

Mass-independent fractionation of Hg isotopes resulting from photochemical self-shielding

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Compact fluorescent lightbulbs (CFLs) are a growing source of Hg pollution. The high-energy environment of the CFLs combined with the known partitioning of Hg into the bulb wall could provide an environment for unusual isotope fractionation that could be used to trace pollution from improper bulb disposal. To investigate this possibility, we analyzed the isotope composition of Hg in CFL glass, phosphor powder, and whole bulbs from CFLs of known ages.

We observed large, mass-independent fractionation of Hg isotopes between Hg embedded in the bulb wall or adsorbed to the phosphor powder and Hg in the liquid and vapor phases, which are the initial reservoir of Hg in the bulb. This fractionation results in enrichment of ¹⁹⁸Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, and ²⁰⁴Hg relative to ²⁰²Hg, the most abundant isotope. Both the amount of Hg embedded in the glass and the magnitude of the isotope enrichment were found to increase with the number of hours of light bulb use. For a CFL used for 3600 hours (with a rated lifetime of 10, 000 hours), the isotopic composition of the Hg in the glass was enriched by 21.8‰, 0.9‰, 3.2‰, 13.6‰, and 9.5‰ for ¹⁹⁸Hg/²⁰²Hg, ¹⁹⁹Hg/²⁰²Hg, ²⁰⁰Hg/²⁰²Hg, ²⁰¹Hg/²⁰²Hg, and ²⁰⁴Hg/²⁰²Hg, respectively, compared to NIST SRM-3133.

This pattern of isotope enrichments is not correlated with mass differences for any of the isotope ratios. In contrast, the other mass-independent effects that have recently been observed in Hg isotopes (i.e. the nuclear volume and magnetic isotope effects) resemble mass-dependent fractionation for the even mass isotopes and are anomalous only for the odd mass isotopes, ¹⁹⁹Hg and ²⁰¹Hg. The fractionation observed here is generally consistent with photochemical self-shielding, which predicts that the most abundant isotope will be the least likely to become ionized. As a result, ²⁰²Hg becomes enriched in the liquid/vapor phase, while all other isotopes become enriched in the glass phase.

Archaeal communities of the Lost City Hydrothermal Field

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The Lost City Hydrothermal Field (LCHF), at 30°N near the Mid-Atlantic Ridge, hosts numerous carbonate-brucite chimneys that are venting pH 9-11, 28-91°C fluids with high concentrations of H₂ (up to 14.4 mmol/kg) and CH₄ (1-2 mmol/kg) derived from serpentinization reactions [1, 2]. Identified archaeal communities include CH₄-cycling Lost City *Methanococcaceales* (LCMS) and ANME-1, which flourish in active and inactive chimneys, respectively, while *Thermococcales* and *Crenarchaeota* appear to belong to the subseafloor microbial communities [3, 4].

The membrane structures of archaea likely reflect physiological adaptation to environmental conditions, such as pH, temperature, nutrient availability, source of energy and/or O₂ levels. Here, we present a study of archaeal membrane lipids of surface samples from actively venting carbonate-brucite towers. They provide a unique opportunity to study metabolic and biochemical processes at the interface between hydrothermal fluids and seawater.

The archaeal lipids include isoprenoid glycerol di- and tetraethers as well as C₂₀, C₂₅, and C₃₀ isoprenoid hydrocarbons. Their carbon isotope compositions ($\delta^{13}\text{C}$ values) vary from -13.9‰ up to +24.6‰, the latter value being by far the highest $\delta^{13}\text{C}$ value ever recorded for a lipid biomarker. We propose that the distributions and $\delta^{13}\text{C}$ values of archaeal biomarkers reflect variability in archaeal assemblages within the LCMS phylotype and in the environmental conditions prevailing in the outer part of the chimneys. Three stages of development of the LCMS biofilm can be distinguished and are discussed in relation to the steep chemical gradients and evolution of hydrothermal fluid flow associated with aging of the carbonate-brucite structures.

- [1] Kelley *et al.* (2005) *Science* **307**, 1428–1434
- [2] Proskurowski *et al.* (2008) *Science* **319**, 604–607
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