Molecular-scale biogeochemical mechanisms affecting the mobility of Hanford Site contaminants

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At the United States Department of Energy's (U.S. DOE's) Hanford Site, uranium (U) and technetium (^{99}Tc) are major risk driving contaminants due to their high solubility in oxidized circumneutral site groundwaters. Migration of these contaminants is predicted through aquifer regions and ultimately to a final discharge into the Columbia River. Consequently, understanding the factors limiting the mobility of these contaminants in the subsurface represents an important step towards reducing the risk of Hanford contaminant migration into the Columbia River. Under anoxic conditions, dissimilatory metal reducing bacteria (DMRB) have potential to limit mobility of these radionuclides in the environment by the enzymatic bioreduction of U(VI) or Tc(VII) to insoluble oxides, $U(IV)O_{2(s)}$ or $Tc(IV)O_{2(s)}$.

Due to our recent discovery of *Shewanella* sp. in sediments from the Hanford Reach of the Columbia River, we have investigated the role of putative redox-active proteins from *Shewanella oneidensis* MR-1 for their role in the transfer of electrons to U(VI) and Tc(VII). Kinetic studies with wild type and mutant resting cells revealed that *c*-type cytochromes were essential for the reduction of U(VI) and formation of extracellular UO_2 nanoparticles independent of the electron donor source. Extracellular nanoparticulate UO_2 accumulated in association with a complex exopolymeric substance (EPS) that contained outer membrane *c*-type cytochromes (OMCs). One EPS-associated OMC was shown to be capable of directly transferring electrons to U(VI) *in vitro*. In contrast, the mechanism of Tc(VII) reduction was found to be dependent on the source of reducing equivalents. The NiFe hydrogenase was involved in the H_2-driven reduction of Tc(VII) presumably through a direct coupling of H_2 oxidation and Tc(VII) reduction. In the presence of lactate, Tc(VII) reduction was slower than H_2-driven reduction and catalyzed directly by OMCs, suggesting that electron donor availability may influence strategies designed to enhance biogenic Tc(VII) reduction. These studies represent important steps towards determining the principal mechanisms that govern the biomineralization and reactivity of these redox reactive contaminants.

Tracking precipitation seasonality and vegetation features in Asian Oligo-Miocene mammal tooth remains

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The carbon isotope difference between C3 and C4 vegetation can be exploited to determine ecological and climatic changes in the past. C3 and C4 plants have $\delta^{13}C$ values averaging approximately -27 and -12‰, respectively. The ratio of C3 to C4 plants in the ecosystem is recorded in the diet of herbivores and eventually in the tooth enamel. Mammalian tooth enamel is enriched by about 14‰ compared to the vegetation. The oxygen isotope ratio in the tooth reflects that of the body water, which is in turn in equilibrium with that of the drinking water. Exploring patterns of C and O uptake in the elemental composition of incrementally grown biological structures such as the retzius striae of the teeth deposited with seasonal or more frequent periodicity give opportunities to improve the climatic and environmental reconstructions. Here we explored spatial variations of stable isotopes within tooth enamel of several asian mammal species (Pakhistan) to reconstruct the Asian Oligo-Miocene seasonal changes in (monsoon) precipitation and diet. Carbon isotopes indicate a mosaïc of savanna and forest ecosystems and high-resolution measurments of oxygen isotopes in tooth enamel show that the Asian monsoon system existed ~14Myr ago.