The utility of EXAFS in discovering novel species relevant to U mobility in reducing environments

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Depleted uranium (^{238}U) is continuously produced from nuclear power generation and is also a widespread contaminant from former U mining and weapons production activities. Most of the current plumes propagate in the subsurface and most spent fuel facilities envision underground storage, where oxygen-deficiency and biological activity can induce reducing conditions. Thus, it is imperative to have a good understanding of the reduced U species governing this contaminant's dispersal. Current reactive transport models assume that the reduction of oxidized and mobile U(VI) to U(IV) leads to the formation of the most insoluble U(IV) mineral UO_2 (uraninite). However, multiple recent examinations of contaminated reduced soils and sediments indicate that U(IV) is stabilized in forms other than uraninite. This discrepancy between model and reality could be a source of significant uncertainty in the prediction of plume propagation or in performance assessments of nuclear storage facilities.

We will present recent U L_{III}-edge EXAFS measurements on contaminated sediments from a reduced sediment layer near a creek at the Savannah River National Laboratory (a site of former U production activities), showing the predominance of U(IV) species that are not uraninite. The data are analyzed in the context of U(IV) spectra from prior work by our group on defined systems, starting with the first observations of phosphate- and carbonate-complexed U(IV) in microbial reactors[1] to more recent observations of adsorbed U(IV) species on mineral surfaces[2]. The ability to discern between non-uraninite U(IV) species formed in the complex biological and mineralogical milieu of a sediment is assessed using standard analysis techniques such as linear combination and shell-by-shell fitting, as well as more advanced techniques such as target transformation and wavelet analysis. The results provide important baseline requirements and sensitivity estimates on the ability of U L_{III}-edge EXAFS spectroscopy to discern between different non-uraninite U(IV) species in the diverse environment of natural sediments.

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[2] D. E. Latta, B. Mishra, R.E. Cook, K. M. Kemner, M. I. Boyanov, "Stable U(IV) complexes form at high-affinity mineral surface sites", *Environ.Sci.Tech*., 48 (3), 1683–1691 (2014); M.I.Boyanov, D.E.Latta, M.M.Scherer, E.J.O'Loughlin, K.M.Kemner, "Surface area effects on the reduction of U^{VI} in the presence of synthetic montmorillonite", *Chemical Geology*, 464 (2017) 110-117