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Electron flux controls fractionation of U isotopes during bacterial reduction of U(VI)

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Microbial reduction of U(VI) is widespread in the environment and several studies have shown that such enzymatic redox transformations are accompanied by mass-independent isotope fractionation. This enrichment of the heavy U-238 in the U(IV) products is in accordance with nuclear field shift theory, whereby the nuclear volume impacts isotope partitioning in addition to the conventional vibrational effect.

The preservation of U isotope signatures in the rock record and their relationship to given redox conditions has led to their use as a paleo-redox proxy. However, fundamental mechanistic information is lacking on the factors that affect the direction and magnitude of the U isotope signature. Recent research has implicated the balance between U(VI) supply and reduction rate as a primary determinant of U isotope fractionation.

To unravel mechanistic processes that could underscore U isotope fractionation, we investigated U(VI)-citrate reduction by *Shewanella oneidensis* in systems in which reaction rates were limited by electron flow from the donor, lactate. U isotope analyses with MC-ICP-MS revealed that the U isotope fractionation magnitude increased with decreasing lactate concentrations, suggesting that electron flux from bacterial metabolism may be an important determinant of isotope fractionation.

To confirm this observation, we purified a key U(VI)-reducing protein from *S. oneidensis* and chemically reduced its Fe-containing heme groups to a range of extents. The fully reduced protein resulted in very limited U isotope fractionation in contrast to the partially oxidized protein which showed significant fractionation. Here, we demonstrate that the redox state of U(VI)-reducing proteins is a key controller of back-reaction, and subsequently, isotope fractionation.

Collectively, these findings suggest that U isotope signatures in nature may be complicated by factors other than the local redox conditions; for example, by spatio-temporal changes in supply of organic matter, as an electron donor for microbial metabolism.