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Reduction of U(VI)-citrate by whole microbial cells and pure enzymes: what controls U isotope signatures?

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Microbial reduction of U(VI) is widespread in the environment, both in pristine and engineered environments. Several studies have shown that such enzymatic redox transformations are accompanied by mass-independent isotope fractionation, with enrichment of the heavy U-238 in the U(IV) products, in accordance with nuclear field shift theory. However, fundamental mechanistic information is lacking on the factors that affect the direction and magnitude of the U isotope signature. Recent research has implicated reaction rate as a primary determinant of U isotope fractionation [1], however, the reasons for this are not well established.

To explore this question, reaction kinetics and associated isotope fractionation during U(VI)-citrate reduction by *S. oneidensis* were assessed. U isotope analyses with MC-ICP-MS reveal relatively constant isotope fractionation factors of ~0.5 ‰, irrespective of reaction rates imposed by biomass concentrations. This is far from equilibrium isotope fractionation of ~2‰, as determined both experimentally and theoretically, using *ab initio* calculations. Second, using a mathematical framework first established for microbial sulfur fractionation [2], we will interpret isotope signatures arising from systems in which reaction rates are limited by electron flow from the donor, lactate.

Additionally, cell-free extracts containing redox-active enzymes derived from cultures of *S. oneidensis* were also reacted with U(VI)-citrate to determine the importance of an intact cellular electron-transport system or membrane transport in controlling microbial U isotope signatures. A fractionation factor of ~1‰ suggests that significant back-reaction is permitted in the absence of whole cells.

Finally, recombinant MtrC [3], a *c*-type cytochrome from *S. oneidensis* with proven U(VI) reducing capacity, was purified and reacted with U(VI)-citrate. Here, binding extents and U(VI)/U(IV) concentrations for both the protein-bound and aqueous phases have been determined and, for the first time, we will report the U isotope signatures for reduction by a single enzyme, independent from confounding factors such as membrane transport or a cellular boundary layer.

These data contribute toward a comprehensive understanding of the mechanistic controls on uranium reduction and isotope fractionation by microorganisms.

[1] Basu et al. (2020), *Environ. Sci. Technol.* 54(4), 2295-2303.

[2] Rees (1973), *Geochim. Cosmochim. Acta* 37, 1141-1162.

[3] Shi et al. (2006) *J. Bacteriol.* 188(13), 4705-4714.