

## Surface complexation of Uranium(VI) on Fe/Mn (hydr)oxides

DAVID M. SHERMAN<sup>1</sup>, CAROLINE L. PEACOCK<sup>1,2</sup> AND CHRIS G. HUBBARD<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, University of Bristol, Bristol BS8 1RJ, UK (dave.sherman@bris.ac.uk)

<sup>2</sup>Present Address: School of Ocean and Earth Science, University of Southampton, Southampton SO14 3ZH, UK

The fate and mobility of U in oxic soils, groundwater and the marine environment is controlled by sorption of  $\text{UO}_2^{++}$  onto nanocrystalline iron and manganese (hydr)oxides. Thermodynamic models for such reactions are needed before we can understand the aqueous geochemistry of U. However, we cannot develop useful thermodynamic models until we have a molecular-level understanding of U sorption and complexation. Previous EXAFS studies of  $\text{UO}_2^{++}$  sorption on FeOOH have been interpreted as indicating an inner-sphere  $>\text{Fe}(\text{OH})_2\text{UO}_2$  surface complex formed by edge sharing with  $\text{FeO}_6$  polyhedra (<sup>2</sup>E complex). However, this complex is at odds with the known surface site densities of FeOOH phases. On goethite, for example, <sup>2</sup>E complexes can only occur on the {210} and {010} planes (space group setting Pnma) which comprise only a small fraction of the surface area. Here, we show that previous EXAFS spectra have been misinterpreted owing to the neglect or incomplete inclusion of multiple scattering. The dominant  $\text{UO}_2^{++}$  surface complex on FeOOH is  $(>\text{FeOH})_2\text{UO}_2(\text{H}_2\text{O},\text{OH})_3$  and  $(>\text{FeOH})_2\text{UO}_2\text{CO}_3$  (<sup>2</sup>C complex) resulting from bidentate corner-sharing with two adjacent  $\text{FeO}_6$  surface polyhedra. Ab initio calculations of U-O and U-Fe distances in the (<sup>2</sup>C) complexes are consistent with the EXAFS results. On goethite, <sup>2</sup>C complexes can form on the {101} planes which comprise nearly all of the reactive surface area; the 2C complex explains the high sorption capacity (>2 wt%) for U(VI) on goethite and, apparently, ferrihydrite.

We developed a surface complexation model to fit a series of sorption experiments of U on goethite and ferrihydrite. Using a 1pK formalism and Basic Stern model for electrostatics, we found we could fit our data using  $(>\text{FeOH})_2\text{UO}_2(\text{OH})$  and  $(>\text{FeOH})_2\text{UO}_2\text{CO}_3$  (<sup>2</sup>C) complexes, consistent with EXAFS results. An analogous model for U sorption onto hexagonal birnessite was developed using the  $(>\text{MnO})_3\text{UO}_2\text{OH}$  and  $(>\text{MnO})_3\text{UO}_2\text{CO}_3$  complexes assuming that  $\text{UO}_2^{++}$  complexes over vacancies in the phyllosomanganate layer. Implications of our models for the fate of U(VI) in soils and aquatic environments will be discussed.

## The Os isotope heterogeneities in the mantle sequence of the Bangong Lake ophiolite, northwestern Tibet

R.D. SHI, X.C. ZHI, B.H. DING AND L. CHEN

CAS Key Lab. of C-M Materials and Environments, School of Earth and Space Sciences, USTC, Hefei 230026, China

Two type harzburgites occur in mantle sequence of the Bangong Lake ophiolite, NW Tibet. Type I is Cpx-bearing harzburgite with  $\text{Cr}^\# = 20\sim 25$  of spinel reflecting 10~15% degrees of partial melting; Type II is Cpx-free harzburgite with  $\text{Cr}^\# = 69\sim 73$  of spinel representing 35~40% degrees of partial melting formed in the suprasubduction zone (SSZ) [1]. In Type I, the  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.12446 to 0.12853) are chondritic and the  $^{187}\text{Re}/^{188}\text{Os}$  ratios (0.44 to 1.77) are suprachondritic reflecting that Re gain recently by basaltic melt percolating during the formation of the Bangong Lake crust 167 Ma ago [2], while in Type II, part of  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.12166 to 0.12896) are subchondritic, this can be explained by Re depletion during ancient partial melting. The old Os isotope model age (>950 Ma) of one Cpx-free harzburgite in a young ophiolitic mantle show that ancient Os isotopic heterogeneities can survive in the Earth upper mantle.

Osmium concentrations tend to decrease from Type I (Cpx-bearing harzburgites, 5.25-5.45ppb) to Type II (Cpx-free harzburgites, 4.4-4.45ppb, one sample is 1.32ppb) indicating that Os does not behave compatibly during melt percolation as it is observed during partial melting, but becomes dissolved and mobilized by the percolating melt [3]. But the heavy serpentinization likely caused the Os loss by the sulphide decomposition in a SSZ environment with high  $f\text{O}_2$ .

This study shows that Type I and II harzburgites of the Bangong Lake ophiolitic mantle have complex and different evolution. However, the Os isotopic features are consistent with a model where the two type harzburgites belong to the same melting regime producing the Bangong Lake oceanic crust. This scenario is also observed early in Troodos ophiolite [3].

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### References

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