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Formation of mixed-valence uranium oxide nanowires during magnetite-mediated reduction

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Uranium (U) biogeochemistry is largely constrained by its redox transformation from soluble hexavalent species (U(VI)) to sparingly soluble tetravalent species (U(IV)). U(VI) reduction by ferrous iron-bearing minerals has been shown to produce crystalline U(IV) in the form of UO_2. There is increasing evidence for the persistence of intermediate pentavalent U (U(V)) during the reduction of U(VI) to U(IV). Indeed, previous work has demonstrated the presence of U(V) in the bulk system during the reduction of U(VI) by preformed magnetite. Additionally, we reported the formation of single U oxide nanocrystals (1-5 nm) followed by their assembly into nanowires that extended from the magnetite surface outward during this process [1]. Over time, the nanowires collapsed into ordered UO_2 nanoclusters. Despite efforts to investigate the spatial localization of U(V) in the above system using U $M_{4,5}$ edge TEM-EELS (transmission electron microscopy-electron energy loss spectroscopy), beam induced reduction precluded accurate measurement of the U valence state within the nanowires.

Current work has focused on mapping the U valence state at the nanoscale. We acquired O K-edge and U $N_{6,7}$-edges spectra from individual nanoparticles within the nanowires and compared the observed features to those from single valence (i.e., UO_2, KUO_3, $BaUO_4$) and mixed-valence (U_4O_9, U_3O_7, U_3O_8) uranium compounds, with the aim to characterize the valence state of the nanocrystals. We found that nanocrystals within nanowires consist of U(IV/V)-bearing phases, mainly U_4O_9 (50% U(IV), 50%U(V)) and U_3O_7 (33% U(IV), 66%U(V)), pointing to the persistence of U(V) in the nanowires (**Figure 1**). In contrast, the nanoclusters (collapsed nanowires) include only UO_2 (U(IV)). This work is the first step in unraveling the mechanistic details of U oxide reduction by magnetite and may shed light on the reduction of other multivalent metals that produce oxides. It also demonstrates the potential of EELS to investigate environmental nanoscale redox processes.

[1] Pan et al., *Nat Commun* **11,** 4001 (2020)

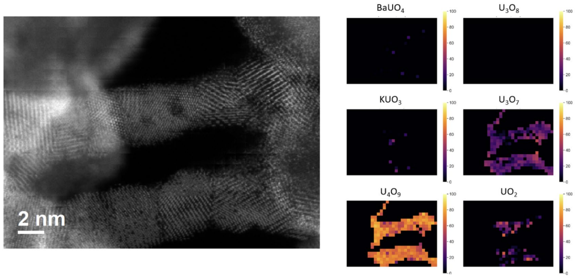

Fig. 1: False-color images showing the fit of the spectrum image data (left) obtained at the O K-edge and U $N_{6,7}$ edges to those of uranium standards.