Summary of Estrade *et al.* 2009 (Geochimica et Cosmochimica Acta)

Estrade et al (2009) perform both equilibrium and dynamic (kinetic) evaporation experiments to measure the isotope fractionation between liquid and gas-phase mercury. Equilibrium experiments gave them $^{202}\alpha^{eq}_{liquid\text{-}vapor}$ values of 1.00086, with the vapor depleted in $\delta^{202}Hg$ by 0.86‰, across the range of temperatures tested. Reyleigh-type dynamic fractionation experiments produced a fractionation factor at 22°C of $^{202}\alpha^{Dyn}_{liquid\text{-}vapor} = 1.0067$, which agrees (within uncertainty) to their re-analysis of historical data ($^{202}\alpha$=1.0076). Equilibrium evaporation experiments display mass-independent fractionation in ^{199}Hg and ^{201}Hg, with $\Delta^{199}Hg = 0.12‰$ and $\Delta^{201}Hg = 0.07‰$, whereas ^{200}Hg was mass-dependent to within the uncertainty of the measurement. Smaller $\Delta^{199}Hg$ and $\Delta^{201}Hg$ anomalies were observed in the dynamic experiments, depending upon the conditions. This data produces a $\Delta^{199}Hg$ / $\Delta^{201}Hg$ slope of 2.0 ± 0.6, which is (within uncertainty) similar to the predicted nuclear volume isotope effect (slope of 2.47), but significantly different from the slopes of 1.00 and 1.36 observed by Bergquiest and Blum (2007) and attributed to magnetic isotope effect. The authors therefore hypothesize that the anomalous isotope fractionation is due to nuclear volume isotope effect.

This study is novel and significant because it demonstrates significant mass-independent fractionation in the odd isotopes of mercury occurring in a simple physical process (*i.e.* evaporation). Although the effect is small, it could potentially be attributed to a nuclear volume isotope effect. Nuclear volume isotope effects are predicted to be observed mostly in reactions where there are changes in redox state causing a change in the electron configuration of the heavy atom. However, in this case a nuclear volume effect is observed where both the product (Hg^0 vapor) and the reactant (Hg^0 liquid) are in the same redox state. Since evaporation of mercury vapor does not involve radicals, it is unlikely that the observed effect could be kinetic in nature. This study is significant in showing that it is possible to observe nuclear volume isotope effects in physical processes with no change in redox state. However, the isotope effects observed in these experiments are unlikely to be relevant in earth surface environments, since the mercury MIF caused by photoreduction of mercury and methylmercury produce a much stronger signal that more closely matches that observed in natural samples.

This study had several strengths. The authors did a good job reviewing the theory and using the theory to explain their experimental results. They also went back and re-analyzed historical literature data from the 1920's, converting it from density data to the modern delta notation and showing that it is consistent with their experiments. In addition, the equilibrium experiments were well designed, although I do not believe they justified strongly enough that they had actually reached equilibrium. I thought the dynamic experiments might be measuring additional isotope fractionations beyond that from evaporation, such as an effect of condensation on the walls, diffusion through the system, or possibly an effect from the large temperature gradient in the system.