

Uranium reduction by magnetite – mechanism of UO_2 formation monitored by STEM, SAED and EELS

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Uranium (U) is a ubiquitous element in the Earth's crust, having a concentration of about 2 ppm. Soluble hexavalent uranium (U(VI)) is reduced and immobilized in anoxic environments. The underlying reduction mechanism is unknown but is likely of critical importance to explain variability in U biogeochemical behaviors. In this study, we focused on the mechanism of reduction of U(VI) by the mixed-valence iron oxide magnetite [1]. Reduction proceeds first through surface-associated U(VI) to form pentavalent U, U(V) [2]. U(V) persists on the surface of magnetite, being reduced to tetravalent UO_2 and forming small clusters (~1-2 nm) inside the nanowires. The nanowires collapse into ordered UO_2 nanoclusters through re-orientation and coalescence of nanoparticles, resembling previous reports for magnetite and U(VI) [3]. This work provides evidence for a transient U nanowire structure that may have implications for uranium isotope fractionation and a molecular-scale understanding of nuclear waste temporal evolution and the reductive remediation of uranium contamination.

Images of U-magnetite samples monitor the structure development during the reduction process, see Fig.1. After 4-hours of reduction, only uranium atoms (bright, contrasted spots) are observed on magnetite surfaces. Whereas the 12-hour sample shows near-surface U nanoparticle formation, the 24-hour samples prevalently contain a small fraction of nanowires formed by individual nanoparticles of well-defined orientations. The 72-hours sample structure contains multiplied and longer nanowires of UO_2 in which we observe the presence of nanoclusters and the initial transition of this morphology. The 5-day sample comprises more nanoclusters; however, some nanowires that did not collapse are still present. Finally, after 4 weeks, only nanoclusters formed by larger nanoparticles are observed.

We performed spatially resolved TEM EELS measurements of the U valence state in the various U-magnetite samples. With a 200 nm parallel probe, we measured the integral intensity of the M_4 and M_5 edges for uranium and calculated the ratio of their edge intensities-the branching ratio- which varies according to the valence, see Fig.2 [4, 5]. We used uranium oxide standards of known valence to calibrate the branching ratio and determine the influence of the electron dose. Electron beam-induced reduction was significantly suppressed at liquid nitrogen temperatures. We observed a decreasing trend of branching ratios for the set of standards, uraninite for U(IV), UMoO_5 for U(V), and UO_3 for U(VI), from 0.6960 ± 0.0046 , 0.6860 ± 0.0063 to 0.6622 ± 0.0093 , providing a reliable reference data to resolve U

valence states. We also performed TEM EELS measurements to atomically resolve the different U valence species within the nanoparticles that comprise nanowires using MLLS fitting and how U valence states temporally evolve in the redox reaction. These findings reported here of the transient valence state and nanowire structure significantly improve our understanding of molecular-scale mechanisms during U(VI)-magnetite interactions and advance our interpretation of the environmental behavior of U species.

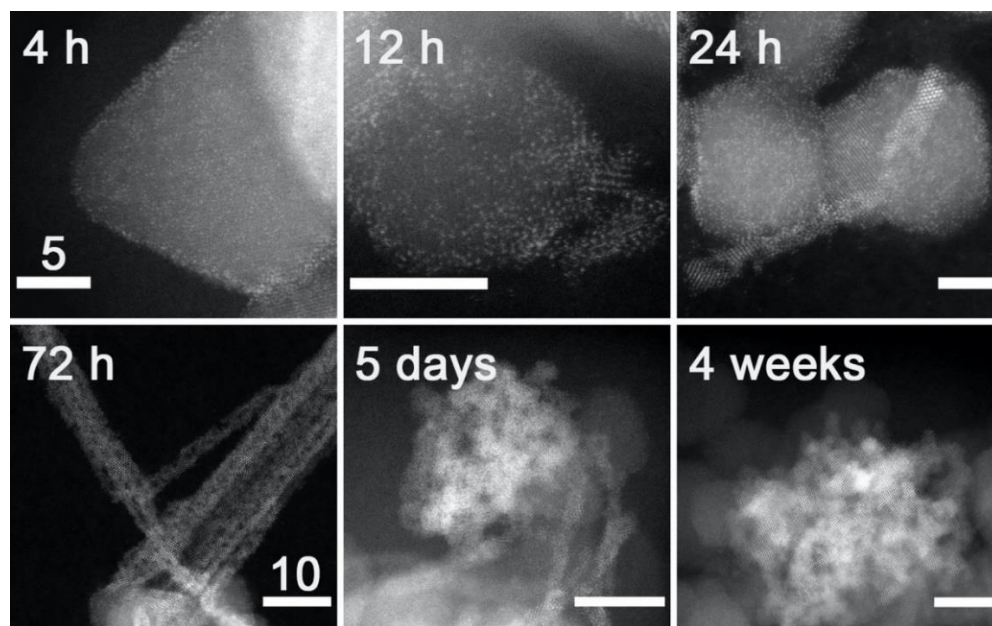


Figure.1: HAADF-STEM images show the structure evolution during the reduction process. Scale bar in nm.

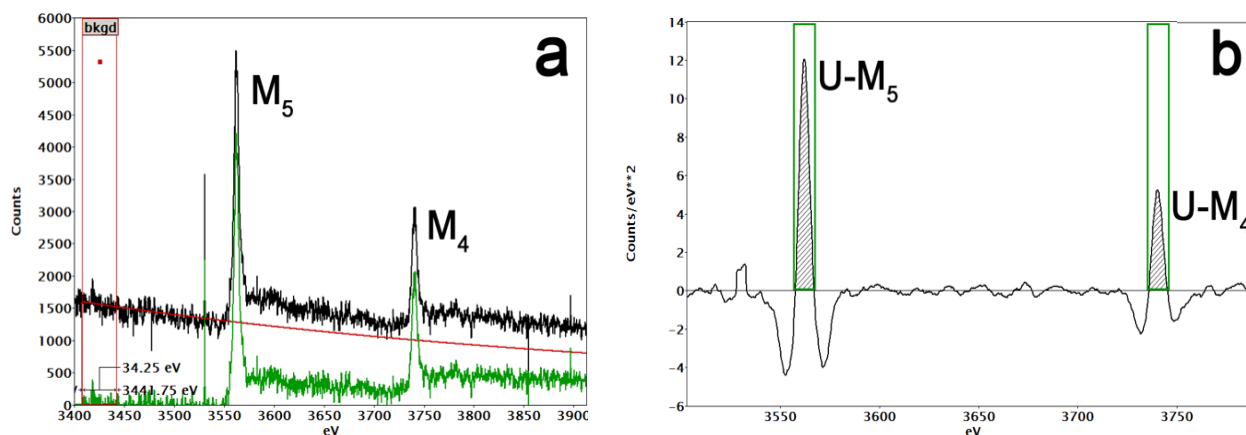


Fig.2: Illustration of EELS spectra analysis. (a) a background-subtracted spectrum (green) compared to the original spectrum (in black); (b) the second derivative of the signal spectrum in (b) and two windows (in green) over the peaks from which the integrated signal was obtained.

References

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