here, we show that, following reduction of U(VI), mineral surfaces can stabilize U(IV) as adsorbed complexes. By using X-ray absorption spectroscopy (XAS) and electron microanalysis techniques we establish that reduction of low surface loadings of U(VI) at model mineral oxide surfaces (rutile and magnetite) results in the formation of inner-sphere U(IV) surface complexes.

We find that U(IV)-mineral surface complexes form both through direct electron transfer between magnetite (Fe_3O_4) and U(VI), as well as by reduction of U(VI) at the TiO_2-water interface by the model soluble electron shuttle AQDS (reduced form: AH_2QDS = 9,10-dihydroxyanthraquinone-2,6-sulfonate). At high U-to-surface area loadings uraninite (UO_2) predominates, but at lower U surface loadings only adsorbed U(IV) is observed. Inner-sphere U(IV)-Ti and U(IV)-Fe complexes predominate at the rutile and magnetite surfaces at different U surface loadings (<2.5 U nm^{-2} for rutile and < 0.075 U nm^{-2} for magnetite). U(IV)-Ti complexes were stable under anoxic conditions for at least a year, whereas at moderate surface loadings (0.15 to 0.075 U nm^{-2}) U(IV)-Fe complexes aged to uraninite over a period of 4 months.

Our results reveal new information about the chemistry of U(IV) in the environment, and indicate that U(IV) forms complexes with mineral surfaces under reducing conditions. Such U(IV) surface complexes might be expected under the lower U-to-mineral surface loadings found in contaminated sediments. Future work is needed to further characterize and incorporate these complexes into geochemical models.