

# Uranium reduction by magnetite: mechanism of UO<sub>2</sub> formation from EELS analysis and density functional theory computations

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Uranium (U) is ubiquitous with an estimated average concentration of 2.7 ppm in the Earth's crust. In anoxic environments, the reduction of hexavalent uranium (U(VI)) to tetravalent U(IV) species results in its immobilisation through a decrease in aqueous solubility. The details of the underlying reduction mechanism remain unknown but of critical importance to explain variability in U biogeochemical behaviors. In this study, we focused on U(VI) reduction by the mixed valence iron oxide magnetite (Fe<sub>3</sub>O<sub>4</sub>). The reduction ultimately yields crystalline uranium as U(IV)O<sub>2</sub>. Investigations of the mechanism of reduction revealed the emergence of uranium oxide nanocrystals (1-5 nm), followed by their self-assembly into nanowires extending away from the magnetite surface [1]. We suggest a reduction pathway that is initiated by U(VI) adsorption to the magnetite surface which subsequently forms pentavalent U(V). U(V) persists in UO<sub>2+x</sub> nanoparticles that self-assemble into nanowires. As reduction continues over time, the nanowires collapse, and uranium is fully reduced to tetravalent UO<sub>2</sub> nanocrystals. However, direct evidence for the formation and persistence of U(V) is lacking. Using electron energy loss spectroscopy (EELS), we analyzed O K-edge and U N-edge spectra of individual uranium oxide nanoparticles within nanowires. This approach allows for the precise spatial characterisation of the valence state of uranium by comparing the fine structures of nanoparticle-derived spectra with spectra from reference mixed valence oxides under identical conditions. However, accurate validation of reference EELS spectra for variable valence uranium oxides requires computational support. We've employed first-principles calculations to simulate the electronic structure and spectral characteristics of six uranium oxide phases with high accuracy, i.e., the single valence compounds U(IV)O<sub>2</sub>, KU(V)O<sub>3</sub>, BaU(VI)O<sub>4</sub> and the mixed valence compounds U<sub>4</sub>O<sub>9</sub>, U<sub>3</sub>O<sub>7</sub>, U<sub>3</sub>O<sub>8</sub>. By integrating computational models with experimental data, we aim to build a robust uranium oxide EELS dataset that allows the investigation

of uranium redox transformations at the nanoscale.

[1] Z. Pan et al., "Nanoscale mechanism of UO<sub>2</sub> formation through uranium reduction by magnetite." *Nature Communications* **11**, 1(2020) 4001, <https://doi.org/10.1038/s41467-020-17795-0>