U Isotope Fractionation: Thermodynamic and Kinetic Controls

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Low temperature fractionation of $^{238}U/^{235}U$ is an emerging tracer in geologic processes such as the oxygenation of the oceans, contaminant transport and high precision geochronology. The relatively large variations in $^{238}U/^{235}U$ are often attributed to isotope fractionation between the oxidation states U(VI) and U(IV), called the nuclear volume effect (NVE). The observed U isotope fractionations in laboratory and field scale experiments, however, rarely yield isotopic fractionations that are consistent with the NVE predictions. The apparent contradiction between NVE predictions and experimental observations raises the possibility that more than one mechanism affects U isotope fractionation.

We present data from U reductive precipitation experiments designed to quantify the important parameters affecting abiotic U isotope fractionation in laboratory experiments and reevaluate data from the published literature. In our experiments U was reduced onto the surfaces of synthetic reductants, primarily FeS, under varying aqueous uranium ($U_{(aq)}$) removal rates. The removal rate of $U_{(aq)}$ was controlled by the concentration of aqueous Ca and by inference the concentration of $Ca_2UO_2(CO_3)_3^0$.

A first order kinetic rate law best describes our reduction experiments with rate constants between 0.05-0.257 h^{-1}. The $^{238}U/^{235}U$ of the residual $U_{(aq)}$ varied by >2‰ and isotopic fractionation factors (α) range from 1.00023-1.00084. The α's are highly correlated with $U_{(aq)}$ speciation and the $U_{(aq)}$ removal rate.

Earlier abiotic U reduction experiments report $\alpha \leq 1.0000$, significantly different from our results. To compare all of the experimental data we calculated the half-life ($t_{1/2}$) of $U_{(aq)}$ for each experiment where possible. The $t_{1/2}$ varies from approximately $10^{2.95}$ to $10^{4.64}$ s and correlates with α. We infer from these data that many of the abiotic reduction experiments are partially to completely recording kinetic U isotope fractionation and not the NVE. Experiments with intermediate α likely record a mixture of NVE and kinetic fractionation effects.