Modeling UO_2 bioprecipitation and reoxidation by Fe(III) (hydr)oxides

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UO_2 reoxidation may impede cleanup efforts where U(VI)-contaminated groundwater is remediated using organic electron donors to reduce U(VI) and precipitate UO_2. We focus here on previously published experiments in which biogenic UO_2 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 UO_2 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

$$2C_3H_5O_3^- + SO_4^{-2} + H^+ \rightarrow 2CH_3COO^- + 2CO_2 + HS^- + 2H_2O \quad (1)$$

Fe (III) reduction

$$2C_3H_5O_3^- + 8Fe^{+3} + 2H_2O \rightarrow 2CH_3COO^- + 2CO_2 + 8Fe^{+2} + 8H^+ \quad (2)$$

U (VI) reduction

$$4UO_2^{+2} + HS^- + 7\,H^+ \rightarrow 4U^{+4} + SO_4^{-2} + 4H_2O \quad (3)$$

HS^- oxidation by Fe (III)

$$HS^- + 8Fe^{+3} + 4H_2O \rightarrow SO_4^{-2} + 8Fe^{+2} + 9H^+ \quad (4)$$

U (IV) oxidation by Fe (III)

$$U^{+4} + 2Fe^{+3} + 2H_2O \rightarrow UO_2^{+2} + 2Fe^{+2} + 4H^+ \quad (5)$$

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, UO_2 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 UO_2 oxidation. Thus, the relative rates of these reactions, and the relative mobility of species involved, control the extent of UO_2 reoxidation. As Fe(II) is produced by reaction (4) and causes the thermodynamic limit of reaction (5) to be reached before that of (4), UO_2 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 SnO_2 at Earth's mantle pressures up to 9 GPa

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In a recent study, Kvasnytsya and Wirth [1] have reproted occurrences of nanoinclusions of Sn-oxides in the Precambrian Samotkan lherzolitic microdiamonds. However, the origin and stability of nano-crystalline SnO_2 at mantle pressures are not yet understood properly. Earlier report on high-presure studies of the electrical resistivity of nano-crystalline SnO_2 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 SnO_2 [2]. On the contrary the high-pressure X-ray diffraction studies by He *et al.* [3] showed that the Nano-crystalline SnO_2 is stable up to 23 GPa, where it undergoes a pressure induced rutile-to- cubic phase tarnsition. The transition pressures were 29 GPa for 14 nm crystallie size and 30 GPa for 8 nm crystllite size. The 3nm SnO_2 is stable up to 40 GPa. [3]. High-pressure studies on nanocrystalline SnO_2 are very important in understanding their presence in the diamonds. In view of these contrasting observations, we stduied the elctrical resistivity of synthetic nano-crystalline Co-doped SnO_2 with different crystallite size of 15nm, 24 nm, 32 nm, 40 nm and pure SnO_2 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 smaple preperation and characterization and the high-pressure set up have been discussed elsewhere [4, 5]. We have found that the the samples of nano-crystalline SnO_2 as well as Co-doped SnO_2 (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.