Quantitative Model for Abiotic Uranium Isotope Fractionation

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The (bio)reduction-oxidation of uranium (U) and the associated changes in solubility are important for many areas of Earth sciences including sedimentary U ore deposits, groundwater remediation, and studies of redox conditions from Earth's sedimentary record. In the last decade observations of natural variations in the U isotope ratio $^{238}U/^{235}U$ have been linked to U reduction, making it a promising tool to quantify this process. One vexing issue in interpreting the observed $^{238}U/^{235}U$ variations is the discrepancy between theoretical predictions of isotope fractionation and both laboratory and field observations. Published data from circumneutral pH lab experiments or field samples are not consistent with the Nuclear Field Shift theory predictions (NFS; equilbrium fractionation >1.001). In our view, in order to use variations of $^{238}U/^{235}U$ to quantify U reduction, a better understanding is needed of the causes of observed variations in $^{238}U/^{235}U$ fractionation.

We combine recently published experimental data and studies of well-constrained environmental systems to interrogate the reasons for variable U isotopic fractionation. In general, processes that (1) favor the stability of aqueous U including aqueous molecules with larger formation constants (e.g. $Ca_2UO_2(CO_3)_3$) or (2) solubilize U(IV) increase the observed U isotope fractionation.

Observed variations in net isotope fractionation can be modeled as a competition between a kinetic mass dependent fractionation (MDF) and an equilibrium isotope fractionation that is the sum of an equilibrium MDF and NFS. The experimental and modeling results suggest that when the half-life of $U(VI)_{aq}$ is $>10^{5.4}$ s the equilibrium fractionation α should be expressed.

Alternately, the magnitude of kinetic MDF may be insignificant and the variations in observed fractionation are best interpreted as incomplete isotopic exchange. Regardless of the correct physical model, it is clear that the chemical properties of aqueous U are important to predicting the magnitude of U isotope fractionation. We will present a revised model for abiotic $^{238}U/^{235}U$ fractionation that is described by the thermodynamic and kinetic properties of corresponding experimental systems.