

Modeling UO₂ bioprecipitation and reoxidation by Fe(III) (hydr)oxides

N. SPYCHER¹, M. ISSARANGKUN², B. STEWART⁴,
S. SENGOR², T. GINN², R. SANI³ AND B. PEYTON⁴

¹Lawrence Berkeley National Laboratory, Berkeley, CA
94720 (nspycher@lbl.gov)

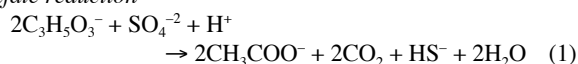
²University of California at Davis, Davis, CA 95616

³SD School of Mines and Technology, Rapid City, SD 57701

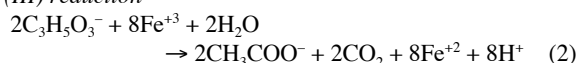
⁴Montana State University, Bozeman, MT 59717

UO₂ reoxidation may impede cleanup efforts where U(VI)-contaminated groundwater is remediated using organic electron donors to reduce U(VI) and precipitate UO₂. We focus here on previously published experiments in which biogenic UO₂ was precipitated using sulfate-reducing bacteria under lactate-limited conditions in the presence of Fe(III) (hydr)oxides. Upon elimination of lactate it was observed that UO₂ reoxidized. The modeling objective is to evaluate kinetic and thermodynamic constraints at play in these experiments. The following basic reaction network is applied, coupled with the dissolution and precipitation of solid Fe and U phases:

Sulfate reduction



Fe (III) reduction



U (VI) reduction



HS⁻ oxidation by Fe (III)



U (IV) oxidation by Fe (III)



The sulfate and initial iron reduction (1 and 2) is microbially-mediated, and modeled using a dual-Monod rate law with biomass growth. U(VI) reduction (3) is tested using both abiotic (unlimited) and biotic (lactate-limited) rates. The oxidation of U(IV) and HS⁻ by Fe(III) (4 and 5) is considered abiotic with reversible rates. In our case, UO₂ reoxidizes only when reaction (3) is set to be lactate-limited. Model results and additional thermodynamic analyses show oxidation of HS⁻ by Fe(III) directly competing with UO₂ oxidation. Thus, the relative rates of these reactions, and the relative mobility of species involved, control the extent of UO₂ reoxidation. As Fe(II) is produced by reaction (4) and causes the thermodynamic limit of reaction (5) to be reached before that of (4), UO₂ reoxidizes to a lesser extent and eventually reprecipitates (reversing 5). Reoxidation is also sensitive to the effect of Fe(II) minerals precipitation on Fe(II) activity.

Nanocrystalline SnO₂ at Earth's mantle pressures up to 9 GPa

B. SREEDHAR¹ AND G. PARTHASARATHY²

¹Indian Institute of Chemical Technology (CSIR), Hyderabad-500607 India (sreedharb@iict.res.in)

²National Geophysical Research Institute (CSIR), Hyderabad-500 606, India (gpngri@rediffmail.com)

In a recent study, Kvasnytsya and Wirth [1] have reported occurrences of nano-inclusions of Sn-oxides in the Precambrian Samotkan lherzolitic microdiamonds. However, the origin and stability of nano-crystalline SnO₂ at mantle pressures are not yet understood properly. Earlier report on high-pressure studies of the electrical resistivity of nano-crystalline SnO₂ showed a phase transition at about 2.4 GPa for 5 nm grain size and decreases to 1.5 GPa for 9 nm grain size of SnO₂ [2]. On the contrary the high-pressure X-ray diffraction studies by He *et al.* [3] showed that the Nano-crystalline SnO₂ is stable up to 23 GPa, where it undergoes a pressure induced rutile-to-cubic phase transition. The transition pressures were 29 GPa for 14 nm crystallite size and 30 GPa for 8 nm crystallite size. The 3nm SnO₂ is stable up to 40 GPa. [3]. High-pressure studies on nanocrystalline SnO₂ are very important in understanding their presence in the diamonds. In view of these contrasting observations, we studied the electrical resistivity of synthetic nano-crystalline Co-doped SnO₂ with different crystallite size of 15nm, 24 nm, 32 nm, 40 nm and pure SnO₂ with 46 nm up to 9 GPa at room temperature. In order to decrease the transition pressure cobalt was added up to 0.05 %. Details of the sample preparation and characterization and the high-pressure set up have been discussed elsewhere [4, 5]. We have found that the samples of nano-crystalline SnO₂ as well as Co-doped SnO₂ (0.05%) are stable up to 9 GPa and the compressibility of the samples increases with the decrease of the crystallite size.

[1] Kvasnytsya & Wirth (2009) *Lithos* **113**, 454.

[2] Thangadurai *et al.* (2005) *J. Phys. Chem. Sol* **66**, 1621.

[3] He Y *et al.* (2005) *Phys. Rev. B* **72**, 212102. [4] Srinivas *et al.* (2009) *J.Phys.Chem.C* **113**, 3543. [5] Parthasarathy (2006)

J. Applied Geophys. **58**, 321.