Uranium(IV) oxide surface reactivity

K.-U. ULRICH[1], A. SINGH[1], S.F. DIXON[1], E. SCHOFIELD[2],
J.R. BARGAR[2] AND D.E. GIAMMAR[1]

[1] Dept. of Energy, Environmental & Chemical Engineering,
Washington University, St. Louis, USA
(k.ulrich@seas.wustl.edu; giammar@wustl.edu)
[2] Stanford Synchrotron Radiation Laboratory, Menlo Park,
USA (bargar@slac.stanford.edu)

The success of bioremediation of uranium-contaminated sites will depend on the long-term stability of the U(IV) oxide formed by microbially induced reduction of soluble U(VI). This contribution is part of a research project establishing the local and long-range structure and reactivity of biogenic uraninite generated under different environmental conditions in comparison to its closest abiotic analog, UO_{2+x} ($0 < x < 0.25$). An abiotic uraninite solid was produced by thermal reduction of uranium peroxide with $H_{2(g)}$, yielding particles with a star-like prism shape and a size of ~700 nm. Powder XRD proved an fcc crystal lattice of cubic uraninite. Its stoichiometry was identical to that of a reference sample of $UO_{2.0}$, as shown by EXAFS spectroscopy.

The dissolution kinetics of abiotic uraninite have been examined in batch and flow-through experiments as a function of pH, dissolved inorganic carbon, and dissolved oxygen. Dissolution rate constants are calculated from a mass balance approach, accounting for equilibrium solubility and the decrease of particle size as dissolution progresses. Batch dissolution experiments under anoxic conditions have shown dissolved uranium concentrations close to or even higher than predicted from published thermodynamic data. In the range of pH 6 to 9, dissolution rate constants were on the order of $1.3\text{-}3.1 \cdot 10^{-13}$ mol m^{-2} s^{-1}, but they increased by two orders of magnitude under atmospheric conditions. Under anoxic conditions, a flow-through experiment has shown an initial U-release peak, suggesting removal of more soluble U phases from the surface. However, carbonate as a complexing agent for U(VI) did not immediately change the dissolution kinetics of abiotic uraninite, but gradually altered its surface toward higher solubility, which was a reversible reaction.

Dissolved U(VI) showed high affinity for abiotic uraninite. Further experiments will quantify the adsorption/desorption reactions and test the effects of other divalent cations such as manganese, calcium, and magnesium. Among factors such as formation conditions, structural properties, and adsorption/desorption behavior, the surface reactivity and dissolution kinetics of uranium oxide are the most important factors for promoting immobilization and long-term stability in the subsurface.

Nd isotope mixing during thermal ionisation mass spectrometry: Implications for accurate ^{142}Nd measurements

D. UPADHYAY, E.E. SCHERER AND K. MEZGER

Zentrallabor für Geochronologie, Institut für Mineralogie,
Univ. Münster, Corrensstr. 24, 48149 Münster, Germany

Deviations from the exponential-law mass-bias curve are observed during some high-precision runs of the La Jolla Nd standard. The resulting measured isotope ratios (X/144) are generally higher than predicted by the exponential law (Fig. 1) and characterized by increased scatter. The onset of the deviations correlates with a distinct change in the mass-bias trajectory (from normal to reverse) of the isotope ratios.

Similar effects during Ca isotope measurements [1] were attributed to isotope mixing during mass spectrometry. For Nd isotopes, the effects of mixing during measurements are not clearly understood even though several studies have documented an apparent breakdown of the exponential mass-bias law [e.g., 2 and 3].

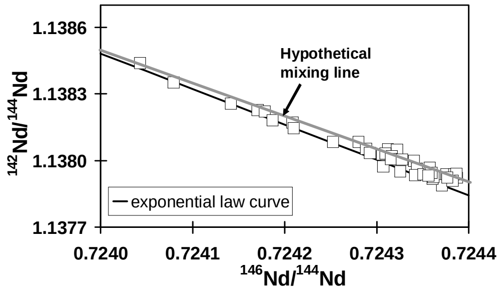

Figure 1: Deviations of the isotope ratios from the exponential curve during a run segment modeled as mixtures of ions from differentially fractionated sample reservoirs

This study shows that the divergence from exponential-law can be modeled as mixtures among reservoirs on the theoretical fractionation curve (Fig. 1). Such differentially fractionated reservoirs can form because of temperature gradients or heterogeneous sample distribution on the filament. Mixing of ions derived from these reservoirs can modify the composition of the ion beams significantly causing deviations from the exponential-law curve. Mixing results in an apparent reversal of mass fractionation because isotopically light ions from less fractionated reservoirs are ionized together with those from more fractionated ones.

Such mixing during mass spectrometry is a great concern when measuring the generally very small ^{142}Nd anomalies because deviations up to 56 ppm have been observed for the ^{142}Nd/^{144}Nd ratios. This deviation is far greater than the variations expected for most applications. The ultimate accuracy and reproducibility of the isotope ratios is dictated by the extent of isotope fractionation and mixing in addition to instrument electronics and ion counting statistics.

[1] Hart and Zindler (1989), *IJMSIP* **89**, 287-301
[2] Caro *et al.* (2003), *Nature* **423**, 428-432
[3] Sharma and Chen (2004), *Prec. Res.* **135**, 315-329.