

Inorganic Uranium Isotope Fractionation is Dependent on Aqueous Speciation

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Low temperature fractionation of $^{238}\text{U}/^{235}\text{U}$ is now recognized in a large number of environmental and geologic settings over at least the past 2.5 Ga. Observations of $^{238}\text{U}/^{235}\text{U}$ variations in marine and terrestrial environments are used to quantify paleo ocean anoxia, the rise of atmospheric oxygen and the fate of contaminant U in the subsurface. The interpretation of variable $^{238}\text{U}/^{235}\text{U}$ in the geologic record is predicated on a limited number of experimental and theoretical studies that have identified inorganic, mass independent U isotope fractionation at high temperature and low pH (1, 2) while experiments at environmentally relevant conditions produce limited or kinetic fractionation (3-5).

We present results from recent inorganic U reduction experiments designed to elucidate the important mechanisms controlling the direction and magnitude of $^{238}\text{U}/^{235}\text{U}$ fractionation. All experiments were conducted at anaerobic conditions in a $\text{N}_2\text{-H}_2\pm\text{CO}_2$ atmosphere. U was reduced onto the surfaces of synthetic uranyl hydroxide with varying solution compositions.

Residual aqueous U concentrations and isotopic compositions were characterized by MC-ICP-MS. U isotopic compositions are reported as $\delta^{238}\text{U}$ normalized to the starting U solution. The U concentration and isotopic data were used to calculate the reaction order and the isotopic fractionation factors. All experiments are consistent with first order reaction kinetics with reaction rate constants between 0.050-0.257 (h^{-1}) and total durations of up to 48 hours. Isotopic fractionation factors (α) range from 1.00023-1.00084 and are correlated with U speciation. A model is presented which describes two U reaction pathways: redox vs. non-redox U removal from the solution. Both processes have an identifiable, unique fractionation factor and the mass balance of these two mechanisms describes the observed fractionation variation.

[1] Bigeleisen (1996) J. Am. Chem. Soc. [2] Fujii et. al. (1978) J Nuc. Sci. [3] Stirling et. al. (2007) EPSL. [4] Rademacher et al (2006) ES&T. [6] Stylo et al (2015) PNAS.