

## **Mobilization of non-crystalline U(IV) by complexation with organic ligands generates U isotope fractionation**

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Uranium mining and processing left a legacy of contamination around the world. Strategies for remediation are commonly based on the reduction of the mobile U(VI) to more immobile U(IV), e.g., by stimulated microbial reduction. It has been demonstrated that the major product of U bioreduction is a non-crystalline U(IV) (NC-U(IV)) species associated with the microbial biomass. NC-U(IV) is not well characterized but is significantly more labile than uraninite (UO<sub>2(s)</sub>). Oxidation or complexation by organic ligands can cause (re)mobilization of NC-U(IV). Organic ligands, for instance derived from humic acids, are present at many contamination sites and may form soluble complexes with U(IV).

Here, we examine the effectiveness of NC-U(IV) mobilization by complexation and the associated U isotope fractionation with a variety of ligands.

First, U(VI) with an initial U concentration of 400 μM was reduced by *Shewanella oneidensis* MR-1 in a phosphate-containing medium (WLP) under anoxic conditions to produce NC-U(IV). Subsequently, U was mobilized with EDTA or citrate (400 μM and 1000 μM) or bicarbonate (500 mM). Samples collected at various time points were analyzed for their U concentration and <sup>238</sup>U/<sup>235</sup>U isotope ratios.

First, all ligands are able to mobilize NC-U(IV) effectively, a larger ligand to U ratio results in faster and more extensive U mobilization. Complexation with EDTA and citrate resulted in an enrichment of <sup>238</sup>U in the mobilized fraction (EDTA: δ<sup>238</sup>U= 0.4-0.7 ‰; citrate: δ<sup>238</sup>U= 0.3 ‰). For bicarbonate, an initial decrease in the mobilized fraction (-0.2 ‰) was followed by an increase (+0.2 ‰) of δ<sup>238</sup>U.

These initial findings indicate that non-redox-related mobilization of U(IV) may result in an opposite isotope fractionation as compared to partial oxidative U mobilization.