New insight into Mercury biogeochemistry from Mercury stable isotopes

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Variation in the natural abundance of mercury isotopes has recently emerged as an important research tool and has shed new light on many long-standing problems in mercury biogeochemistry. Research is progressing on several fronts including: 1) the systematic determination of Hg isotope fractionation factors for important biotic and abiotic reactions, 2) the application of Hg isotope measurements to the tracing of specific Hg sources in the environment, and 3) the application of Hg isotope measurements to investigating Hg biogeochemical transformations in the environment.

Mercury isotope fractionation has been observed to result from both the classical isotope effect and the magnetic isotope effect [1]. The classical isotope effect depends on the nuclear mass selectivity of reactions and is mass dependent (MDF, reported as δ^{202}Hg), whereas the magnetic isotope effect depends on the nuclear spin selectivity of certain reactions and is mass independent (MIF, reported as Δ^{199}Hg and Δ^{201}Hg) [1]. MDF has been quantified for a wide range of biotic and dark abiotic reactions and is particularly useful in tracing specific sources of Hg pollution in rivers, lakes and estuaries. MIF has been quantified for photochemical radical-pair reactions involving DOC in aquatic systems [1] and for photochemical radical-pair reactions involving halogens in snow [2], and is finding use as a measure of the degree of photochemical reduction of Hg (II) and MeHg in the environment. The ratio of MDF to MIF and the ratio of Δ^{199}Hg to Δ^{201}Hg hold great promise for elucidating the nature of reaction mechanisms for important reactions that control the mobility and toxicity of mercury [1-3].

Some of the recent applications and future directions for mercury isotope research will be discussed. Particular emphasis will be placed on studies addressing the sources of Hg to open-ocean fisheries and the question of whether significant amounts of Hg are methylated in the open ocean [4]. Recent findings on atmospheric Hg isotopes and how they can be used to investigate transport to, and deposition of, mercury to arctic regions [2] will also be discussed.

[1] Bergquist & Blum (2009) *Elements* **5**, 353–357. [2] Sherman *et al.* (2010) *Nature Geosci.* doi,10.1038/ngeo758. [3] Zheng & Hintelmann (2009) *GCA* **73**, 6704–6715. [4] Senn *et al.* (2010) *ES&T* doi,10.1021/es902361j.

Mercury isotopes in the late Archean Mount McRae Shale

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The Mount McRae shale in Australia displays peaks in Mo and Re concentration interpreted to have resulted from the input of O_2 to the Earth's atmosphere and oceans in the Archean, ~50 million years before the 2.22 to 2.45 Ga Great Oxidation Event [1]. This allows investigation of whether the biogeochemistry of Hg recorded in its concentration [Hg] and both mass dependent fractionation (MDF, δ^{202}Hg) and mass independent fractionation (MIF, Δ^{199}Hg) was different in an anoxic world, and whether the Hg record is consistent with the hypothesis of O_2 addition to the atmosphere and oceans.

MDF of Hg has been observed during biotic, dark abiotic and photochemical reactions, whereas MIF of Hg has been observed during photochemical radical pair reactions [2]. Hg exists in the present-day atmosphere as gaseous Hg (0) with a residence time of ~1 year, and is deposited only after atmospheric oxidation to Hg (II). The most important atmospheric oxidant is believed to be O_3, although halogens can be important in areas of strong marine influence. Hg is oxidized from crustal sulfides by O_2, and complexes strongly with organic matter during riverine transport.

We analyzed 20 samples of the McRae shale for [Hg] and isotopic composition. [Hg] displays a sharp peak rising from ~250 ppb to ~1550 ppb and then dropping back to ~250 ppb in sync with the Mo and Re peaks. Δ^{199}Hg for these samples shifts from +0.15‰ before the Mo and Re peaks to ~0‰ and then remains at this value. δ^{202}Hg shifts from -0.85 to -1.0 at the time of the Mo and Re peaks. Before the purported O_2 input MIF and MDF were identical to Pleistocene organic-rich sediments from the Meditteranean [3], suggesting a similar degree of photochemical Hg reduction in the Archean anoxic atmosphere. The shifts in [Hg], δ^{202}Hg, and Δ^{199}Hg in sync with the Mo and Re peaks can be explained by oxidative weathering of crustal or submarine sulfides, which would have enhanced delivery of Hg to the ocean and overwhelmed the photochemical Hg MIF signal with crustal or mid-ocean hydrothermal [4] sources.

[1] Anbar *et al.* (2007) *Science* **317**, 1903–1906. [2] Bergquist & Blum (2007) *Science* **318**, 417–420. [3] Gehrke *et al.* (2009) *GCA* **73**, 1651–1665. [4] Sherman *et al.* (2009) *EPSL* **279**, 86–96.