Investigating the potential microbial reduction of U(V)

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The molecular mechanism of hexavalent uranium (U(VI)) reduction to tetravalent, U(IV), species remains partly unclear in metal-reducing bacteria such as Shewanella oneidensis MR-1. Recent evidence converges to the conclusion that U(VI) is reduced to pentavalent U(V) by a one-electron transfer. We capture the U(V) intermediate using the unusual properties of the synthetic dpaea ligand, which forms a stable aqueous complex with U(V) at pH 7. The U(V)-dpaea complex allows us to circumvent the propensity of U(V) to disproportionate to U(VI) and U(IV) and provides the opportunity to investigate the fate of the U(V) species formed. An emerging consensus attributes U(IV) formation to the disproportionation of U(V) to U(VI) and U(IV). However, this step in the reduction mechanism of U(VI) still requires clearer experimental evidence. Here, we propose to elucidate the mechanism of this/these electron transfer(s). We combine ion exchange chromatography, UV-vis spectrometry, luminescence, and U M4-edge High Resolution X-ray Absorption Near Edge Structure spectroscopy to investigate U(VI) reduction to U(V) and U(V) transformation to U(IV) using a collection of mutant strains of S. oneidensis MR-1. These strains lack genes for which the corresponding proteins are hypothesized to catalyse electron transfer. While the system studied here is not directly relevant to environmental systems, it provides the unique opportunity to probe for microbial reduction of U(V).