Contamination of the subsurface with hexavalent U is an unfortunate consequence of uranium mining and processing around the world. U(VI), the hexavalent oxidation state, is soluble and thus its mobility off site is a significant concern. A bioremediation strategy that is being considered is microbially-mediated U(VI) reduction to tetravalent U [U(IV)], a relatively insoluble U valence state. This approach relies on naturally present microbes able to use U(VI) as an electron acceptor, thereby reducing it to U(IV).

While nanoparticles of the mineral uraninite were long thought to be the sole product of microbial U(VI) reduction, other U(IV) products were identified in laboratory and field studies. In particular, a product dubbed monomeric U(IV) – an operationally defined species – that has a tuft-like appearance, is coordinated to phosphate and is found in a variety of settings including remediated field sediments.

However, many questions remain as to (a) the structure, composition and reactivity of monomeric U(IV) and (b) its mechanism of formation. In this study, we use X-ray absorption spectroscopy, X-ray microspectroscopy, Fourier transform infrared spectroscopy, electron microscopy and wet chemical approaches to investigate the structure and composition of monomeric U(IV). We use in-field deployment to probe the lability of this compound and laboratory experiments to investigate chemical and biological controls on its formation.

By combining the wealth of data accumulated from the various approaches, we propose a model for the preferential formation of monomeric U(IV) over uraninite in natural and remediated sediments.