

Mechanisms of Uranium Isotope Fractionation

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The redox chemistry of uranium (U) has been utilized for various applications including remediating U contamination, determining redox conditions in the ancient oceans, and processing U ore [1]. While U(VI) is soluble and mobile in natural waters, U(VI) reduction to relatively insoluble U(IV) leads to accumulation of U in sediments and removal from solution. [U] in modern and ancient aqueous systems are impacted by numerous chemical and physical processes, so [U] do not provide a direct proxy for U(VI) reduction. A more direct indicator of U(VI) reduction is the ²³⁸U/²³⁵U ratio, which is strongly affected by reduction, but not by other processes [1]. Typically, U(VI) reduction preferentially involves ²³⁸U(VI), driving ²³⁸U/²³⁵U of remaining U(VI) to lower values. Prior studies of microbial U(VI) reduction consistently observed the preferential reduction of ²³⁸U(VI) [2]. Previous evidence pointed towards no isotopic preference or even slight preferential reduction of ²³⁵U(VI) during abiotic reactions [2]. However, a recent study has demonstrated that ²³⁸U/²³⁵U can be fractionated during abiotic reduction and that solution chemistry controls the extent of fractionation [3], but the mechanisms inducing the isotopic fractionation are still unknown. Without improved understanding of these mechanisms, proper utilization of ²³⁸U/²³⁵U remains uncertain

By conducting numerous batch experiments, we investigated the mechanisms controlling U isotopic fractionation during abiotic reduction. By changing several chemical parameters, including pH, bicarbonate, Ca, and Mg concentrations, we observed the impact of aqueous chemistry on isotopic fractionation. U(VI) reduction with Fe(II) sulfide resulted in preferential removal of ²³⁸U(VI) in most experiments. Our results suggest that the extent of U(VI) adsorption to Fe(II) sulfide controls the magnitude of fractionation with less adsorption inducing a greater isotopic fractionation. Forthcoming experiments with aqueous sulfide, U(VI)-reducing microbes, and microbial proteins will further evaluate the extent to which adsorption is a controlling mechanism on fractionation and what other processes impact isotopic fractionation during reduction.

[1] Andersen *et al.* (2017) *Rev. Mineral. Geochem.* **82**, 799-850. [2] Stylo *et al.* (2015) *PNAS* **112**, 5619-5624. [3] Brown *et al.* (2018) *PNAS* **115**, 8688-8693.