Kinetic versus Equilibrium Mercury Isotope Effects During Homogenous and Surface Catalyzed Mercury(II) Reduction by Iron(II)

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Mercury (Hg) is a global pollutant that poses a risk to humans and the environment. The environmental mobility and bioavailability of Hg is largely determined by its speciation and redox state. In anoxic geochemical settings with high iron (Fe) contents and low organic matter concentrations as can be found in groundwater aquifers, an important reaction which controls Hg chemistry is direct Hg(II) reduction by dissolved or surface-bound Fe(II). This process has further been shown to be catalyzed by the presence of Fe(III)-mineral surfaces.

Hg isotope analysis has been successfully used to trace Hg transformation processes, for example, to distinguish between photochemical reduction and other non-photochemical reduction pathways. Biotic as well as abiotic reduction of Hg(II) to Hg(0) fractionate Hg isotope ratios in a way that light isotopes are enriched in the produced Hg(0). Additionally, small but variable mass independent fractionation (MIF) effects have been observed. The use of Hg isotopes to differentiate between reduction pathways relies on the assumption that these invoke characteristic fractionation factors and are not overprinted by secondary processes such as isotope exchange between product and reactant.

To assess the applicability of Hg isotope ratios as a tracer for different reduction pathways kinetic experiments with continuous removal of Hg(0) after the reduction of Hg(II) by dissolved Fe(II) and surface catalyzed reduction by Fe(II) sorbed on goethite and boehmite were compared with closed system experiments that allowed isotope exchange between Hg(II) and Hg(0) in solution after the partial reduction. The results of the kinetic experiments could be described by a Rayleigh model with mass dependent fractionation ($\varepsilon^{202/198}$Hg) in the range of -2.1 to -2.9 ‰. A small positive MIF of odd-mass Hg isotopes was observed in all experiments. The δ^{199}Hg/δ^{201}Hg slope was consistent in all kinetic experiments (1.5-1.6) indicating that the MIF was likely caused by the nuclear volume effect. The closed system experiments on the other hand indicated a large potential for isotope exchange between of coexisting Hg(II) and Hg(0) to overprint the initial kinetic effects. Our results have important implications for the application of Hg isotopes in the investigation of Hg(II)-Hg(0) redox systems.