Mercury isotope fractionation during abiotic transmethylation reactions

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Experiments modeling abiotic methylation of mercury were performed by using methylcobalamin, methyltin, acetic acid and dimethylsulfoxide as the methyl donor compounds. Mercury isotope ratios were measured by using multi-collector ICP-MS for both methylmercury and inorganic Hg(II). Abiotic methylation of mercury in the dark was accompanied by mass-dependent Hg isotope fractionation with isotope fractionation factors, product/substrate, ranging from 0.9985 to 0.9995 in terms of delta 202/198Hg values and with undetectable Hg isotope anomalies. The radical substitution reactions releasing a methyl radical in solution in the dark facilitated formation of methylmercury and increased the magnitude of the concomitant mass-dependent Hg isotope effect but were not capable of producing any measurable mass-independent anomaly in the isotopic composition of mercury. In contrast to methylation in the dark, photochemical methylation of mercury was accompanied by both mass-dependent and mass-independent Hg isotope fractionation. The latter resulted in selective enrichment of the 199Hg and 201Hg isotopes in methylmercury and was attributed to the magnetic isotope effect. These data highlight the fact that the light-assisted methylation of mercury produces a unique mass-independent Hg isotope signature that can be used in tracing the origin of this highly toxic compound.