Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.5965

Mercury stable isotope fractionation during aqueous photoreduction in sulfidic environment

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Mercury (Hg) is a global pollutant with complex transformations in the environment. The fractionation of Hg stable isotopes has been widely used as a powerful tracer for Hg cycling, for that it exhibits unique mass independent fractionation (MIF), particularly during photochemical reactions. The aqueous photoreduaction of various Hg(II) speices is a critical process controlling Hg cycles and one of the major processes that generate MIF. However, the mechanism of Hg MIF during photoreduction has not been fully understood. Previous studies on Hg isotope fractionation during photoreduction have mostly focused on oxic aquatic environment where Hg(II) is dominantly complexed by organic matter, but there is no systematic study in sulfidic water, where Hg(II) is complexed by sulfide. Previous studies have shown that the sign and magnitude of Hg MIF are sensitive to the type of ligands and dissolved oxygen in solution. Thus Hg MIF has the potential to act as a proxy of ocean redox changes. We have demonstrated that Hg MIF in black shale can record photic zone euxinia (PZE, shallow anoxic and sufide rich condition in ancient ocean), which may have played a critical role in mass extinction and the evolution of life. Here we experimentally investigate Hg isotope fractionation during photoreduction of Hg(II) in sulfide-rich water, which is representative of PZE in ancient ocean and in some anoxic coatsal settings in modern environment. Our goals were to further understand the mechanism of Hg MIF in its photochemistry, and develop the use of Hg MIF as a paleoredox proxy.

We observed both mass dependent fractionation with enrichment of heavier isotopes in the reactant Hg(II) and significant negative MIF that caused depletion of odd mass isotopes in Hg(II). This negative direction is opposite to the positive MIF previously observed in photoreduction in oxic waters, but is similar to the MIF during photoreduction of Hg(II) complexed by reduced organic thiol. More details of the experiment are still in progress to investigate the effects of Hg speciation, and irradiation wavelength and other environment parmeters on Hg MIF.