U(IV) complexation by sedimentary organic matter

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Uranium contaminates many sites throughout the world. Within the United States, mine waste is a partuclarly ubiqitous problem as exemplified by Rifle, Co where U groundwater concentrations exceed the EPA limit as a result of past mining activities. Thin lenses of organic matter-rich, anoxic sediments (referred to as naturally reduced zones, NRZs) are distributed within the aquifer. Our group has recently shown that these sediments harbor up to 95% of the total U in the aquifer, mainly as U(IV) species, which are non-crystalline and more labile than biogenic uraninite (UO_2) [1]. Thus, the NRZ sediments may act as a source of U, maintaining the groundwater U plume.

Knowledge of the U(IV) speciation is thus key to modeling efforts that seek to elucidate U transport within the aquifer. However, the speciation of the non-crystalline U(IV) in the NRZ sediments is currently unknown: U may be complexed by Fe or Si functional groups on mineral surfaces or with P or C funtional groups associated with natural organic matter (NOM) [1].

To investigate the speciation of U(IV) in the NRZ sediments, we employ a model system containing homogenized partially-decayed plant material innoculated with Rifle groundwater and incubated with U(VI) under anoxic conditions (which leads to U(IV) production). The model includes a mixture of degraded plants materials and living and dead microbial biomass, thus providing a simplified analogue of sedimentary NOM. We investigate the NOM and NOM-mineral models using a combination of extended X-ray absorption fine structure (EXAFS) spectroscopy to obatin bulk U speciation, scanning transmission X-ray microscopy (STXM) to co-locate U with organic macromolecules, microbes and minerals, and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) to co-locate U with morphological features (e.g. cells), C, P, Si and Fe. Our work provides insight into U(IV) speciation in complex organic-rich sedimentary environments.

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