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

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The fate and mobility of U in oxic soils, groundwater and the marine environment is controlled by sorption of UO2++ 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 UO2++ sorption on FeOOH have been interpreted as indicating an inner-sphere >Fe(OH)2UO2 surface complex formed by edge sharing with FeO6 polyhedra (2E complex). However, this complex is at odds with the known surface site densities of FeOOH phases. On goethite, for example, 2E 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 UO2++ surface complex on FeOOH is (>FeOH)2UO2(OH)3 and (>FeOH)2UO2CO3 (2C complex) resulting from bidentate corner-sharing with two adjacent FeO6 surface polyhedra. Ab initio calculations of U-O and U-Fe distances in the (2C) complexes are consistent with the EXAFS results. On goethite, 2C 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 (>FeOH)2UO2(OH) and (>FeOH)2UO2CO3 (2C complexes) consistent with EXAFS results. An analogous model for U sorption onto hexagonal birnessite was developed using the (>MnO)3UO2OH and (>MnO3)2UO2CO3 complexes assuming that UO2++ complexes over vacancies in the phyllomanganate 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

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Two type harzburgites occur in mantle sequence of the Bangong Lake ophiolite, NW Tibet. Type I is Cpx-bearing harzburgite with Cr# = 20~25 of spinel reflecting 10~15% degrees of partial melting; Type II is Cpx-free harzburgite with Cr# = 69~73 of spinel representing 35~40% degrees of partial melting formed in the suprasubduction zone (SSZ) [1]. In Type I, the 187Os/188Os ratios (0.12446 to 0.12853) are chondritic and the 187Re/188Os 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 187Os/188Os 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 ophiolite 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 serpentinitization likely caused the Os loss by the sulphide decomposition in a SSZ environment with high fO2.

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