Fractionated Mercury Isotope in Sediments: A quest for processes

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Introduction

Analyses of mercury isotopes in sediments from lakes and oceans have revealed mass independent fractionation (MIF) effects. Sediments form an important sink for mercury in natural water. MIF of Hg isotopes can provide constraints on models of Hg cycling in aquatic systems.

Experiment

Approximately 1-2 gm of wet sediment is dissolved in 5-7 ml of aquaregia for 24 hours and filtered. The sample solution was diluted and reduced with SnCl$_2$ in a hydride generator and Hg(0) vapor was measured in a Thermo-Finnigan Neptune MC-ICPMS. Isotope ratios $^{199}$Hg/$^{202}$Hg, $^{199}$Hg/$^{202}$Hg, $^{200}$Hg/$^{202}$Hg, $^{200}$Hg/$^{202}$Hg and $^{204}$Hg/$^{202}$Hg have been measured, using a standard-sample bracketing technique. Sample isotope ratios are measured relative to the NIST SRM 3133 mercury standard. When corrected for mass dependent fractionation, only values for $^{199}$Hg/$^{202}$Hg and $^{201}$Hg/$^{202}$Hg yield non-zero residuals. These residuals are expressed as $\Delta^{199}$Hg and $\Delta^{201}$Hg respectively and have negative or positive values indicating depletion or enrichment.

Results

Lake Erie and Yucatan limestone are enriched in the odd A isotopes (0.06 ‰ to 0.5 ‰). The absolute value of enrichment/depletion generally increases with the depth of the sediment but is not correlated with the total concentration of Hg in the sediments. The primary species of Hg in sediments are Hg(II) and MeHg. The former is scavenged from the water column because of its high reactivity with particulates and MeHg is produced in the anaerobic sediments by sulfate reducing bacteria. Lab experiments have shown that photo-reduction of Hg(II) and MeHg in water yields residual water enriched in the odd_A isotopes (positive $\Delta^{199}$Hg and $\Delta^{201}$Hg) and liberates elemental Hg that should be depleted in $\Delta^{199}$Hg and $\Delta^{201}$Hg (Bergquist and Blum, 2007).

Discussion

Lake Erie and Yucatan sediments might have a large proportion of Hg derived from the water column that retain the odd A isotope enrichment signature. Florida lake and spring sediments were highly enriched in organics and exhibit negative values of $\Delta^{199}$Hg and $\Delta^{201}$Hg (Figure 1). Likely, some of the Hg is associated with the organics as well. The slight depletion of the odd N isotopes in these sediments might be due to the organics, mostly plant materials that derive their $^{199}$Hg and $^{201}$Hg depletion from the atmosphere and they overwhelm the proportion of enriched $^{199}$Hg and $^{201}$Hg signature that comes from the adsorped Hg(II) in water. From the range of values of the $\Delta^{201}$Hg/$\Delta^{199}$Hg ratios, we infer multiple isotope effects responsible for the MIF, as we have reported in fish tissue (Das and Odom, 2007) and as inferred by Ghosh et al. (2008).

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References