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Experimental evidence for mass-independent fractionation of even-mass mercury isotopes related to the nuclear volume effect

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Investigating stable mercury (Hg) isotope ratios is a novel approach for tracing biogeochemical transformations of this global pollutant in environmental systems. The Hg isotope system is unique in the sense that it encompasses not only mass-dependent (MDF) but also multiple types of mass-independent fractionation (MIF) in both experimental and natural systems. One of the processes causing MIF for heavy elements such as Hg is the nuclear volume effect (NVE) which occurs during kinetic and equilibrium reactions and can exceed the magnitude of the conventional mass difference effect (MDE). It is well established that the NVE can cause significant MIF of odd-mass Hg isotopes (^{199}Hg, ^{201}Hg) because they have slightly smaller nuclear charge radii than predicted by a linear scaling with mass (based on ^{198}Hg and ^{202}Hg). Small deviations from this linear relationship have also been theoretically predicted for the even-mass isotopes ^{200}Hg and ^{204}Hg, but the effect was so far believed to be negligible.

In this study, we investigated Hg isotope fractionation during Hg(II) reduction by Fe(II) by analyzing both reactants and products of laboratory experiments. Reduction of Hg(II) by dissolved Fe(II) led to MDF with enrichment factors (up to -2.4‰) that are larger than for other abiotic reduction pathways. A positive MIF of odd-mass Hg isotopes was observed in all experiments (E^{199}Hg up to 0.34±0.02‰ and E^{201}Hg up to 0.21±0.02‰) with a consistent $\Delta^{199}Hg/\Delta^{201}Hg$ slope of ≈1.6 indicating that the MIF was likely caused by the NVE. Additionally, we report the first experimental evidence for small MIF of even-mass Hg isotopes related to NVE (E^{200}Hg up to 0.04±0.01‰ and E^{204}Hg up to −0.05±0.01‰), which aligns with theoretical predictions based on the non-linearity of nuclear charge radii (Figure 1).

Our results provide further insights into Hg isotope fractionation systematics and constraints for the interpretation of Hg isotope signatures. Despite the small magnitude of the documented even-mass MIF caused by the NVE, we suggest that this effect should be considered when interpreting small even-mass MIF signals detected in environmental samples, which are frequently assumed to be solely produced by atmospheric processes.

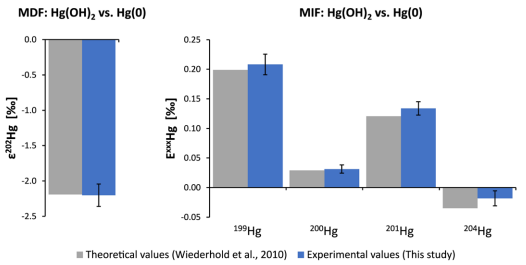

Figure 1: *Comparison of theoretical and experimentally determined extent and direction of MDF and odd- and even-mass MIF by the NVE for $Hg(OH)_2$ relative to Hg(0) vapor. Error bars represent 2SE of regressions of linear Rayleigh plots. Theoretical values are based on Wiederhold et al., ES&T, 44, 11 (2010), doi: 10.1021/es100205t.*