Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.36430

Control of uranium speciation on isotope fractionation during microbial reduction: the example of the U-carbonate system

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Uranium (U) mobility in the environment is largely controlled by its redox chemistry. Under oxic conditions, hexavalent U(VI) forms highly soluble complexes with organic and inorganic ligands. Reduced, tetravalent U(IV) commonly precipitates in the absence of strong organic ligands. Pentavalent U(V) forms as a transient intermediate in the reduction process.

Microbial U(VI) reduction can be mediated by dissimilatory metal- and sulfate-reducing bacteria and commonly leads to U isotope fractionation ($\delta^{238}U$) with an enrichment of heavy ^{238}U in the U(IV) product. This characteristic, mass-independent fractionation behavior has led to the emergence of $\delta^{238}U$ as bioremediation marker and paleoredox proxy. Mechanistically, U reduction can occur via two distinct pathways, which share an initial enzymatic reduction of U(VI) to U(V). Subsequently, U(V) disproportionates or can be enzymatically reduced to U(IV). Both pathways have been invoked during microbial U(VI) reduction.

The diagnostic capacity of $\delta^{238}U$ is limited by an incomplete understanding of factors controlling the extent of fractionation, including the effect of U speciation and the role of a U(V) intermediate. We aim to address these subjects in a U(VI)-carbonate system, since carbonate species are expected to dominate aqueous U speciation across different ecosystems, including freshwater and seawater environments.

We aim to discriminate between the abovementioned reduction pathways and their associated isotope fractionation utilizing the dissimilatory metal reducing organism *Shewanella oneidensis* MR-1. To do so, we varied the bicarbonate concentration which, in turn, impacts U speciation. We followed U reduction in batch incubations over time, combining ICP-MS, U(VI)-luminescence and U M_4-edge HERFD-XANES with $\delta^{238}U$ measurements. Bicarbonate concentration influenced the reduction rate and mechanism with periodic re-emergence of aqueous U in ICP-MS and luminescence data, attributed to U(V) disproportionation. Only the highest tested bicarbonate concentration expressed the expected mass-independent Rayleigh-type fractionation, whereas lower bicarbonate systems fractionated slightly in a mass-dependent direction.

We suggest a shift from a disproportionation-controlled reduction to two consecutive electron transfers along the bicarbonate concentration axis. Our results highlight the control of U speciation and the associated reduction mechanism on $\delta^{238}U$, illustrating the fact that U fractionation may not always operate in the mass-independent direction commonly expected for microbial reduction.