

Theoretical study of uranium isotope fractionation in aqueous and crystalline species

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Despite the radioactivity of all isotopes of uranium, $^{238}\text{U}/^{235}\text{U}$ ratios of geologic materials indicate chemical fractionation processes similar to those observed in stable isotopic systems. Fractionation between U(IV) and U(VI) species is typically $\sim 1\%$ at ambient temperatures, allowing the U-isotope system to be used as a proxy for oxygenation changes through geologic time. Reduced U(IV) species tend to have higher $^{238}\text{U}/^{235}\text{U}$ than U(VI) species due to the nuclear field shift effect, which works in the opposite direction of the mass dependent fractionation [1,2].

Building on previous theoretical calculations [3] to include more complex and geologically relevant materials, this study combines the first principles estimates of the field shift and mass dependent components of fractionation to determine the net equilibrium isotopic fractionation for a variety of U-bearing phases in solution and crystals.

Our results indicate that redox state is the major control on U-isotope fractionation, with smaller yet measurable effects due to speciation. Based on inner-shell shell hydration models of $\text{U}^{4+}_{(\text{aq})}$ and $\text{UO}_2^{2+}_{(\text{aq})}$ and a periodic boundary condition model of UO_2 -uraninite, we estimate a 1.0‰ fractionation between U(IV) and U(VI) species in solution, and a 1.3‰ fractionation between $\text{UO}_2^{2+}_{(\text{aq})}$ and $\text{UO}_2_{(\text{s})}$, at 25°C, compared to experimental determinations of 1.1‰ and 1.6‰, respectively[4,5]. We find that solvation modestly affects predicted fractionations (by up to 0.2‰) involving aqueous uranyl-carbonate species, which dominate the modern seawater uranium budget. We estimate that $\text{CaUO}_2(\text{CO}_3)_3^{2-}_{(\text{aq})}$ is lighter than $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3_{(\text{aq})}$ by $\sim 0.2\%$, in apparent disagreement with the mechanism invoked to explain slightly elevated $^{238}\text{U}/^{235}\text{U}$ in aragonite precipitated under alkaline conditions[6]. Finally, models of U-substituted zircon and other U-bearing analogues for silicate melts suggest that zircon crystallization from U(V) and/or U(VI) bearing melts may generate measurable fractionations throughout the range of silicate melting and crystallization temperatures in the Earth's crust and upper mantle.

[1] Bigeleisen (1996) *J Am Chem Soc* 118:3676–3680, [2] Nomura et al. (1996) *J Am Chem Soc* 118:9127–9130, [3] Abe et al. (2008) *J Chem Phys* 129:164309, [4] Wang et al. (2015) *GCA* 150:160–170 [5] Wang et al. (2015) *GCA* 158:262–275, [6] Chen et al. (2016) *GCA* 188:189–207