

$^{238}\text{U}/^{235}\text{U}$ fractionation during U(VI) reduction by synthetic magnetite

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The ratio of the two major uranium (U) isotopes, $^{238}\text{U}/^{235}\text{U}$, varies in natural environments depending on biogeochemical conditions [1]. This isotopic signature is proposed as a tool to distinguish between abiotic and biotic U reduction in paleo and modern redox processes [2]. Experimental findings indicate that strong U isotope fractionation (with high $^{238}\text{U}/^{235}\text{U}$ in the product) occurs during biotic U reduction, while during abiotic reduction, fractionation is either negligible or opposite in direction [2, 3].

However, in order to use U isotopes as a robust marker for biological processes, it is critical to understand the mechanistic processes of biotic and abiotic reduction with regard to U isotope fractionation. Here, we tackle reduction mediated (abiotically) by the Fe(II)-bearing mineral magnetite. From the limited data available [2], there appeared to be a dependence of the fractionation behavior on the uranium surface loading of the magnetite.

To test this hypothesis, we systematically investigated the effect of U(VI) loading on the rate of U reduction and the isotopic fractionation in a batch configuration. The reduction was monitored over time with inductively coupled plasma mass spectrometry (ICP-MS) to capture the reduction progress over time and isotopic fractionation was probed by multi-collector ICP-MS. Finally, the products in the solid phase were characterized with X-ray absorption spectroscopy. We observed that, at low U loadings, ^{235}U was preferentially reduced resulting in an isotope enrichment factor of 2.89 and 1.5 ‰. In contrast, at higher loadings, isotope fractionation was muted. Additionally, we confirmed the two-phase reduction kinetics previously observed. Independently from the loading, little to no fractionation occurs in the first phase of reduction, while the light isotope is preferentially reduced during the second phase (but only at low loading).

We also investigated the role of phosphate ligands on the reduction and isotopic fractionation of U. Previous work has shown that the product of uranium reduction by phosphate-reacted magnetite is not uraninite (as usually expected for abiotic reduction), but rather non-crystalline U(IV) [4].

[1] Weyer et al. (2008), *Geochimica and Cosmochimica Acta* 72, 345-359. [2] Stylo et al. (2015), *PNAS* 112, 5619–5624. [3] Basu et al. (2014), *Geochimica and Cosmochimica Acta* 136, 100-136. [4] Veeramani et al. (2001), *Geochimica and Cosmochimica Acta* 75, 2512-2528.