Isotopic signature of uranium bioreduction

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Engineered remediation of U could occur via chemical reactions (abiotic pathways) and/or microbial processes (biotic pathways). The role of direct enzymatic activity in remediation processes remains unresolved due to the inability to discriminate biotic from abiotic redox transformations of U in sediments. In the present study, we show that the isotopic signature generated by microbial reduction of U(VI), i.e., the accumulation of the heavy ^{238}U isotope in the formed U(IV) phase, is readily distinguishable from that originating from abiotic uranium reduction. The latter exhibits either no U isotope fractionation (in the case of reduction by mackinawite, peat or aqueous S(-II)) or significant enrichment of the light ^{235}U isotope in the formed U(IV) phase (in the case of reduction by magnetite, green rust or aqueous Fe(II)). Thus, based on our experiments, biotic U and abiotic U reduction tend to fractionate U in opposite directions [1].

We explored possible mechanistic explanations for these findings. The isotopic signature associated with biotic reduction could be due to a kinetic effect or to near-equilibrium fractionation. This is because, for uranium, the nuclear field shift dominates equilibrium isotope fractionation and results in the preferential accumulation of the heavy isotope in the reduced valence state [2]. The lack of isotope fractionation for sulfide- or organic-mediated reduction may be attributed to direct two-electron transfer from organic matter or S(-II) to U(VI).

Regardless of the mechanistic underpinnings, these uranium isotopic signatures could be utilized to constrain the contribution of biotic U reduction in remediation studies. For example, direct enzymatic reduction likely contributes substantially to U immobilization at the U-contaminated site in Rifle (Colorado, USA) based on the reported accumulation of the ^{235}U isotope in the groundwater during remediation [3].

[1]Stylo, M. et al., Uranium Isotope Fingerprint Biotic Reduction. *Proc. Natl. Acad. Sci. U.S.A* **accepted**. [2]Schauble, E. A. *Geochim. Cosmochim. Acta* **2007,** *71*, 2170-2189. [3]Bopp, C. J. et al., *Environ. Sci. Technol.* **2010,** *44*, 5927-5933.