

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

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MIRACOSA

This work is carried out within the MIRACOSA project (Mercury isotope ratios as a tool to trace and quantify Hg species transformations in contaminated soils and aquifers).

In this project, a combination of different analytical methods is used to elucidate the pathways of Hg in the subsurface of two HgCl₂-contaminated "industrial legacy" sites.

The goal is to improve the understanding of Hg species transformation processes and ultimately the risk assessment and remediation design at such sites.

STUDY GOALS AND HYPOTHESES

Redox transformations are important processes for mercury (Hg) stable isotope fractionation. Determining fractionation factors for specific Hg redox transformations enables stable Hg isotope techniques to be used as a tool to trace biogeochemical processes.

Previous studies showed that reduced Fe species and Fe(II)-bearing minerals such as magnetite, green rust, siderite, mackinawite or vivianite are capable of reducing Hg(II) to Hg(0) ¹⁻⁷.

These processes may be important in environments with low organic matter concentration and changing redox conditions such as groundwater aquifers or temporarily saturated soils ⁸⁻¹⁰. Increased emission of Hg(0) to the atmosphere, as well as a reduction of the bioavailable Hg(II) pool that may be methylated may result from the reduction of Hg(II) to Hg(0).

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 anoxic conditions. The goal is to determine isotope fractionation factors for each of the investigated redox reactions.

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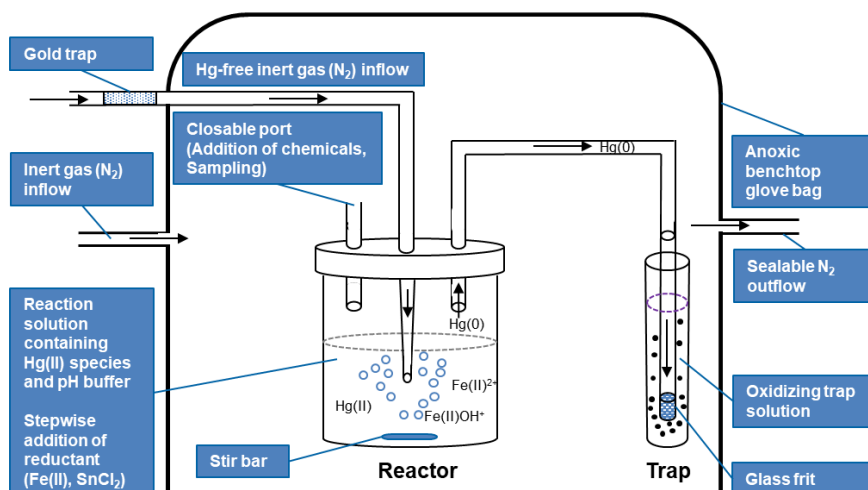
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Figure 1: Schematic overview of the experimental setup for the Hg(II) reduction combined with purge and trap

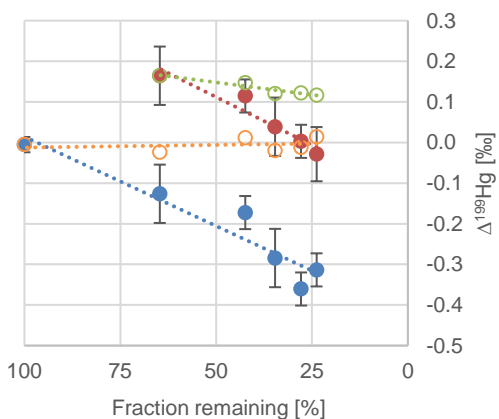
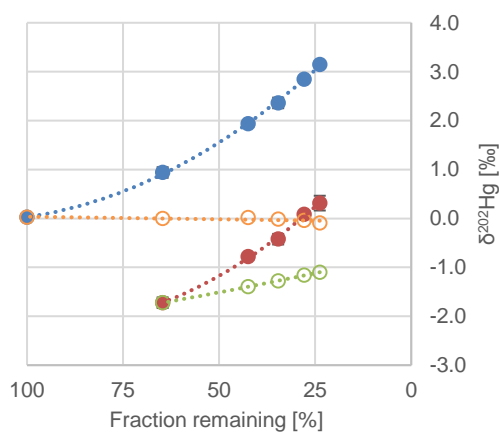


Methods

The reducing agents are added stepwise to reduce fractions of Hg until complete reduction. The produced $\text{Hg}^{(0)}$ is purged into an oxidizing trap solution with N_2 gas at a low flow rate.

Total Hg concentrations in reactor and trap samples are measured with CV-AAS/AFS and isotopic composition determined by CV-MC-ICP-MS ^{11,12}.

Similar to previous studies ¹³ different amounts of SnCl_2 were initially used as reducing agent to test the experimental setup.



● Reactor ● Inst. Product
○ Cum. Product ○ Balance

Figure 2: Mass dependent (MDF, top) and mass independent (MIF, bottom) isotope fractionation during the stepwise reduction of $\text{Hg}^{(II)}$ by SnCl_2 . Filled circles are results from measured samples (reactor, traps), empty circles are calculated.

RESULTS & DISCUSSION

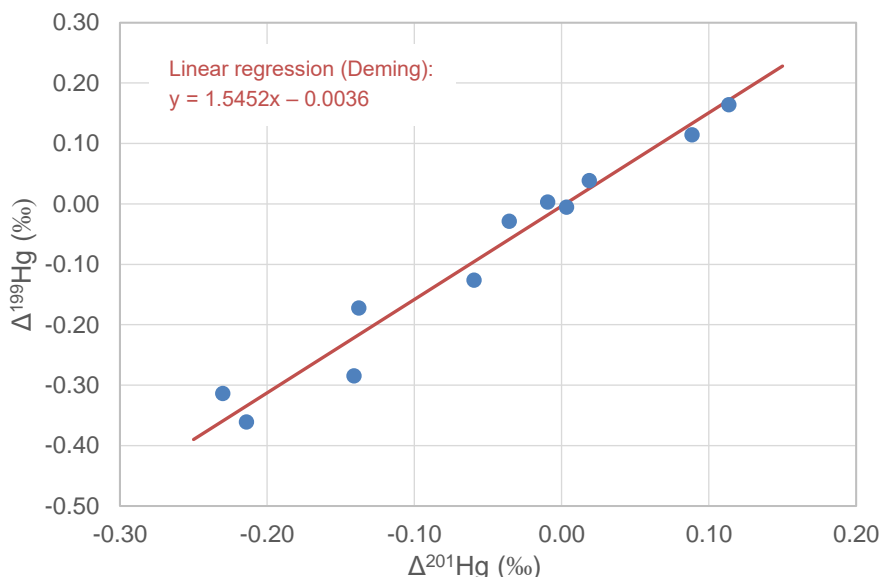


Figure 3: $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ during reduction by SnCl_2 . The solid line represents a linear regression accounting for errors in x and y direction ($\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope).

During the reduction by SnCl_2 we observed consistent isotopic trends which could be described by a Rayleigh model fit (Figure 2).

Mass dependent fractionation
($\epsilon^{202}\text{Hg} = -2.75 \pm 0.07\text{‰}$) and mass independent fractionation of odd-mass Hg isotopes ($E^{199}\text{Hg} = +0.32 \pm 0.04\text{‰}$) were observed (Figure 2).

The observed MDF is larger than previously reported values of $-1.56 \pm 0.11\text{‰}$ and $-1.77 \pm 0.11\text{‰}$ ¹³.

The slope of the linear regression of $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ was calculated to be 1.55 ± 0.22 (2SE of linear regression). This indicates that the MIF was likely caused by the nuclear volume effect (NVE) (Figure 3).

The observed $\Delta^{199}\text{Hg}/\Delta^{201}\text{Hg}$ slope is in good agreement with theoretical predictions and previously reported experimental values of 1.5 - 1.6 ^{13,14}.

Both $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ are positive for the product $\text{Hg}^{(0)}$ and negative for the reactant $\text{Hg}^{(II)}$ as a result of NVE, which is the opposite direction compared to photoreduction.

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OUTLOOK

In subsequent experiments different amounts of Fe^(II) in solution are used as reducing agent. First results show that Hg^(II) can be reduced and trapped using a Fe^(II) stock solution prepared from Fe^(II)Cl₂ salt.

In second step, surface catalyzed reduction using Fe^(II) adsorbed to different mineral surfaces is studied. Additionally, experiments are carried out with Fe^(II)-bearing minerals.

The results produced from this study will be useful for the interpretation of field data from temporarily anoxic groundwater bodies at contaminated sites (e.g. ^{8,9}).

Most important, this study will add much needed fractionation factors to the toolbox of Hg stable isotope fractionation as a tracer for biogeochemical transformations.

The insights from the experiments will further contribute to the understanding of the interplay between Hg and Fe biogeochemical cycles and redox transformations.

REFERENCES

- (1) Wiatrowski, H. A.; Das, S.; Kukkadapu, R.; Ilton, E. S.; Barkay, T.; Yee, N. Reduction of Hg(II) to Hg(0) by Magnetite. *Environ. Sci. Technol.* **2009**, *43* (14), 5307–5313. <https://doi.org/10.1021/es9003608>.
- (2) Pasakarnis, T. S.; Boyanov, M. I.; Kemner, K. M.; Mishra, B.; O'Loughlin, E. J.; Parkin, G.; Scherer, M. M. Influence of Chloride and Fe(II) Content on the Reduction of Hg(II) by Magnetite. *Environ. Sci. Technol.* **2013**, *47* (13), 6987–6994. <https://doi.org/10.1021/es304761u>.
- (3) O'Loughlin, E. J.; Kelly, S. D.; Kemner, K. M.; Csencsits, R.; Cook, R. E. Reduction of AgI, AuIII, CuII, and Hg II by FeII/FeIII Hydroxysulfate Green Rust. *Chemosphere* **2003**, *53* (5), 437–446. [https://doi.org/10.1016/S0045-6535\(03\)00545-9](https://doi.org/10.1016/S0045-6535(03)00545-9).
- (4) Ha, J.; Zhao, X.; Yu, R.; Barkay, T.; Yee, N. Hg(II) Reduction by Siderite (FeCO₃). *Appl. Geochemistry* **2017**, *78*, 211–218. <https://doi.org/10.1016/j.apgeochem.2016.12.017>.
- (5) Bone, S. E.; Bargar, J. R.; Sposito, G. Mackinawite (FeS) Reduces Mercury(II) under Sulfidic Conditions. *Environ. Sci. Technol.* **2014**, *48* (18), 10681–10689. <https://doi.org/10.1021/es501514r>.
- (6) Amirbahman, A.; Kent, D. B.; Curtis, G. P.; Marvin-Dipasquale, M. C. Kinetics of Homogeneous and Surface-Catalyzed Mercury(II) Reduction by Iron(II). *Environ. Sci. Technol.* **2013**, *47* (13), 7204–7213. <https://doi.org/10.1021/es401459p>.
- (7) Charlet, L.; Bosbach, D.; Peretyashko, T. Natural Attenuation of TCE, As, Hg Linked to the Heterogeneous Oxidation of Fe(II): An AFM Study. *Chem. Geol.* **2002**, *190* (1–4), 303–319. [https://doi.org/10.1016/S0009-2541\(02\)00122-5](https://doi.org/10.1016/S0009-2541(02)00122-5).
- (8) Richard, J. H.; Bischoff, C.; Ahrens, C. G. M.; Biester, H. Mercury (II) Reduction and Co-Precipitation of Metallic Mercury on Hydrous Ferric Oxide in Contaminated Groundwater. *Sci. Total Environ.* **2016**, *539*, 36–44. <https://doi.org/10.1016/j.scitotenv.2015.08.116>.
- (9) Debure, M.; Grangeon, S.; Robinet, J. C.; Madé, B.; Fernández, A. M.; Lerouge, C. Influence of Soil Redox State on Mercury Sorption and Reduction Capacity. *Sci. Total Environ.* **2020**, *707*. <https://doi.org/10.1016/j.scitotenv.2019.136069>.
- (10) Peretyashko, T.; Charlet, L.; Grimaldi, M. Production of Gaseous Mercury in Tropical Hydromorphic Soils in the Presence of Ferrous Iron: A Laboratory Study. *Eur. J. Soil Sci.* **2006**, *57* (2), 190–199. <https://doi.org/10.1111/j.1365-2389.2005.00729.x>.
- (11) Grigg, A. R. C.; Kretschmar, R.; Gilli, R. S.; Wiederhold, J. G. Mercury Isotope Signatures of Digests and Sequential Extracts from Industrially Contaminated Soils and Sediments. *Sci. Total Environ.* **2018**, *636*, 1344–1354. <https://doi.org/10.1016/j.scitotenv.2018.04.261>.
- (12) Brocza, F. M.; Biester, H.; Richard, J.-H.; Kraemer, S. M.; Wiederhold, J. G. Mercury Isotope Fractionation in the Subsurface of a Hg(II) Chloride-Contaminated Industrial Legacy Site. *Environ. Sci. Technol.* **2019**, *53* (13), 7296–7305. <https://doi.org/10.1021/acs.est.9b00619>.
- (13) Zheng, W.; Hintelmann, H. Nuclear Field Shift Effect in Isotope Fractionation of Mercury during Abiotic Reduction in the Absence of Light. *J. Phys. Chem. A* **2010**, *114* (12), 4238–4245. <https://doi.org/10.1021/jp910353y>.
- (14) Wiederhold, J. G.; Cramer, C. J.; Daniel, K.; Infante, I.; Bourdon, B.; Kretschmar, R. Equilibrium Mercury Isotope Fractionation between Dissolved Hg(II) Species and Thiol-Bound Hg. *Environ. Sci. Technol.* **2010**, *44* (11), 4191–4197. <https://doi.org/10.1021/es100205t>.