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

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The ratio of the two major uranium (U) isotopes, $^{238}U/^{235}U$, varies in near-surface environments depending on biogeochemical conditions [1]. Strong U isotope fractionation (with high $^{238}U/^{235}U$ in the product) occurs during enzymatic U reduction [2]. In contrast, during abiotic U reduction, U isotope fractionation is either negligible or is opposite in direction to that during enzymatic reduction. Thus, U isotope signatures were proposed as a tool to distinguish between abiotic and biotic processes in U(VI) reduction [3] and may be used to deconvolute the mechanism of U reduction leading to remediation in the subsurface.

Previous research has also shown that Fe(II)-bearing minerals exhibit two distinct fractionation behaviors [3]. An initial reduction phase during which no fractionation is observed, followed by a slower reduction phase during which the light isotope is preferentially reduced. This work further investigates the mechanism(s) responsible for this peculiar isotopic fingerprint.

We hypothesized that the availability of reactive Fe(II) surface sites controls the reduction rate, and potentially the isotopic fractionation behavior. In the cases in which there are excess Fe(II) surface sites, direct reduction of U(VI) to U(IV) can occur, resulting in no fractionation. However, when Fe(II) surface sites become limiting, the mineral may only reduce U(VI) to U(V). Subsequently, U(V) disproportionates to U(IV) and U(VI). Either the one-electron transfer or the disproportionation step (or both) may result in the isotopic fractionation observed.

To test this hypothesis, we assessed U(VI) reduction by magnetite at varying surface loadings in a batch configuration. The reduction progress was monitored by inductively coupled plasma mass spectrometry (ICP-MS) and isotopic fractionation probed by multi-collector ICP-MS. Further, we characterized the U products in the solid phase with XAS techniques to confirm the extent of reduction. Preliminary results support the two-phase reduction kinetics reported previously and isotopic data are pending.

[1] Weyer et al. (2008), *Geochimica et Cosmochimica Acta* **72**, 345-359. [2] Basu et al. (2014), *Geochimica et Cosmochimica Acta* **136**,*100-113*. [3] Stylo et al. (2015), **PNAS** accepted.