Nuclear volume isotope fractionation of mercury, thallium, and other heavy elements.

E.A. SCHAUBLE

Dept. of Earth and Space Sciences, UCLA ;
schauble@ucla.edu

First-principles estimates of nuclear-volume (a.k.a. field-shift) and mass-dependent stable isotope fractionation of mercury and thallium will be presented. This study is motivated by recent observations of fractionations that appear to be much larger (2‰ or more) than can be explained by mass-dependent mechanisms operating at equilibrium. While the magnitude of mass-dependent fractionations is expected to decrease with increasing atomic mass, scaling roughly as $\delta m/m^2$, fractionations driven by isotopic variation in nuclear volume should increase. Isotopic variation in nuclear volume is not linear, and might be detectable as anomalous odd-even staggering in isotope abundance ratios. These effects are expected to be largest when species with different valence *s*-electron occupancies equilibrate – suggesting a particular relevance to redox processes separating Hg^0 or Tl^+ ($6s^2$) from Hg^{2+} or Tl^{3+} ($6s^0$).

Relativistic Dirac-Hartree-Fock calculations are used to estimate shifts in molecular energies caused by isotopic substitution. Each nucleus is modelled as a spherically symmetric Gaussian charge distribution. Vibrational contributions to mass-dependent fractionation are estimated using a combination of experimental and *ab initio* models. The results suggest ~2-3‰ higher $^{205}Tl/^{203}Tl$ in $Tl^{3+}_{(aq)}$ than in $Tl^{+}_{(aq)}$ at 25ºC, and ~2-3‰ higher $^{202}Hg/^{198}Hg$ in $HgCl_{2(g)}$ than in $Hg^0_{(g)}$. $Hg(CH_3)_2$ and $Hg(CH_3)Cl$ are intermediate between Hg^0 and $HgCl_2$. Nuclear volume contributes more to the total fractionation than mass-dependent effects for most of the studied molecules. Nuclear-volume fractionation correlates with coordination number and the electronegativity of bond partners. Odd-even staggering effects of 0.1-0.4‰ are predicted for Hg^{2+}-molecules vs. Hg^0 at 25ºC. A survey of the periodic table suggests ≥ 0.1‰ even-odd staggering effects only occur in period 5-7 elements (~Mo-U).