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Environmental stability of U(V) and its isotopic signature in magnetite

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Uranium (U) contamination in some subsurface environments is a legacy of mining and processing activities. Uranium isotopic signatures are frequently used to monitor efforts of U reduction and immobilization, however, the mechanistic details of associated isotope fractionation are yet poorly understood. Previous studies on the mechanism of U(VI) abiotic reduction by Fe(II)-bearing reducing agents, such as magnetite, sometimes implicated the formation of pentavalent U, U(V), incorporated in solid structures[1,2]. Related isotope fractionation of such a one-electron transfer reduction of U(VI) to U(V) species is yet unknown. Here, we present a co-precipitation study, in which U(VI) was reduced during the synthesis of magnetite[3]. Spectroscopic techniques, M_4 and L_3 HERFD-XANES both confirmed U(V) as the dominant species after reduction, with EXAFS supporting U(V) incorporation into magnetite as uranate(V). Adsorbed U(VI) on magnetite showed that the light isotope remained in unreduced U(VI) ($\delta^{238}U$ = -0.89±0.04‰), suggesting preferential reduction of heavy isotope to the reduced surface U(IV) species ($\delta^{238}U$ = 0.3-0.5‰). U remaining within the solid phase after removal of surface U(VI) and U(IV) consisted of 96% U(V) with a slightly light isotope signature ($\delta^{238}U$ = -0.11±0.02‰). When the coprecipitated U(VI)/U(V)/U(IV)-containing magnetite was either equilibrated with a solution containing heavy U(VI) ($\delta^{238}U$ = 5‰) or exposed to ambient conditions for re-oxidation, the isotope signature of incorporated U(V) remained stable, suggesting no isotope exchange between incorporated U(V) and surface/aqueous U(VI) species. Overall, the results appear to support the persistence of a stable light U(V) signature within magnetite in isolation from environmental conditions. This finding may have implications for the interpretation of either light or undetectable U isotope signatures in iron-rich rocks[4].

1. Ilton et al., (2010), 44, 170–176. 2. Huber et al., (2012), 96, 154–17. 3. Pidchenko et al., (2017), 51, 2217–2225. 4. Wang et al., (2018), 238, 438-452