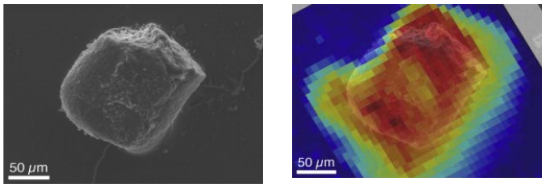
Metal Detection

Bioreduced iron generates reduced technetium that may resist remobilization

Technetium-99 is a metal formed during nuclear reactions and can be released into the environment during nuclear fuels reprocessing. It is highly mobile in its most oxidized state, Tc(VII), and much less mobile in its reduced state, Tc(IV). Technetium contamination of groundwater is a chief concern at the Department of Energy's Hanford Site, where ^{99}Tc has leaked from nuclear waste storage tanks to depths of 60 meters in the vadose zone, which is the region above the water table. Using resources at the DOE's EMSL, researchers found that ^{99}Tc in natural subsurface sediments that has been reduced by Fe(II) associated with certain mineral phases may be exceedingly resistant to oxidation and, therefore, remobilization.



^{99}Tc-containing particle isolated from oxidized FRC sediment: backscattered electron micrograph (left) and electron microprobe energy dispersive X-ray analysis (right).

The research team, comprising scientists from Pacific Northwest National Laboratory and Argonne National Laboratory, examined two sediments that differed in mineralogy and aggregation state. One was obtained from the upper Ringold Formation near the Hanford Site and the other from the Field Research Center (FRC) at the Oak Ridge Site. Both sediments contained Fe(III) and Mn(III/IV) as redox active phases, although the FRC sediment also contained different Fe-phyllosilates minerals. The researchers used a *Shewanella*, a metal-reducing bacterium, to reduce manganese and iron oxides in the sediments. Iron in the bioreduced sediments, in turn, reduced Tc(VII) to Tc(IV). During the subsequent oxidation phase, the researchers measured Tc release from the sediments and found that Tc(IV) in the Ringold Formation sediment was oxidized and released much more rapidly and extensively than in the FRC sediment. The researchers used tools at EMSL and the Advanced Photon Source at Argonne National Laboratory to characterize sediment-associated ^{99}Tc and then used EMSL's X-ray microprobe, electron microprobe, X-ray absorption spectroscopy, and micro X-ray diffraction to analyze the FRC sediment and Tc-containing particles isolated from the sediment. These analyses revealed an oxidation-resistant Tc(IV) phase that exists with Fe(III) within iron-containing micas in the FRC sediment. The mica particles were a mineral phase called celadonite.

Scientific Impact: This work offers insights into electron exchange at the microbe-mineral interface and its effect on the fate and transport of subsurface contaminants. This research was performed as part of EMSL's Biogeochemistry Grand Challenge and supports EMSL's goal to predict biological functions from molecular and chemical data.

Societal Impact: Subsurface contaminants such as ^{99}Tc pose serious health risks. This study helps researchers better understand the biogeochemical processes influencing the fate and transport of ^{99}Tc and may lead to better predictions of its migration in the subsurface and new insights into remediation strategies at nuclear facilities worldwide.

Reference: Fredrickson JK, JM Zachara, AE Plymale, SM Heald, JP McKinley, DW Kennedy, C Liu, and P Nachimuthu. 2009. "Oxidative Dissolution Potential of Biogenic and Abiogenic TcO_2 in Subsurface Sediments." *Geochimica et Cosmochimica Acta* 73:2299-2313.

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