

Mechanism for Mercury Isotope Fractionation during Aqueous Photodecomposition

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Stable isotope fractionation during chemical reactions has traditionally been assumed to result from differences in molecular or atomic properties due to a difference in atomic mass resulting from an isotopic substitution. This type of phenomenon is denoted mass dependent fraction (MDF). The theoretical framework for MDF was developed from transition state theory and has been useful in the study of stable isotope geochemistry. However, current theories fail to explain the large MDF of mercury (Hg) isotopes, as the relative isotopic mass differences for Hg is small. Traditional explanations for MDF also break down for photochemical reactions involving Hg in aquatic systems, where the isotope fractionation appears to be independent of mass, and reactions exhibit mass independent fractionation. This is in part because the assumptions for MDF do not apply to photochemical reactions in which the excitation of an electron by a photon involves the jump from a ground state to an excited state, and this excited state cannot be described within transition state theory.

The photochemical decomposition of Hg complexes in natural waters is one of the least understood areas of the Hg cycle despite its major role in limiting the Hg available for bioaccumulation in the food-web. We will discuss both *in vitro* and *in vivo* reactions, and quantum chemistry modelling approaches that can be used to investigate Hg stable isotope fractionation during photochemical decomposition. We will conclude our discussion with the implications of our findings to the interpretation of Hg stable isotope measurements in Pacific and Atlantic Ocean foodwebs.