Nanoscale mechanism of formation of UO_2 through uranium reduction by magnetite

ZEZHEN PAN[1], BARBORA BARTOVA[1], THOMAS LAGRANGE[1], KRISTINA O. KVASHNINA[2], SERGEI BUTORIN[3], NEIL HYATT[4], MARTIN STENNETT[4], RIZLAN BERNIER-LATMANI[1,*]

[1]Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland (* rizlan.bernier-latmani@epfl.ch); [2]Helmholtz Zentrum Dresden-Rossendorf, Dresden, Germany; [3]Uppsala University, Sweden; [4]University of Sheffield, UK

Uranium (U) is a ubiquitous element in the Earth's crust and can be found as a contaminant in the subsurface as a result of legacy ore mining and processing activities. Hexavalent U (U(VI)) can be immobilized through redox processes catalyzed by microorganisms and reduced minerals or chemical species. In anoxic subsurface environments, the mixed valence iron oxide, magnetite, is reported to form, for instance through biological reduction of ferrihydrite. Magnetite is well known to reduce U(VI) to tetravalent U (U(IV)) producing UO_2 [1]. Furthermore, the formation of an intermediate valence U species (U(V)) has been reported during the precipitation of magnetite in the presence of U(VI) [2] but has not been evidenced in the case of pre-formed magnetite reacting with U(VI).

Here, we tackle the mechanism of reduction of U(VI) by magnetite. We use a combination of scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and high energy resolution fluorescence-detected x-ray absorbance near-edge spectroscopy (HERFD-XANES) to probe the time-dependent transformation of U(VI) incubated with pre-formed magnetite. We observe that the reduction proceeds first through the the formation of surface-associated U(V), which persists until it is further reduced to form UO_2 nanocrystals. The nanocrystals assemble into nanowires that extend from the magnetite surface outward. Within the nanowires, these nanocrystals exhibit random orientations. Over time, through nanoparticle re-orientation and coalescence, the nanowires collapse into ordered UO_2 nanoclusters, resembling those previously reported for magnetite and U(VI) [3]. Overall, this work provides new insight into the molecular mechanism of formation of UO_2 and evidence for the growth of transient U nanowire structures.

[1] O'Loughlin *et al*. ES&T **44**, 1656–1661 (2010); [2] Pidchenko *et al.* ES&T **51**, 2217–2225 (2017); [3] Latta *et al*. ES&T **48**, 1683–1691 (2014).