

A potential mechanism to explain even Hg isotope mass independent fractionation

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Mass independent fractionation (MIF) of even mass number mercury (Hg) stable isotopes is observed in rainfall globally, and is used to quantify atmospheric Hg deposition pathways. The chemical reaction and underlying even-Hg MIF mechanism are unknown however, and suggested to be caused by Hg photo-oxidation on aerosols at the tropopause. In this study we investigate the Hg isotope composition of free tropospheric gaseous elemental Hg⁰ and oxidized Hg forms at the high altitude Pic du Midi Observatory. We observe that gaseous oxidized Hg has positive $\Delta^{199}\text{Hg}$, $\Delta^{201}\text{Hg}$, $\Delta^{200}\text{Hg}$, and negative $\Delta^{204}\text{Hg}$ signatures, similar to rainfall Hg, and we document rainfall Hg $\Delta^{196}\text{Hg}$ to be near-zero. Cloud water and rainfall Hg show enhanced odd-Hg MIF compared to gaseous oxidized Hg, indicating the occurrence of in-cloud aqueous Hg photoreduction. Hg MIF observations of free tropospheric Hg⁰ dynamics show how net Hg⁰ oxidation in the lower free troposphere leads to opposite even- and odd-MIF in Hg⁰ and oxidized Hg. We postulate that even-Hg MIF takes place by a ligand induced magnetic isotope effect. Hyperfine coupling of nitrogen or chlorine ligand nuclear spin with even Hg isotope electron spin in aqueous aerosol Hg-ligand radical pairs then causes even-Hg MIF during Hg photoreduction.