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Subsurface Conditions Controlling Uranium Retention Pathways

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Microbial uranium reduction in the subsurface can sequester substantial quantities of this toxic element, but the long-term fate depends upon the specific phases produced via reduction. Within natural environments, uranium often correlates with iron rather than existing as a discrete uranium oxide phase; uranium incorporation into iron oxides is a mechanism that can explain the co-occurrence of these two elements and may represent a natural attenuation pathway for uranium. Further, incorporated uranium within Fe (hydr)oxides appears stable with respect to oxidative dissolution, representing a potential means for long-term sequestration of uranium in the subsurface. Within this project we are examining uranium reduction pathways and mechanisms.

We have examined the divergent fate of uranium being either incorporated within iron oxides or reduced to U(IV) solids. Our experiments reveal that: U(V) is incorporated into Fe oxides, calcium concentration has a determining effect on the dominant reaction pathway, (iii) U incorporated into Fe oxides across a broad range of conditions. Uranium valence state was measured using x-ray photoelectron spectroscopy, and U sequestration mechanisms were identified and quantified using extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray powder diffraction, and transmission electron microscopy (TEM). Depending on the reaction conditions, 12 to 80% of total U is incorporated into goethite. Uranium incorporation was a particularly dominant retention pathway at U concentrations ~50 µM. However, Ca limits both incorporation of U(V) into Fe oxides and reduction to U(IV). Calcium experts a progressive inhibition of reduction to U(V) or U(IV) even at Ca:Fe ratios in excess of 2.6, rendering greater proportions of aqueous U(VI). We deduce that through the formation of the dicalcium uranyl carbonato complex, Ca blocks that active electron transfer coordinate for Fe(II). A mass expression for the exchange of Fe-Ca in the ternary complex describes the regulatory role of calcium (and by association other ternary complexing divalent cations).

In sum, our results demonstrate that complex reaction pathway for uranium reduction and illustrate that U incorporation can be a major U retention pathway. Ultimately, it is critical to recognize that multiple retention processes of uranium will occur in the subsurface , which must be considered in the long-term fate of this hazardous element.