

Mass-dependent and mass-independent fractionation of Hg isotopes in aquatic systems

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Mercury is a globally distributed and highly toxic pollutant, the mobility and bioaccumulation of which is dependent on its redox cycling. Hg isotope analysis by MC-ICPMS is an important new tool for identifying Hg sources and tracking Hg transformations in the environment (Smith *et al.*, 2005; Jackson *et al.*, 2006; Bergquist *et al.*, 2006; Kritee *et al.*, 2007), with most measured natural samples displaying mass-dependent isotope fractionation (MDF). A small body of data suggests that natural samples also display mass-independent isotope fractionation (MIF) of the odd Hg isotopes (Jackson *et al.*, 2006; Bergquist *et al.*, 2006).

Reduction of Hg species to Hg(0) vapor is an important pathway for removal of Hg from aqueous systems into the atmosphere and occurs by abiotic and biotic mechanisms. In laboratory experiments, we find that photochemical reduction of both Hg⁺² and CH₃Hg⁺ by natural sunlight leads to large MIF of the odd isotopes (²⁰¹Hg, ¹⁹⁹Hg) and preferential retention of the odd isotopes in the reactant (soluble) phase. Also, the relationship between MIF for the two odd isotopes of Hg is significantly different for the two photo-reduction pathways (Hg⁺² to Hg⁰ versus CH₃Hg⁺ to Hg⁰). In contrast, both biological reduction (Kritee *et al.*, 2006) and dark abiotic organically-mediated reduction follow MDF.

Natural samples from aquatic ecosystems preserve both MDF and MIF. In fish, MDF increases with the size and Hg concentration of the fish suggesting MDF may be useful in understanding Hg bioaccumulation (similar to δ¹⁵N). Fish also display a large range in MIF (4‰) with MIF always having positive values. Additionally, the relationship between the MIF of the two odd isotopes in fish has a similar slope to the slope found for photo-reduction of CH₃Hg⁺. Since fish bioaccumulate CH₃Hg⁺, fish may be recording the extent to which CH₃Hg⁺ is lost via photochemical reduction in an aquatic ecosystem. Fish populations from different locations have different MIF values, but mostly display similar MIF within a location. This suggests that MIF is preserved in the food web and could be used to quantify photo-reduction of CH₃Hg⁺ of an ecosystem. Both MDF and MIF of Hg isotopes hold promise for quantifying and understanding Hg pathways and bioaccumulation in the environment.

References

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CO₂-bearing fluid inclusions in upper mantle xenoliths from Tihany (western Hungary): Minimum trapping pressures and trace element compositions

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In this study, microthermometry, Raman microspectroscopy and LA-ICP-MS analysis of dense CO₂-rich fluid inclusions hosted in orthopyroxenes from spinel peridotite xenoliths of the subcontinental lithospheric mantle from Tihany (western Hungary) were carried out.

Discussion

Petrographically two types of fluid inclusions are distinguished. Based on microthermometry, two different density ranges were observed. The CO₂-densities, together with the geothermometry of the peridotites based on orthopyroxene/clinopyroxene equilibrium, suggest that the studied xenoliths represent two, physically distinct domains in the lithospheric mantle, one shallow and one deeper. Raman microspectroscopy confirms that the fluid inclusions consist mostly of pure CO₂, but rarely H₂S is also observed.

For multi-element analysis in situ LA-ICP-MS was used to identify elements associated with the CO₂ fluid inclusions in orthopyroxene. LIL elements such as K, Ba and Rb which are incompatible to the host orthopyroxene, were found to be concentrated at the CO₂ inclusions.

Conclusion

Since a precise geobarometer for the spinel peridotite stability field is not available yet, the minimum trapping pressure estimation from CO₂ fluid inclusions provides the best method available for pressure estimation in these mantle rocks. The CO₂ fluid inclusions in the studied peridotites suggest ~12°C/km temperature gradient for the upper mantle 8 million years ago when the xenoliths were brought to the surface by the host basalt.

The results of LA-ICP-MS analysis suggest that the orthopyroxenes and the enclosed fluids have very different trace element compositions. These results also suggest that the CO₂-rich fluids are important agents for transporting incompatible trace elements in the lithospheric mantle.