Molecular- and nano-scale structure and reactivity of biogenic Uranium(IV) oxide

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Bioremediation has been proposed and extensively researched as an *in situ* immobilization strategy for uranium contamination in the subsurface with nanoparticulate uraninite (UO_2) being the commonly reported product. Little detail is known about the structure and reactivity of this material, but based on comparison to its closest abiotic analog, UO_{2+x} ($0 < x < 0.25$), we expect that it is complex and disordered. In addition, it has been predicted that the nanoparticulate form would induce strain and dramatically increase the solubility.

In this study, the local-, intermediate and long-range atomic and nano-scale structure of biogenic UO_2 (formed at varying pH using *Shewanella oneidensis* strain MR-1) was characterized using EXAFS, SR-based powder diffraction and TEM. The lattice parameter of the nanoparticulate phase is seen to be consistent with bulk UO_2. There is no evidence for hyperstoichiometry or strain of the particles, the latter indicating that surface energy is relatively modest. In agreement with this structural analysis, the surface-area normalized dissolution rate of the biogenic UO_2 was found to be comparable to that of coarser, synthetic $UO_{2.00}$.

Chemical and valence state imaging of mineral intergrowths using X-ray photo-emission electron microscopy

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Valence state ratios of the first row transition metals can be used as a measure of the redox conditions of geological, planetary and environmental processes. Additionally, the textural relationships between minerals provides a record of the formation history, stability and alteration events of natural materials. By measuring and imaging the crystal chemistry of multivalent elements in minerals, whilst maintaining the spatial integrity of the mineral microstructure, a detailed understanding of the complex processes involved with the formation of natural materials can be developed.

X-ray Photo-Emission Electron Microscopy (XPEEM) has the capability to provide precisely this sort of information. With an area selectivity ranging from the nanometer scale up to several hundreds of microns, quantitative valence state images can be obtained, nondestructively, from the same material prepared for electron microscopy. To demonstrate the efficacy of the technique and its application we used XPEEM to study mineral intergrowths such as weathered magnetite [1], Mn-hollandite hydrothermal veins [2], oxidised magnesiowustite (Fig. 1) and polygenetic Co-Cu-Fe sulphide microtextures.

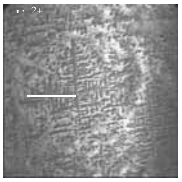

Figure 1: Valence-state images of magnetite exsolution in magnesiowustite. Scale bar is 10 µm.

More detailed XPEEM studies [3] have been performed on oceanic materials such as metal sulphide precipitates exhumed from hydrothermal vents present at mid-ocean ridges and Mn nodules from the Madeira Abyssal Plain in the Atlantic Ocean. The speciation of oxygen has been investigated in the Santa Catharina meteorite and studies of chromite grains in Martian basalts may provide information relating to the evolution of magma chambers on Mars.

[1] Smith *et al.* (1998) *J Sync Rad* **5**, 1108-1110. [2] Smith *et al.* (2004) *Mineral Mag* **68**, 859-869. [3] Smith *et al.* (2003) *J. de Phys IV* **104**, 373-376.