

Unforeseen Reaction Pathways of U(VI) with Fe(II) Limiting U(IV) Formation

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Uranium contamination of soil and fresh water is found worldwide, posing risks to human health and the environment on all continents except Antarctica. Dissolved concentrations and the coupled propensity for transport of U vary extensively depending on U speciation. In surface and subsurface environments, U redox state is the primary determinant of U solubility, with U(VI) occurring as the soluble uranyl moiety, and U(IV) as sparingly soluble uraninite or particulate organic matter-bound phase. Thus, understanding U reduction pathways, and mechanisms promoting or inhibiting these pathways, is essential for understanding U cycling and the risk imposed by this contaminant. Here, we reveal two such mechanisms linked to concentrations of calcium or carbonate that control U(VI) reduction and the solid phase products.

The first mechanism is a kinetic constraint on electron transfer to U(VI) imposed by calcium in the ternary calcium uranyl carbonate complexes. We performed a series kinetic experiments, in which we varied the initial proportion of total calcium uranyl carbonate species (mono- and di-), to probe the impact of calcium on U(VI) reduction. U reduction by Fe(II)_{aq} slows as U speciation shifts entirely to the calcium uranyl carbonate species, despite thermodynamic conditions that favor reduction.

The second mechanism is precipitation of a mixed U(V)/U(VI)-carbonate phase immediately following the first electron transfer, but before a second electron transfer can proceed, limiting U(IV) formation. We characterized the reaction products from the kinetic experiments with HERFD-XANES, EXAFS, and TEM. We find that the products are an amorphous Fe(III) solid and a mixed U(V)/U(VI)-carbonate phase. No uraninite was detected in the solid. Precipitation U(V)/U(VI)-carbonate phase inhibits uraninite formation.

In sum, we show that both calcium and carbonate can inhibit formation of U(IV). Furthermore, alongside other work documenting U(V), our results suggest that the concentration of U(V)-stabilizing ligands, as well as that of ions competing for those ligands, control the proportions of U(V) and U(IV) produced by reduction of U(VI).