Uranium(V) persists as uranium oxide nanowires during U(VI) reduction by magnetite

Zezhen Pan[1,*], Barbora Bártová[1,2], Thomas Lagrange[2], Sergei Butorin[3], Neil C. Hyatt[4], Martin C. Stennett[4], Kristina Kvashinina[5], Rizlan Bernier-Latmani[1]

[1] EML, École polytechnique fédérale de Lausanne, Lausanne, 1015, Switzerland (* zezhen.pan@epfl.ch)
[2] CIME, École polytechnique fédérale de Lausanne, Lausanne, 1015, Switzerland
[3] Uppsala University, 75236, Sweden
[4.] University of Sheffield, S10 2TN, UK
[5] European Synchrotron Radiation Facility, Grenoble, 38000, France

The mechanism of U(VI) reduction by magnetite has been studied extensively. However, the presence and the role of pentavalent U species in the reductive process are still unclear as some studies report uraninite(IV) on the surface[1,2] while others observed U(V) incorporated in iron oxide structures as the final products.[3,4] Additionally, little is known about the morphology of U species during the reduction process. Here, we probe the removal of aqueous U(VI) from solution by reductive precipitation onto the surface of preformed magnetite. Bulk measurement with spectroscopic techniques, M4- and L3-edge HERFD-XANES, both confirmed that U(VI) was slowly reduced to lower valence states over 4 weeks. M4-edge spectra reinforce the formation and persistence of U(V) as the dominant valence state over a long duration, which was not expected for reduction by preformed magnetite at neutral pH conditions. In parallel, nanoscale observation by STEM-imaging showed progressive formation of nanocrystals (1-2 nm diameter) on/near the surface of magnetite followed by the arrangement of the nanoparticles into nanowires. The nanowires persisted for weeks but eventually disappeared and only uraninite nanoclusters remained. The M5, M4 branching ratio obtained from EELS spectra on nanowires enables the spatially-resolved determination of U valence states at the nanoscale and further suggests that U(V) is associated with the nanowires. Our study demonstrated the presence and persistence of U(V) in nanowires comprised of nanoparticles, which can significantly affect U reactivity, stability and bioavailability in environments with slow reduction processes.

1. Latta et al., (2012), 46, 778−786. 2. Latta et al., (2014), 48, 1683−1691. 3. Ilton et al., (2010), 44, 170–176. 4. Huber et al., (2012), 96, 154–17.