Mass Independent Fractionation of Mercury Isotopes Archived in a Peat Core

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Introduction

The levels of mercury (Hg) in aquatic systems and the food chain, its global dispersion by the atmosphere, the toxicity of organo-Hg species, and an ever increasing anthropogenic input, combine to produce a serious public health problem. Isotopic tracing of Hg can help identify its sources, transport and/or processes of methylation. Isotopic variations in the seven stable isotopes of Hg arise from differences in nuclear mass, nuclear spin and nuclear volume. We report precise Hg isotope measurements that have revealed natural variations in the isotopic composition of Hg that promise to provide powerful new constraints on the dynamics of the mercury cycle.

Experiment

A peat core, previously shown to contain a 2000-year atmospheric Hg depositional record, was cut into 5-cm thick slices. From splits of six distributed slices cellulose was extracted and sent for dating by the ^{14}C method. Mercury was leached from peat samples using concentrated HCl and H_2O_2. A hydride generator was used to produce a stream of cold Hg vapor that was introduced into the ion source of the Thermo-Finnigan *Neptune* MC-ICP-MS at the Plasma Analytical Facility, NHMFL. Mercury isotopes were measured by a standard-sample bracketing technique against the Hg standard NIST SRM 3133 and recorded as $\delta^{A}Hg$ values. $\delta^{A}Hg$ (‰)= $[(^{A}Hg/^{202}Hg)_{sample}/(^{A}Hg/^{202}Hg)_{NIST3133} -1] \times 1000$. $\Delta^{A}Hg$ values express permil residuals after correction for mass-dependent isotope fractionation. The precision of isotope ratio measurement is about ±0.1 ‰.

Results and Discussion

Mercury deposited in the peat has been interpreted by previous workers as a record of atmospheric Hg. The most striking result of our measurements is that the odd-mass isotopes (^{199}Hg and ^{201}Hg) are deficient in the peat cores relative to the even-mass isotopes (^{198}Hg, ^{200}Hg, ^{202}Hg, ^{204}Hg). Mass-independent fractionation (MIF) of mercury isotopes can arise either from smaller nuclear volumes of odd-mass relative to even-mass isotopes (Nuclear Volume Effect, NVE), or from the magnetic isotope effect (MIE) due to the non-zero nuclear spin of odd-mass isotopes. A sample of Spanish moss exhibited MIF effects with nearly equal ^{199}Hg and ^{201}Hg depletions up to 1 ‰, while the ^{199}Hg and ^{201}Hg depletions recorded in the peat core are smaller, <0.4 ‰ (Ghosh et al., 2008). Variations in the slope of the correlation between $\Delta^{199}Hg$ and $\Delta^{201}Hg$ provide constraints on the relative contributions of NVE and MIE, with the magnetic isotope effect appearing to be the dominant source of MIF (Ghosh et al., 2008).

Conclusions

We report precise Hg isotope compositions for Hg from peat cores that reveal the presence of mass independent isotope fractionation effects that can be used as tracers of either distinct sources of Hg or of distinct processes, *e.g.*, photochemical oxidation or binding of elemental Hg to organic matter.

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References

Ghosh, S. *et al*. Geochemistry, Geophysics, Geosystems, in press (2008).