



# Mass-independent fractionation of even mercury isotopes

Hongming Cai · Jiubin Chen

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**Abstract** Practically all physical, chemical, and biological processes can induce mass-dependent fractionation of mercury (Hg) isotopes. A few special processes such as photochemical reduction of Hg(II) and photochemical degradation of methylmercury (MeHg) can produce mass-independent fractionation (MIF) of odd Hg isotopes (odd-MIF), which had been largely reported in variable natural samples and laboratory experiments, and was thought to be caused by either nuclear volume effect or magnetic isotope effect. Recently, intriguing MIF of even Hg isotopes (even-MIF) had been determined in natural samples mainly related to the atmosphere. Though photo-oxidation in the tropopause (inter-layer between the stratosphere and the troposphere) and neutron capture in space were thought to be the possible processes causing even-MIF, the exact mechanism triggering significant even Hg isotope anomaly is still unclear. Even-MIF could provide useful information about the atmospheric chemistry and related climate changes, and the biogeochemical cycle of Hg.

**Keywords** Mass-independent fractionation · Even mercury isotopes · Processes producing even-MIF · Mechanisms triggering even-MIF · Self-shielding · Neutron capture

## 1 Introduction

Mercury (Hg) is a globally distributed and highly toxic pollutant [1–3]. It virtually exists in all natural ecosystems on earth. In recent years, more and more Hg has been emitted into earth's biogeochemical system by human activities such as the burning of fossil fuel and cement production [4]. Unlike other heavy metals, Hg has a stable gaseous form ( $\text{Hg}^0$ ) that has a residence time of  $\sim 1$  year in the atmosphere [5, 6]. Thus, Hg released by point sources can be transported far from the sources in the atmosphere and may affect the ecosystems even in remote regions after deposition (e.g., the Arctic and Antarctic) [7–12]. More importantly, mercury can be methylated into neurotoxic and bioaccumulative methylmercury (MeHg), which can pose serious threat to the human health via fish or rice consumption [13–15]. Therefore, it is critical to fully understand the source, transformation, and fate of Hg in the environment in order to appropriately target the remediation of Hg contamination and maintain emission of Hg at the sustainable levels [16]. Although significant progress has been made in previous research on Hg biogeochemical cycle, many processes involved in Hg transformation and dispersion in variable ecosystems still remain unidentified or unquantified. Some new approaches are thus needed to be developed for better understanding the conundrums of identifying Hg source and ascertaining Hg fate in the environment. The recently developed Hg stable isotope method sheds new insight into tracing pollution sources and behavior of Hg in nature [7, 17–21].

To date, more than 100 papers have been published on Hg isotope ratios, which demonstrated the potential of Hg isotope in tracing the source, processes and the fate of Hg in the atmosphere, biosphere, lithosphere, and hydrosphere [22].

H. Cai · J. Chen (✉)  
State Key Laboratory of Environmental Geochemistry,  
Institute of Geochemistry, Chinese Academy of Sciences,  
Guiyang 550081, China  
e-mail: chenjiubin@vip.gyig.ac.cn

H. Cai  
University of Chinese Academy of Sciences, Beijing 100049,  
China

These studies have reported very large mass-dependent fractionation (MDF,  $\delta^{202}\text{Hg}$ ) of Hg isotopes in natural samples (up to 20 ‰ of  $\delta^{202}\text{Hg}$ ) due to its active chemical property. In addition to MDF, recent studies reported significant mass-independent fractionation (MIF,  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$ ) of odd Hg isotopes (odd-MIF) in natural samples, rendering Hg, a heavy metal having significant MIF in nature [3, 7, 23–25]. The magnetic isotope effect (MIE) and the nuclear volume effect (NVE) are thought to be the most possible mechanisms causing such odd-MIF [3, 26–35]. Unlike MDF, only a few processes can cause odd-MIF, such as photochemical reduction, abiotic dark reduction, evaporation, and photodegradation [3, 30, 31, 34].

Intriguingly, MIF of even isotopes (even-MIF) has recently been observed mainly in atmospheric samples (up to +1.24 ‰) [24, 36–42]. Since no even-MIF was reported in laboratory experiments up to now and the two causes of odd-MIF (MIE and NVE) unlikely produce significant even-MIF [27, 32, 36, 38, 43], the mechanisms and the processes triggering even-MIF remain unclear. Interestingly, only samples related to the atmosphere display such even isotope anomaly, indicating the potential of even-MIF as a useful tracer of upper atmosphere contribution.

Several papers have previously reviewed Hg isotope systematics [7, 20–22, 44–46]. Here, we give a careful review of publications on even Hg isotope anomalies, with a main focus on sample strategies and possible processes and mechanisms triggering MIF of even Hg isotopes. Our newly measured results from Tibetan and Guiyang precipitation were also added in the data set to show that even-MIF is a phenomenon largely distributed in the world.

## 2 Mercury isotope ratio nomenclature

Hg has seven stable isotopes:  $^{196}\text{Hg}$ ,  $^{198}\text{Hg}$ ,  $^{199}\text{Hg}$ ,  $^{200}\text{Hg}$ ,  $^{201}\text{Hg}$ ,  $^{202}\text{Hg}$ , and  $^{204}\text{Hg}$ , with approximate abundance of 0.155 %, 10.04 %, 16.94 %, 23.14 %, 13.17 %, 29.73 %, and 6.83 %, respectively. Mass-dependent fractionation (MDF) refers to the fact that the distribution of different Hg isotopes in variable materials or phases is proportional to their isotopic masses during the physical, chemical, and biological processes. The MDF of Hg isotopes is expressed as  $\delta$  (‰) notation defined as:

$$\delta^x\text{Hg} = \left[ \frac{(^x\text{Hg}/^{198}\text{Hg})_{\text{sample}}}{(^x\text{Hg}/^{198}\text{Hg})_{\text{std}}} - 1 \right] \times 1000, \quad (1)$$

where  $x$  represents 199, 200, 201, 202, and 204 amu, std is the international NIST SRM 3133 standard suggested by Blum and Bergquist [47].

The MIF refers to any chemical or physical process that aims to separate isotopes, where the amount of separation

is not in proportion to different mass of the isotopes [48]. MIF is reported in “capital delta” notation ( $\Delta^x\text{Hg}$ ; the deviation from MDF in units of per mil, ‰), calculated from the differences between the measured isotope value and the theoretically predicted isotope value using the MDF fractionation law:

$$\Delta^{199}\text{Hg} = \delta^{199}\text{Hg} - 0.252 \times \delta^{202}\text{Hg}, \quad (2)$$

$$\Delta^{200}\text{Hg} = \delta^{200}\text{Hg} - 0.502 \times \delta^{202}\text{Hg}, \quad (3)$$

$$\Delta^{201}\text{Hg} = \delta^{201}\text{Hg} - 0.752 \times \delta^{202}\text{Hg}, \quad (4)$$

$$\Delta^{204}\text{Hg} = \delta^{204}\text{Hg} - 1.493 \times \delta^{202}\text{Hg}. \quad (5)$$

Blum and Bergquist [47] had measured the isotopic composition of UM-Almaden and suggested that all laboratories adopt UM-Almaden as a secondary standard to get consensus values and correct the analytical bias.

## 3 Mainstream observation of odd-MIF

The odd-MIF were reported in a large set of environmental, geological, and biological samples, including atmospheric samples [23–25, 36–39, 42, 49, 50], sediments [49, 51–67], soils [37, 68–70], peats [71], rocks [72], coals [24, 68, 73, 74], mosses and lichens [50, 75–77], human hairs [78–80], plants [37, 50, 81], fishes [3, 62, 78, 80–83], and even seabirds [53, 84]. Blum et al. [22] have given a detail description of these data in a recent review article.

The odd-MIF has been proven to occur in laboratory experiments. Bergquist and Blum [3] firstly studied Hg isotopic fractionation during the photoreduction of Hg(II) and photodegradation of MeHg. Their results showed that the residual Hg(II) was enriched in odd Hg isotopes. Zheng and Hintelmann [33] found that the photoreduction of Hg(II) was controlled by Hg/DOC ratio, and the reactant Hg(II) was enriched in  $^{199}\text{Hg}$  and  $^{201}\text{Hg}$ . Different types of ligands may induce opposite magnetic isotope effects during photochemical processes. For example, Zheng and Hintelmann [35] showed that during the photochemical processes of S-containing ligands, magnetic isotopes ( $^{199}\text{Hg}$  and  $^{201}\text{Hg}$ ) were specifically enriched in the product ( $\text{Hg}^0$ ) rather than in the reactant Hg(II). Odd-MIF was also reported in abiotic processes. During the evaporation of liquid Hg, a small positive  $\Delta^{199}\text{Hg}$  was observed in gaseous elemental Hg ( $\text{Hg}^0$ ) [31, 32]. Zheng and Hintelmann [34] also reported a small positive odd-MIF in the reactant during the abiotic dark reduction of Hg(II).

Unlike MDF of Hg isotopes that occur in most of equilibrium and kinetic processes, odd-MIF has only been found in several specific processes (see above discussion). The nuclear volume effect and the magnetic isotope effect were thought to be the two possible mechanisms triggering odd-

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