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Mercury isotope fractionation during dark abiotic reduction of Hg(II) by dissolved and surface-bound Fe(II) species

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For many metals, including mercury (Hg), the transformation between different redox states is an important process for stable isotope fractionation. Identifying fractionation factors for specific Hg redox transformations therefore enables stable Hg isotope techniques to be used as a tool to trace biogeochemical processes and improve our understanding of the transport and fate of Hg in the environment. Previous studies demonstrated that reduced iron (Fe) species and Fe^(II)-bearing minerals such as magnetite, green rust, siderite or vivianite are capable of reducing Hg^(II) to Hg^(I) and Hg⁽⁰⁾. These processes may be important in environments with low organic matter concentration and changing redox conditions such as groundwater aquifers or temporarily flooded soils.

In this study homogeneous and heterogeneous redox reactions of Hg^(II) with dissolved Fe^(II) and Fe^(II)-bearing minerals are investigated in batch experiments under oxygen-free conditions in a glove bag. Mercury stock solutions prepared from NIST-3133 in a glass batch reactor are continuously stirred to minimize local reducing zones and wrapped in aluminum foil to prevent photoreduction. The reducing agents are added stepwise to reduce fractions of Hg until complete reduction is achieved. The produced Hg⁽⁰⁾ is continuously purged into an oxidizing trap solution (40% inverse aqua regia with BrCl) with nitrogen gas at a low flow rate. After each reduction step solution aliquots are taken from the reactor and the trap is exchanged. Total Hg concentrations in reactor and trap samples are then measured with CV-AAS/AFS and isotopic compositions determined with CV-MC-ICP-MS.

Initially, different amounts of SnCl₂ were used as reducing agent to test the experimental setup similar to [1]. For this experiment we observed consistent isotopic trends which could be described by a Rayleigh model fit with mass dependent fractionation ($\epsilon^{202}\text{Hg} = -2.75 \pm 0.07\text{‰}$) as well as mass independent fractionation of odd-mass Hg isotopes ($E^{199}\text{Hg} = 0.32 \pm 0.04\text{‰}$). The slope of the linear regression of $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ of 1.52 ± 0.1 indicates that the MIF was likely caused by the nuclear volume effect. In subsequent experiments different amounts of a Fe^(II) stock solution prepared from Fe^(II)Cl₂ are used as reducing agent. Additionally, experiments are carried out with Fe^(II)-bearing minerals and Fe^(II) adsorbed to mineral surfaces.

The results produced from this study will be very useful for the interpretation of field data from

temporarily anoxic groundwater bodies at contaminated sites (e.g. [2]). The insights from the experiments will further contribute to the understanding of the interplay between Hg and Fe biogeochemical cycles and redox transformations. Most importantly, it will add much needed fractionation factors to the toolbox of Hg stable isotope fractionation as a tracer for biogeochemical transformations.

[1] Zheng, W., Hintelmann, H. (2010) Nuclear field shift effect in isotope fractionation of mercury during abiotic reduction in the absence of light. *J. Phys. Chem. A*, 114(12), 4238–4245.

[2] Richard, J.-H., Bischoff, C., Ahrens, C.G.M., Biester, H. (2016) Mercury(II) reduction and co-precipitation of metallic mercury on hydrous ferric oxide in contaminated groundwater. *Sci. Tot. Environ.* 539, 36–44.