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Bioreduction of U(VI) in the presence of phosphate

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Phosphate/phosphoryl moieties are ubiquitous in biological and environmental systems and can potentially affect the speciation of uranium during natural attenuation or stimulated bioremediation processes. The reactivity between U(VI) and phosphate has been studied extensively, but the significant influence of phosphate groups on the formation of reduced U(IV) species has only recently been recognized. We will compare and contrast the bioreduction of dissolved and solid-phase U(VI) by Gram-positive and Gram-negative metal-reducing bacteria (Shewanella, Anaeromyxobacter, Geobacter, and Desulfitobacterium) in the presence and absence of phosphate, from the perspective of solid-phase U speciation as determined by U L-edge x-ray absorption spectroscopy (XANES and EXAFS). In all cases examined, the presence of phosphate at concentrations of $P/U > 1$ led to the formation of reduced, inner-sphere complexed U(IV)-phosphate species that prevented the lowest-solubility U(IV) mineral uraninite (UO_2) from forming over at least several months. In the absence of phosphate, nanoparticulate uraninite or complexed non-uraninite U(IV) species were observed (depending on the system and conditions), suggesting that the interplay between the chemical conditions at the location of electron transfer to U(VI) control the U(IV) product and subsequently the stability of reduced U. The importance of non-uraninite U(IV) species will be discussed in the context of their predominance in biostimulated sediments from the Oak Ridge field site in the United States.