ABSTRACT: Recent field studies show that both uraninite and non-crystalline U(IV) are produced following biological metal and sulfate reduction of aquifers containing uranium. This objective of this work was to develop enhanced molecular-scale understanding of the biogeochemical factors controlling the formation and stability of these species in the subsurface. The chemical conditions present during bioreduction were systematically examined to identify specific groundwater solutes favoring the formation of non-crystalline U(IV). Sulfate and silicate were found to promote the formation of the non-crystalline U(IV) product while others such as calcium, magnesium and sodium did not. Phosphate also promotes non-crystalline U(IV) formation. Additionally, the formation of this product was linked to the biological response of \textit{Shewanella oneidensis} MR-1 cells to U(VI). In the presence of these solutes, cells produced abundant exopolymeric substances (EPS). Scanning transmission X-ray microscopy (STXM) revealed that U was co-localized with EPS when non-crystalline U(IV) was produced and with the cell surface when UO$_2$ was produced. Cell viability assays showed that cells producing EPS were more viable than those producing UO$_2$.

The biogeochemical redox cycling of S and Fe and its impact on U(IV) speciation and stability in field-biostimulated Rifle, CO IFRC aquifer sediments was evaluated using X-ray absorption spectroscopy, X-ray microscopy, electron microscopy, and chemical extractions. These findings show that zero-valent sulfur is relatively abundant prior to and during sulfate reduction. The onset of microbial sulfate reduction corresponds with the formation of FeS coatings and a sharp escalation of U(IV) accumulation rates. Intriguingly, U(IV) speciation is not appreciably impacted by the onset and intensity of sulfate reduction, suggesting that bacteria play direct and profound roles in stabilizing U(IV) under all conditions examined.

Further, we characterized the reactivity of crystalline and non-crystalline U(IV) products by exposing chemogenic UO$_2$, biogenic UO$_2$ or non-crystalline U(IV) to various complexants and oxidants and then evaluating the release of U as well as changes in solid-phase speciation. Reactivity assay reagents included ammonium nitrate and fluoride under anoxic conditions and dissolved oxygen and persulfate as oxidants. The results show that non-crystalline U(IV) is more readily mobilized by complexation either form of UO$_2$, and that persulfate is a potent oxidizer of all forms of U(IV). U L$_{III}$ edge x-ray absorption spectroscopy confirmed that non-crystalline U(IV) was more susceptible to rapid oxidation than UO$_2$.

This work provides detailed new process models and quantitative parameters that inform biogeochemical models of uranium redox transitions in aquifers.