

Experimental determination of kinetic mercury isotope fractionation during reduction of Hg(II) by dissolved Fe(II) and Fe(II)-bearing minerals

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Reduction of divalent mercury (Hg) to Hg(0) is an important pathway for controlling Hg emissions from terrestrial and aquatic ecosystems to the atmosphere. Dissolved Fe(II) and Fe(II)-bearing minerals such as magnetite, green rust, siderite, mackinawite and vivianite have been shown to be capable of causing dark abiotic reduction of Hg(II). Transformations between different redox states are major drivers of Hg stable isotope fractionation during biogeochemical cycling. To use stable Hg isotope techniques as a tool for tracing such redox transformations in the environment, it is necessary to determine fractionation factors for the respective process.

Homogeneous and heterogeneous reduction of Hg(II) with dissolved Fe(II) and Fe(II)-bearing minerals, respectively, was investigated in batch experiments under anoxic conditions. The Hg(0) produced by these reactions was continuously removed by purging with N₂ into an oxidizing trap solution. Solution aliquots were taken from the reactor and the trap to record isotope ratios by CV-MC-ICP-MS both in the residual fraction and the product. Homogeneous reduction experiments with dissolved Fe(II) showed consistent isotopic trends which could be described by a Rayleigh model, indicating a kinetically-controlled reaction. Both mass dependent fractionation, with an enrichment of light Hg isotopes in the product, as well as mass independent fractionation, with an anomalous depletion of odd-mass Hg isotopes in the product, were observed. The $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope indicated that the MIF was likely caused by the nuclear volume effect. First data of heterogeneous batch experiments with Fe(II) sorbed on Al oxide (boehmite) as reductant highlighted the influence of Hg(II) sorption to the mineral surface on the investigated system.

The results of this study will be useful for the interpretation of field data, for example from (temporarily) anoxic groundwater bodies at contaminated sites. By adding new fractionation factors to the toolbox of Hg stable isotope fractionation as a tracer for biogeochemical transformations, our experimental insights will contribute to the understanding of the biogeochemical cycling and exchange mechanisms of Hg species within and between different environmental compartments.