

## Nanoscale mechanism of uranium reduction by magnetite

BARBORA BARTOVA<sup>1</sup>, ZEZHEN PAN<sup>2</sup>, THOMAS LAGRANGE<sup>1</sup>, QINGYIN XIA<sup>1,3</sup>, NICOLAS GAUQUELIN<sup>4</sup>, AMIR H TAVABI<sup>5</sup>, JOHAN VERBEECK<sup>4</sup>, RAFAL E DUNIN-BORKOWSKI<sup>5</sup> AND RIZLAN BERNIER-LATMANI<sup>1</sup>

<sup>1</sup>Ecole Polytechnique Fédérale de Lausanne (EPFL)

<sup>2</sup>Fudan University

<sup>3</sup>China University of Geosciences (Beijing)

<sup>4</sup>University of Antwerp

<sup>5</sup>Forschungszentrum Jülich

Presenting Author: rizlan.bernier-latmani@epfl.ch

Uranium (U) is a ubiquitous element in the Earth's crust and its biogeochemical behavior is largely constrained by its redox transformation from soluble uranium hexavalent species (U(VI)) to sparingly soluble tetravalent species (U(IV)). U(VI) reduction by mineral phases has been shown to produce crystalline U in the form of U(IV)O<sub>2</sub>, but also to form persistent pentavalent U (U(V)). Magnetite (Fe<sub>3</sub>O<sub>4</sub>) is an Fe(II)-bearing iron oxide and experimental studies have shown that the co-precipitation of U(VI) and magnetite resulted in the formation of a stable U(V) coordination in the iron oxide mineral phases [1].

A study [2] reported the formation of single U oxide nanocrystals (1-5 nm) followed by the formation of nanowires that extended away the magnetite surface (Figure 1). Over time, the nanowires collapsed into ordered UO<sub>2</sub> nanoclusters. U(IV) was suggested as the dominant valence state in the nanowires. However, due to the sensitivity of U(V) under the beam, reduction of U(V) species may occur, and the presence of mixed valence states may be overlooked. Besides the beam sensitivity issue, robustly discriminating between UO<sub>2</sub> and UO<sub>2+x</sub> (0 < x < 1), representing mixed valence uranium oxides such as U<sub>3</sub>O<sub>8</sub>, is challenging.

Here, we present O K-edge and U N-edge electron energy loss spectroscopy spectra from individual uranium oxide nanoparticles within the nanowires in order to characterize the valence state of individual nanocrystals by comparing their fine structure to references mixed oxides measured in the same conditions.

The mechanism that emerges at the scale of individual nanoparticles (1-5 nm) is the initial reduction of U(VI) to U(V) at the magnetite surface, producing mixed valence oxides UO<sub>2+x</sub> that self-assemble into nanowires. These nanowires are stable as long as no further reduction occurs but reduction to UO<sub>2</sub> results in the collapse of nanowires into nanoclusters.

The reduction of U(VI) by magnetite represents an example of heterogeneous reductive precipitation that, due to the properties of uranium, can be resolved at the near atomic scale and reveal the complexity of electron transfer from mineral to metal.

[1] Pidchenko et al. *Environ. Sci. Technol.*, **51**, 2217–2225 (2017).

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

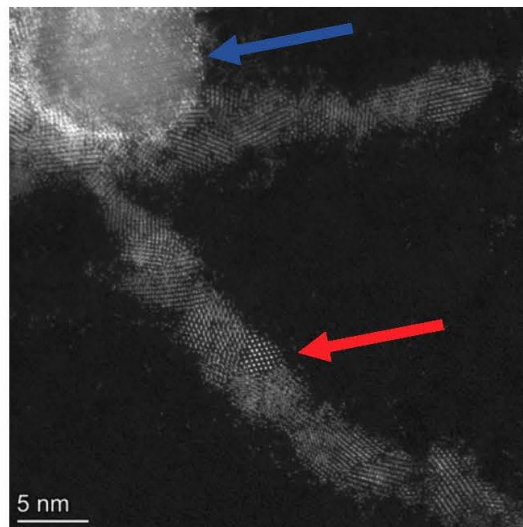


Fig. 1: Magnetite particle (blue arrow) with UO<sub>2+x</sub> nanoparticles self-assembled into nanowires (red arrow).