Review

Application of the stable-isotope system to the study of sources and fate of Hg in the environment: A review

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ARTICLE INFO

ABSTRACT

With the improvement of analytical methods and the development of multiple-collector inductively coupled plasma-mass spectrometry (MC-ICP/MS), research on non-traditional stable isotope (Cu, Zn, Fe, Se, Mo, Cr, Hg) in geochemistry has made tremendous progress in the past decade. Recent studies have demonstrated that both organic and inorganic reactions may cause Hg isotope fractionation, and variations of Hg isotopic composition in the environment have been successfully employed to explain Hg pollution history, Hg sources and tracking Hg pathways in nature. Furthermore, Hg isotopic fractionation studies can be a powerful tool in the calibration of global Hg cycling models. Stable isotope geochemistry of Hg is therefore becoming a new frontier subject in earth sciences. Based on summarizing previous research, this paper outlines the main advances in the study of Hg stable isotopes with particular emphasis placed on a brief explanation of Hg isotope analytical techniques, possible Hg isotope fractionation mechanisms observed in both natural and experimental processes, Hg isotope composition variations in different environmental matrices, and the application prospects of the Hg stable isotopes in environmental geosciences.

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1. Introduction

Mercury is a globally distributed and extremely toxic pollutant (Fitzgerald et al., 1998; Lamborg et al., 2002a). Both inorganic and methylated Hg (MeHg) species have severe health effects on biota. Among the different species of Hg, MeHg is of utmost concern to public health because of its ability to get bioaccumulated in fish (Clarkson, 1993). Exposure of Hg to humans may cause damage to the central nervous system, heart and immune system (US EPA, 1997).

The sources and fate of Hg need to be fully understood so that remediation is appropriately targeted and emissions are maintained at sustainable levels (Weiss et al., 2008). Both anthropogenic sources, coal combustion (Anthoni, 1997; Feng et al., 2002; Wang et al., 2000; Hassett et al., 2004), waste incineration (Ferraz and Afonso, 2003; Mukherjee et al., 2004), metal refining and manufacturing (Feng et al., 2004a; Streets et al., 2005; Wu et al., 2006) and chlor-alkali production (Qi et al., 2000; Landis et al., 2004; Southworth et al., 2004), and natural processes, geothermal activity (Ferrara et al., 2000; Loppi, 2001; Nriagu and Becker, 2003), evasion from surficial soils (Gustin, 2003; Gustin et al., 2003), water bodies (Lindberg and Zhang, 2000; Mason et al., 2001; Zhang and Lindberg, 2001; Gardfeldt et al., 2003; Feng et al., 2005), vegetation surfaces (Lindberg et al., 2008; Feng et al., 2004b), wild fires (Brunke et al., 2001; Ericksen and Gustin, 2004), re-emission of deposited mercury (Schroeder and Munthe, 1998), transport Hg to the environment. The global-scale sources, sinks, rates and loads of Hg in the surficial environment have been established generally (Mason et al., 1994). The global anthropogenic Hg emission to the atmosphere is estimated to be 2200 tons a^{-1} (Pacyna et al., 2006), and the global natural Hg emission of 1800–5800 tons a^{-1} (Bergan et al., 1999; Shia et al., 1999; Mason and Sheu, 2002; Lamborg et al., 2002b; Gustin, 2003). Such a significant yet uncertain emission quantity can considerably influence model results for atmospheric Hg (Lin et al., 2006, 2007; Gbor et al., 2007).

Great progress has been made towards establishing the geochemistry of non-traditional stable isotopes (Cu, Zn, Fe, Se, Mo, Cr, Hg) by the development of multiple-collector inductively coupled plasma-mass spectrometry (MC-ICP/MS) in the past decade. Investigations of isotopic variations of these elements have provided important information on a range of problems including planetary geology, the origin and evolution of life, crust and mantle evolution, climate change, and the genesis of natural resources (Johnson et al., 2004). Mercury has an active redox chemistry, volatile inorganic (Hg^0) and organic [(CH$_3$)$_2$Hg], and a tendency to form covalent bonds, thus kinetic effects may also play an important role in Hg isotopic fractionation(Fein and William-Jones, 1997; Smith et al., 2005; Bergquist and Blum, 2007). Research on the Hg isotope system is becoming more and more popular in tracking and quantifying Hg pathways during biogeochemical processes. The first ever session on stable Hg isotopes was held during the recent 9th International Conference on Mercury as a Global Pollutant, where 10 reports and 16 submitted abstracts were dedicated to natural Hg isotope variations (http://www.mercury2009.org/).

This paper summarizes the main advances in the study of Hg stable isotopes with particular emphasis placed on a brief explanation of Hg isotope analytical techniques, possible Hg isotope fractionation mechanisms observed in both natural and experimental processes, Hg isotope composition variations in different environmental matrices, and the application prospects of Hg stable isotopes in environmental geosciences.

2. Mechanisms of fractionation and notion nomenclature

The basics of stable-isotope fractionation are well established and reviewed elsewhere (Criss, 1999; Hoefs, 2004), for Hg, the most important principles are summarized. Because isotope variations in nature are small, differences are expressed as ‰ deviations relative to a reference standard in δ unit, where $\delta > 0$ is considered heavy and $\delta < 0$ light, if the heavier isotope is in the numerator.

$$\delta^{xxx}\mathrm{Hg}(‰) = \left\{ \left[\frac{{}^{xxx}\mathrm{Hg}/{}^{198}\mathrm{Hg}_{\mathrm{sample}}}{{}^{xxx}\mathrm{Hg}/{}^{198}\mathrm{Hg}_{\mathrm{NISTSRM3133}}} \right] - 1 \right\} \times 1000$$

where xxx is the mass of a Hg isotope between 196 and 204 amu (Blum and Bergquist, 2007). There is currently no Hg standard with an isotopic composition certified with adequate accuracy for reference in natural Hg isotope studies. Individual laboratories have used in-house standards to calculate ‰ deviations, for example ERM AE639, NIST-1641d, NIST-1641c, NIST-3133. Blum and Bergquist (2007) have compared several of these reference standards, with NIST-3133, which is distributed as a 10.00 ± 0.02 mg/g solution in 10% HNO$_3$, being thought to be an ideal universally adopted Hg isotope reference standard because of its low matrix effects.

The partitioning of stable isotopes of a certain element between two substances, A and B, is described by the isotopic fractionation factor α:

$$\alpha_{A/B} = R_A/R_B$$

where R_A and R_B are the ratios of the heavy to light isotopes in the molecules or phases A and B, respectively. Because α is very close to 1, the very useful relationship:

$$10^3 \ln \alpha_{A/B} \approx \delta_A - \delta_B = \Delta_{A-B}$$

is derived, where Δ_{A-B} is the fractionation between phases A and B, reflecting equilibrium or kinetic partitioning.

Equilibrium fractionation arises during isotope exchange when the forward and backward reaction rates of the isotope that lead to isotope redistribution are identical. Kinetic fractionation occurs when the reaction is unidirectional and reaction rates are mass-dependent. Fractionation exists because bonds with the lighter isotope and lower atomic mass are broken faster. A very important kinetic fractionation process—Rayleigh distillation fractionation (RDF)—occurs when reaction products are irreversibly separated from the reactant reservoir, potentially leading to extreme fractionation (Weiss et al., 2008).

Mass-independent fractionation (MIF) for Hg has been predicted on the basis of nuclear field shift theory (Bigeleisen, 1996; Schauble, 2007) and the magnetic isotope effect (Buchachenko

et al., 2004, 2007). In these instances, $\delta^{202}Hg$ is used to determine the predicted mass-dependent values of $\delta^{204}Hg$, $\delta^{201}Hg$, $\delta^{200}Hg$ and $\delta^{199}Hg$ using a kinetic mass-dependent fractionation law. MIF is reported in "capital delta" notation ($\Delta^{xxx}Hg$, deviation from mass dependency in units of permil, ‰) and is the difference between the measured $\delta^{xxx}Hg$ and the theoretically predicted $\delta^{xxx}Hg$ value using the following formulas (Blum and Bergquist, 2007):

$$\Delta^{204}Hg \approx \delta^{204}Hg - (\delta^{202}Hg * 1.493)$$
$$\Delta^{201}Hg \approx \delta^{201}Hg - (\delta^{202}Hg * 0.752)$$
$$\Delta^{200}Hg \approx \delta^{201}Hg - (\delta^{202}Hg * 0.502)$$
$$\Delta^{199}Hg \approx \delta^{199}Hg - (\delta^{202}Hg * 0.252)$$

To evaluate and compare the isotope data obtained in different laboratories, Blum and Bergquist (2007) suggested that all laboratories adopt an in-house secondary standard solution (UM-Almadén) to report the analytical uncertainties. For different environmental matrices, Estrade et al. (2010) also provided creditable Hg isotope values of several reference materials.

3. Mercury isotope analytical techniques

Stable Hg isotope analysis has a remarkably long history that began almost 100 a ago with the characterization of its isotopes by Aston (1920). Brönsted and von Hevesy (1920) reporting on the fractionation of Hg isotopes by vacuum distillation and pycnometry detection, implied that fractionation of the isotopes in nature was possible. Further Hg isotopic compositions were measured in a series of samples and materials with variable success by several techniques, including Neutron activation analysis (NAA) (Jovanovic and Reed, 1990; Reed and Jovanovic, 1990; Kumar and Goel, 1992), gas-source mass spectrometry (Nier and Schlutter, 1986; Lauretta et al., 2001), Q-ICP–MS (Jackson, 2001), SC-ICP/MS (Klaue and Blum, 2000; Klaue et al., 2000; Evans, 2001; Hintelmann et al., 2001) and ICP-time-of-flight-MS (ICP-TOF-MS) (Jackson, 2001). The results of these studies demonstrated large fractionation of Hg isotopes by natural activities, but are still considered questionable, largely owing to the low precision of these instruments (Lauretta et al., 2001; Foucher and Hintelmann, 2006).

High-precision measurements of Hg isotope ratios are now made mostly by MC-ICP/MS, precision of which is superior to that of both thermal ionization mass spectrometry and SC-ICP–MS (Foucher and Hintelmann, 2006). MC-ICP–MS consist of three major components: an ion source, a mass analyzer, and a detection unit (Weiss et al., 2008). The ion source is a high-temperature plasma, which enables the ionization of elements with high ionization potential, this includes elements such as Hg that were previously impracticable or impossible to analyze. The mass analyzer consists of different focusing setups that reduce the kinetic-energy spread of ions entering the mass spectrometer and focus the ion beam, as well as an electromagnet that separates the ions according to their mass. Finally, the detection unit consists of a collector array, which measures ion beams of different isotopes at the same time, leading to an acceptable precision for ratios. A thorough description of current mass spectrometers can be found elsewhere (Becker, 2005).

3.1. Introduction system

Traditional Hg concentration analysis involves pre-concentration of Hg onto Au traps followed by thermo-reductive desorption (Crock, 1996; Ridley and Stetson, 2006). Sample introduction by thermal release has advantages that include minimum potential contamination by reagents, increased sample throughput, and the possibility of in situ spatially resolved analysis, but it produces a transient signal, often of very short duration to acquire data, which is inherently more difficult to precisely evaluate for isotope ratios. Another problem is the poor external reproducibility for environmental materials, partly due to sample heterogeneity (Xie et al., 2005). Sonke et al. (2008) presented a new off-line technique (Fig. 1a), where amalgamated elemental Hg^0 is volatilized from the Au trap in an Ar gas stream and temporarily stored in a large volume gas tight syringe. Elemental $Hg^0_{(g)}$ contained in the syringe is then injected on-line into the MC-ICP–MS interface using a syringe pump at a continuous flow rate, which results in a steady state Hg signal.

Klaue and Blum (2000) and Klaue et al. (2000) originally introduced cold vapor multi-collector inductively coupled plasma-mass spectrometry as a viable technique for exploring the natural variations in Hg isotope abundance. This approach relies on a continuous generation of Hg^0 vapor by reduction to create a steady and continuous signal (Fig. 1b). In general, such techniques require higher amounts of Hg but tend to greatly improve external precisions of the measurements. The details of the CV generation apparatus have been formerly described (Foucher and Hintelmann, 2006).

3.2. Mass bias correction

3.2.1. Elemental spike

The approach of using an element with mass and ionization potentials close to those of the analyte for mass bias correction has been successfully applied in high precision isotope measurement by MC-ICP–MS, such as Tl for Pb (Albarède and Beard, 2004). Blum and Bergquist (2007) suggested correcting instrumental mass bias by simultaneous measurement of the certified Th isotope standard (NIST-997). Since most high-precision Hg isotope measurements are being made by introduction of a cold Hg vapor into the MC-ICP–MS plasma source, a dry Tl aerosol can be generated using a desolvating nebulizer, mixed with the Hg vapor in a gas–liquid separator, and then simultaneously introduced into the plasma. An exponential fractionation law can be used to determine the instrumental mass bias factor β (Albarède et al., 2004) for Tl, which is subsequently applied to achieve an exponential mass bias correction of Hg isotope abundances.

3.2.2. Sample-standard bracketing

Mass spectrometers favor the transmission of heavy isotopes in preference to lighter ones, and this effect needs to be corrected (Albarède et al., 2004). For the highest precision and accuracy, the simplest technique is standard sample bracketing, in which a Hg bracketing standard is measured before and after each sample. Temporal drift in mass bias is presumed to be constant over a short time period. The bracketing standards can then be used to correct for additional instrumental mass bias by interpolating the instrumental mass bias between the two bracketing standards and applying this correction to the sample (Blum and Bergquist, 2007).

4. Mercury isotope fractionation in natural and experimental processes

Elemental $Hg^0_{(g)}$ has an extended tropospheric residence time entailing global-scale transportation and interhemispherical boundary-layer mixing ratio homogeneities (Schroeder and Munthe, 1998; Johansson et al., 2001). Multiple pathways including anthropogenic sources and emissions through water–air and other natural interfaces result in the transport of Hg^0 to the atmosphere (Cheng and Schroeder, 2000; Temme et al., 2005) (Fig. 2).

Elemental Hg is oxidized in the gaseous phase to inorganic molecular Hg species (RGM) by ozone and reactive halogen spe-
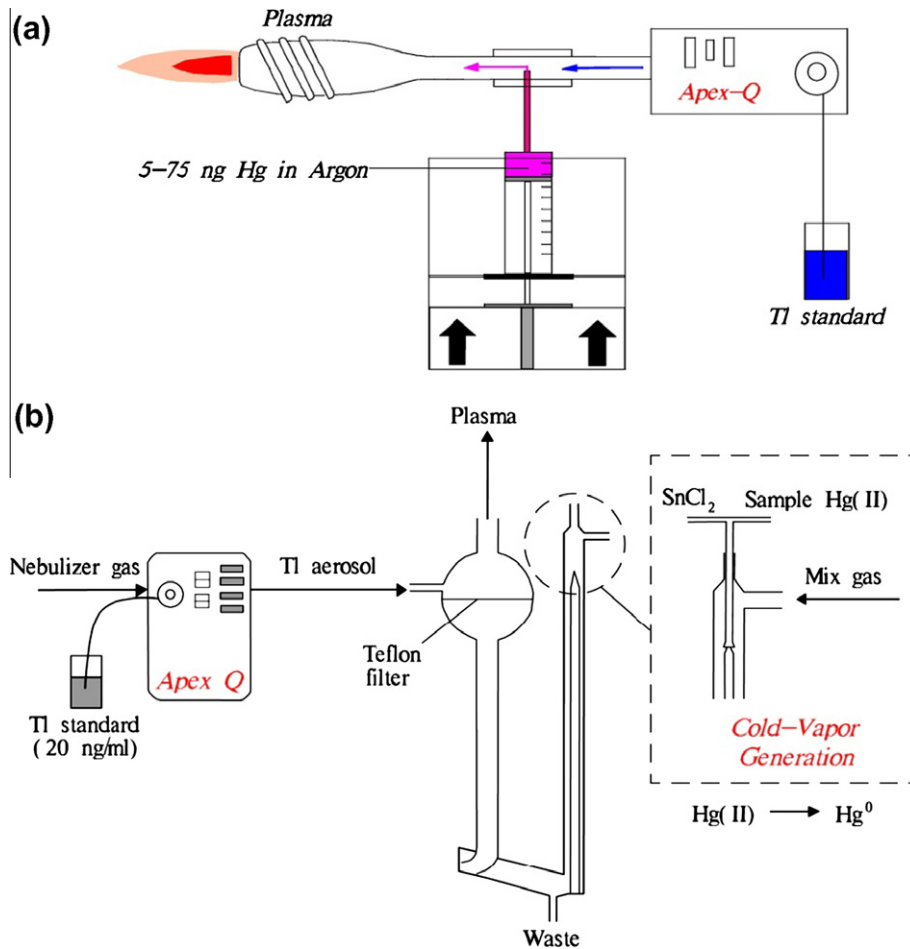
Fig. 1. A schematic of introduction systems for Hg stable isotope analysis. (a) Drawing of the cold vapor syringe injection (CVSI) interface for introduction of gaseous Hg[0] into the MC-ICP–MS (Sonke et al., 2008). (b) Illustration of the sample introduction system for Hg isotope ratio measurements (Foucher and Hintelmann, 2006).
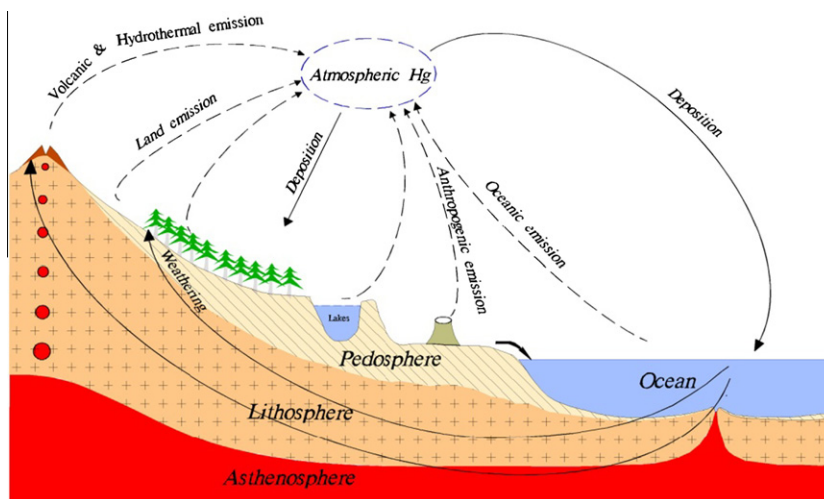
Fig. 2. Conceptual view of the global Hg biogeochemical cycle.

cies, In turn semi-volatile RGM is prone to physical atmospheric removal and becomes deposited to land and oceanic surfaces (Douglas et al., 2008). As depicted in Fig. 3, once deposited into aquatic environments, Hg^{2+} undergoes complexation and transformation,

both by biological and non-biological processes. Aerobic microorganisms which have the capability to make an enzyme called mercuric reductase, can reduce Hg^{2+} to Hg^0. Anaerobic SO_4-reducing bacteria cause methylation of Hg^{2+} to MeHg by non-specific mech-

anisms. Reduction and methylation can also occur abiologically (Morel et al., 1998). But the relative importance of these transformations of Hg is a contested issue (Barkay et al., 2003).

The ability to use stable isotope ratios of Hg as an indicator of Hg biogeochemical processes in environmental management depends on well founded constraints on the extent of fractionation (i.e., values of fractionation factors) during all the transformation processes known to be a part of the global and regional Hg biogeochemical cycles. It can be extremely useful to stipulate which pathway (biological vs. non-biological) regarding Hg in a given environment is the most important, thus helping to direct remediation efforts in an appropriate direction. Recent experimental work and analyses of natural samples have revealed both mass-dependent and mass-independent isotope fractionation effects in Hg (Fig. 4). In studies published to date, fractionation factors ranging from 1.0004 to 1.0067 have been reported (Table 1). The proposed framework helps to explain the variation in the extent of Hg stable-isotope fractionation in natural systems, furthering the promise of Hg isotope ratios as a tool in determining the role of microbial Hg
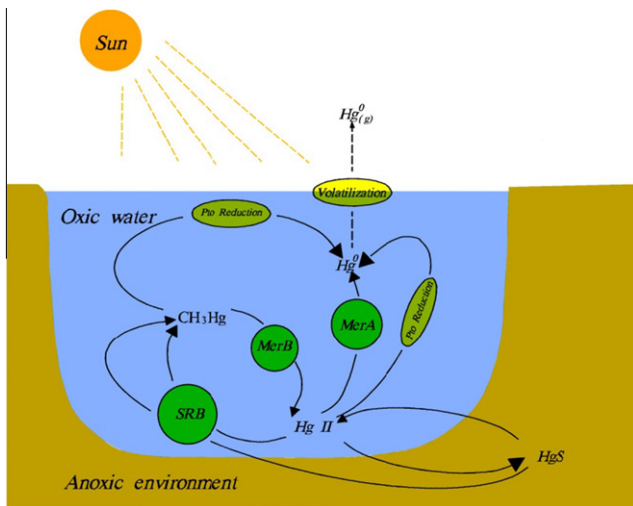

Fig. 3. Hg transformation in aquatic systems (Schaefer et al., 2002).

transformations in the environment. Table 1 provides a general guide to the effects that biogeochemical processes have on isotopic fractionation.

4.1. Reduction

4.1.1. Photo reduction

In the laboratory, Bergquist and Blum (2007) studied photochemical reduction of aqueous Hg^{2+} and $MeHg^+$ by natural sunlight in a quartz reaction vessel with dissolved organic C (DOC), which resulted in MDF of even Hg isotopes. In all the experiments, isotopic fractionation followed Rayleigh-type fractionation in such a way that lighter isotopes were preferentially reduced and removed from the vessel. The rate of the $MeHg^+$ photo-reduction was slower than the rate of Hg^{2+} photo-reduction, but resulted in larger isotopic fractionation ($^{202}\alpha = 1.00130$ and 1.00170) than the Hg^{+2} experiments ($\alpha = 1.00060$). No detectable $MeHg^+$ was reduced during the dark abiotic control experiment, but 20% of the Hg^{2+} was reduced after 300 min in the Hg^{2+} dark control experiments, where the resulting isotopic fractionation was larger than in Hg^{+2} photo-reduction ($\alpha = 1.00200$). This dark abiotic Hg^{2+} reduction probably resulted from organically mediated reactions.

They also observed dramatic MIF (up to 2.5‰) of odd isotopes of Hg in the photochemical reduction. As the photo-reduction of Hg progressed, odd isotopes were preferentially retained in the reactor, where the slower $MeHg^+$ photo-reduction displayed larger MIF than the Hg^{2+} photo-reduction at the same extent of reaction. The relationship between MIF for the two odd isotopes of Hg is significantly different for the two photo-reduction pathways. Plotting $\Delta^{199}Hg$ versus $\Delta^{201}Hg$ reveals a significant difference in the relationship between the two odd isotopes for the photo-reduction of Hg^{2+} ($\Delta^{199}Hg/\Delta^{201}Hg \approx 1.00$) versus $MeHg^+$ ($\Delta^{199}Hg/\Delta^{201}Hg \approx 1.36$) (see Fig. 4). Additionally, the degree of MIF was larger for the higher-DOC experiment. In contrast, there is no MIF displayed in the dark abiotic reduction experiments (Bergquist and Blum, 2007).

4.1.2. Microbial reduction
4.1.2.1. MerA. Kritee et al. (2007) investigated the isotopic fractionation of Hg by Hg^{2+} resistant (HgR) bacteria expressing the mercu-
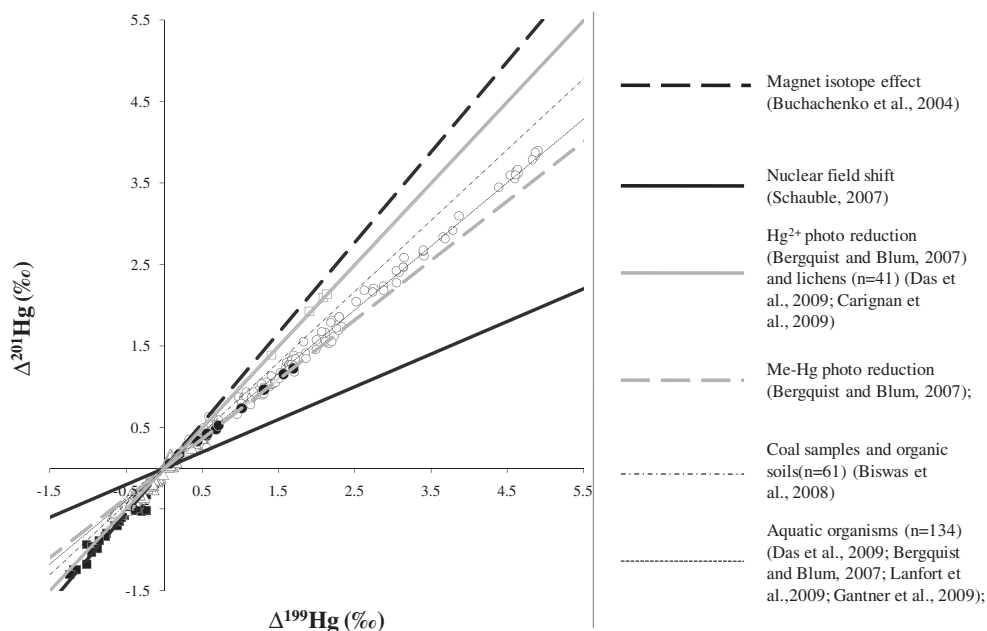

Fig. 4. MIF records in different environmental matrices (based on published data).

Table 1
Direction and magnitude of Hg isotope fractionation during different biogeochemical processes.

Type	A	B	$^{202}\alpha_{A/B}$	Δ_{A-B} (‰)	References
Chemical reactions					
Photo reduction	$CH_3Hg^+_{(aq)}$	$Hg^0_{(g)}$	1.0013–1.0017	0.6	Bergquist and Blum (2007)
Photo reduction	$Hg^{2+}_{(aq)}$	$Hg^0_{(g)}$	1.0006	1.5	Bergquist and Blum (2007)
UV photolysis reduction	$Hg^{2+}_{(aq)}$	$Hg^0_{(g)}$	1.0006	1.34	Yang and Sturgeon (2009)
Dark organically medicated reduction	$Hg^{2+}_{(aq)}$	$Hg^0_{(g)}$	1.0020	1.7	Bergquist and Blum (2007)
Chemical reduction ($SnCl_2$)	$Hg^{2+}_{(aq)}$	$Hg^0_{(g)}$	1.0004	1.17	Yang and Sturgeon (2009)
Chemical reduction ($NaBH_4$)	$Hg^{2+}_{(aq)}$	$Hg^0_{(g)}$	1.0004	1.08	Yang and Sturgeon (2009)
Chemical reduction (ethylation with NaBEt4)	$Hg^{2+}_{(aq)}$	$Hg^0_{(g)}$	1.0012	3.59	Yang and Sturgeon (2009)
Volcanic emission	$Hg^0_{(p)}$	$Hg^0_{(g)}$	1.00135	1.63	Zambardi et al. (2009)
Absorption	$Hg^{2+}_{(aq)}$	$Hg(OH)_2$	–[a]	0.62	Wiederhold et al. (2010)
Biological reactions					
MerA	$Hg^{2+}_{(aq)}$	$Hg^0_{(g)}$	1.0013–1.0020	1.6	Kritee et al. (2007, 2008)
MerB	$CH_3Hg^{2+}_{(aq)}$	$Hg^0_{(g)}$	1.0004	0.4	Kritee et al. (2009)
Methylation	$Hg^{2+}_{(aq)}$	$CH_3Hg^+_{(aq)}$	1.0026	1.0	González et al. (2009)
Physical reactions					
Evaporation	$Hg^0_{(1)}$	$Hg^0_{(g)}$	1.0067	6.5	Estrade et al. (2009)
Volatilization	$Hg^0_{(aq)}$	$Hg^0_{(g)}$	1.0004–1.0005	1.48	Zheng et al. (2007)
Evaporation	$Hg^0_{(1)}$	$Hg^0_{(g)}$	1.0009	0.8	Estrade et al. (2009)

[a] Lack of data.

ric reductase (MerA) enzyme (a gram negative strain Escherichia coli JM109/pPB117) at different temperature. The isotopic composition of both the reactant Hg^{2+} added to the growth medium and volatilized product Hg^0 was measured. In all the cases, these experiments showed reduction preferentially among the lighter isotopes of Hg according to Rayleigh fractionation with the best estimates of α values ranging from 1.0013 to 1.0020. Similarly, Kritee et al. (2008) studied the extent of Hg stable-isotope fractionation during reduction of Hg^{2+} by two Hg(II)-resistant strains, *Bacillus cereus* 5 and the thermophile *Anoxybacillus* sp. FB9 [which actively detoxify Hg(II) by the *mer* system] and a Hg(II)-sensitive metal reducing anaerobe, *Shewanella oneidensis* MR-1 [which reduces Hg(II) at low concentrations]. During experimental reduction of Hg(II), the Hg(II) remaining in the reactor became progressively enriched with heavy isotopes with time and underwent mass-dependent RDF with α value of 1.0016.

4.1.2.2. MerB. Kritee et al. (2009) reported the extent of fractionation of Hg stable isotopes during degradation of MeHg$^+$ to volatile elemental Hg and CH_4 via the microbial Hg resistance (mer) pathway in Escherichia coli carrying a Hg resistance (*mer*) genetic system on a multi-copy plasmid. Following microbial degradation of MeHg$^+$, the MeHg$^+$ remaining in reactors became progressively heavier (increasing $\delta^{202}Hg$) with time and underwent mass-dependent RDF with a fractionation factor α = 1.0004. No MIF was observed in any of the microbial MeHg$^+$ degradation experiments indicating that the isotopic signature left by *mer* mediated MeHg$^+$ degradation is significantly different from fractionation observed during DOC mediated photo-degradation of MeHg$^+$.

4.1.3. Chemical

Yang and Sturgeon (2009) investigated possible Hg isotopic fractionation during the reduction/volatilization process. In the laboratory, volatilization of Hg from the aqueous phase was achieved by chemical reduction of NIST-3133 Hg standard solution with $SnCl_2$ and $NaBH_4$ reductants, by alkylation with $NaBEt_4$ or by UV photolysis. These reactions induced significant isotope fractionation with maximum values of 1.17‰, 1.08‰, 1.34‰, and 3.59‰ for $\delta^{202}Hg$ relative to the initial isotopic composition in the solution following 85–90% reduction of the Hg by $SnCl_2$, $NaBH_4$, UV

photolysis, and ethylation with $NaBEt_4$, respectively. For the even isotopes, MDF was found to be dominant in all reactions studied with relatively small fractionation factors of 1.00043–1.00055 for the reduction experiments and a larger fractionation factor of 1.0012 for the ethylation process.

4.2. Evaporation and condensation

4.2.1. Volatilization

Volatilization plays an important role in the biogeochemical cycle of Hg at various kinds of natural interfaces. Zheng et al. (2007) presented the first systematic investigation of kinetic isotope fractionation during the volatilization of Hg^0 dissolved in aqueous solution to the gas phase. Elemental Hg was generated in situ by reducing Hg^{2+} using $SnCl_2$ and subsequently purged into a trapping solution. The concentration and isotope ratios of Hg in both the trapping solution and the Hg^0 remaining in solution were measured at different time intervals. It was demonstrated that the pattern of isotope fractionation during volatilization following a RDF with an observed maximum $\delta^{202}Hg$ value of 1.48‰. Fractionation factors of 1.00044 and 1.00047 were obtained in two independent experiments.

4.2.2. Evaporation and condensation

Evaporation (distillation) of liquid Hg can take place in a variety of industrial applications such as refining processes. Elemental Hg has an exceptionally high saturation vapor pressure for being a metal element and is easily a subject of liquid–vapor changes. Estrade et al. (2009) investigated liquid–vapor Hg isotope fractionation under equilibrium and dynamic conditions. Equilibrium evaporation experiments were performed in a closed glass system under atmospheric pressure between 0 and 22 °C, showing a constant liquid–vapor fractionation factor of 1.00086. Dynamic evaporation experiments were conducted in a closed glass system under vacuum conditions. Both residual liquid and condensed vapor fractions were analyzed by MC-ICP/MS. The dynamic evaporation experiments displayed RDF behavior with α = 1.0067. The evaporation experiments also resulted in MIF with condensed Hg vapor enriched in odd ^{199}Hg and ^{201}Hg isotopes.

4.3. Volcanic emissions

Zambardi et al. (2009) studied possible Hg isotope fractionation in the active volcanic system of Vulcano Island, Italy. They measured the stable isotopic compositions of Hg in condensate Hg-tot(fum) as well as $Hg^0_{(g)}$ and particulate Hg(p) in the plumes of four fumaroles. Relative to the NIST-3133 Hg standard, the stable isotopic compositions of Hg samples were $\delta^{202}Hg$-tot$_{(fum)}$ = −0.74‰, $\delta^{202}Hg^0_{(g)}$ = −1.74‰, and $\delta^{202}Hg_{(p)}$ = −0.11‰. The enrichment of heavy isotopes in $Hg_{(p)}$ and light isotopes in $Hg^0_{(g)}$ relative to Hg-tot measured in the fumarolic condensate demonstrated that gas-particle fractionation was occurring after the volcanic gas was expelled into the atmosphere. A fit according a first order Rayleigh equilibrium condensation isotope fractionation yielded α = 1.00135.

4.4. Methylation

González et al. (2009) reports novel results on the stable-isotope fractionation of Hg caused by micro-methylation of Hg^{2+} under fermentation conditions. They measured the isotopic composition of Hg^{2+} and $MeHg^+$ in these cultures as a function of time and calculated delta-values for both species versus the starting material (NIST-3133) as a delta-zero standard, and resulted in MDF of the Hg isotopes for both Hg^{II} substrate and produced $MeHg^+$. Such a process occurred under the exponential growth of the bacteria which preferentially methylate the lighter isotopes of Hg. Assuming that RDF happens during micro-methylation, it is equivalent to a α fractionation factor of 1.0026.

4.5. Absorption

The fate and mobility of Hg is strongly influenced by absorption to organic matter. The thiol (mercapto -SH) group are, in quantitative terms, the most dominant complexing entity of Hg^{2+} present in natural organic matter. Wiederhold et al. (2010) reported experimental and computational results on the equilibrium Hg isotope fractionation between dissolved Hg^{2+} species and thiol-bound Hg. Mercuric chloride and nitrate solutions [in the latter $Hg(OH)_2$ is a major species] were equilibrated (24 h, dark) in parallel batches with varying amounts of resin with thiol-functional groups resulting in different fractions of thiol-bound and free Hg. The experimentally determined $\delta^{202}Hg$ revealed that thiol-bound Hg was enriched in the lighter Hg isotopes by 0.55‰ and 0.62‰ relative to dissolved Hg^{2+}. No significant MIF was measured. The result implies that significant equilibrium Hg isotope fractionation may occur in nature without redox transformation taking place.

5. Mercury isotopes in various environmental matrices

Unlike Pb, all 7 natural mercury isotopes (^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, and ^{204}Hg) are stable, there is no radiogenic source of Hg, and any isotopic variation would clearly be the result of fractionation processes (Foucher and Hintelmann, 2006). Using MC-ICP/MS, observations on both terrestrial samples and experimental studies demonstrate substantially large fractionations as high as ∼7‰ (Fig. 5).

5.1. Rocks and hydrothermal ores

Mercury isotopic composition of Hg minerals is mainly determined by the original materials and the processes occurring in the hydrothermal systems. In hydrothermal regions, the hot fluid can be sourced either from a magma or surrounding country rock, where it leaches, concentrates, and transports Hg and other metals from the volcanic rocks, and finally deposits them in epithermal ore deposits as native Hg or a variety of Hg minerals (Smith et al., 2005). Cinnabar is the dominant Hg-bearing ore mineral in Hg mines worldwide, although minor ore minerals such as elemental Hg, meta-cinnabar (β-HgS), calomel (Hg_2Cl_2) and montroydite (HgO) are found in some deposits (Stetson et al., 2009). Hintelmann and Lu (2003) evaluated a worldwide selection of cinnabar samples from epithermal deposits of different ages from a wide variety of geologic settings. The overall variation of $\delta^{202}Hg$ is approximately 1.7‰.
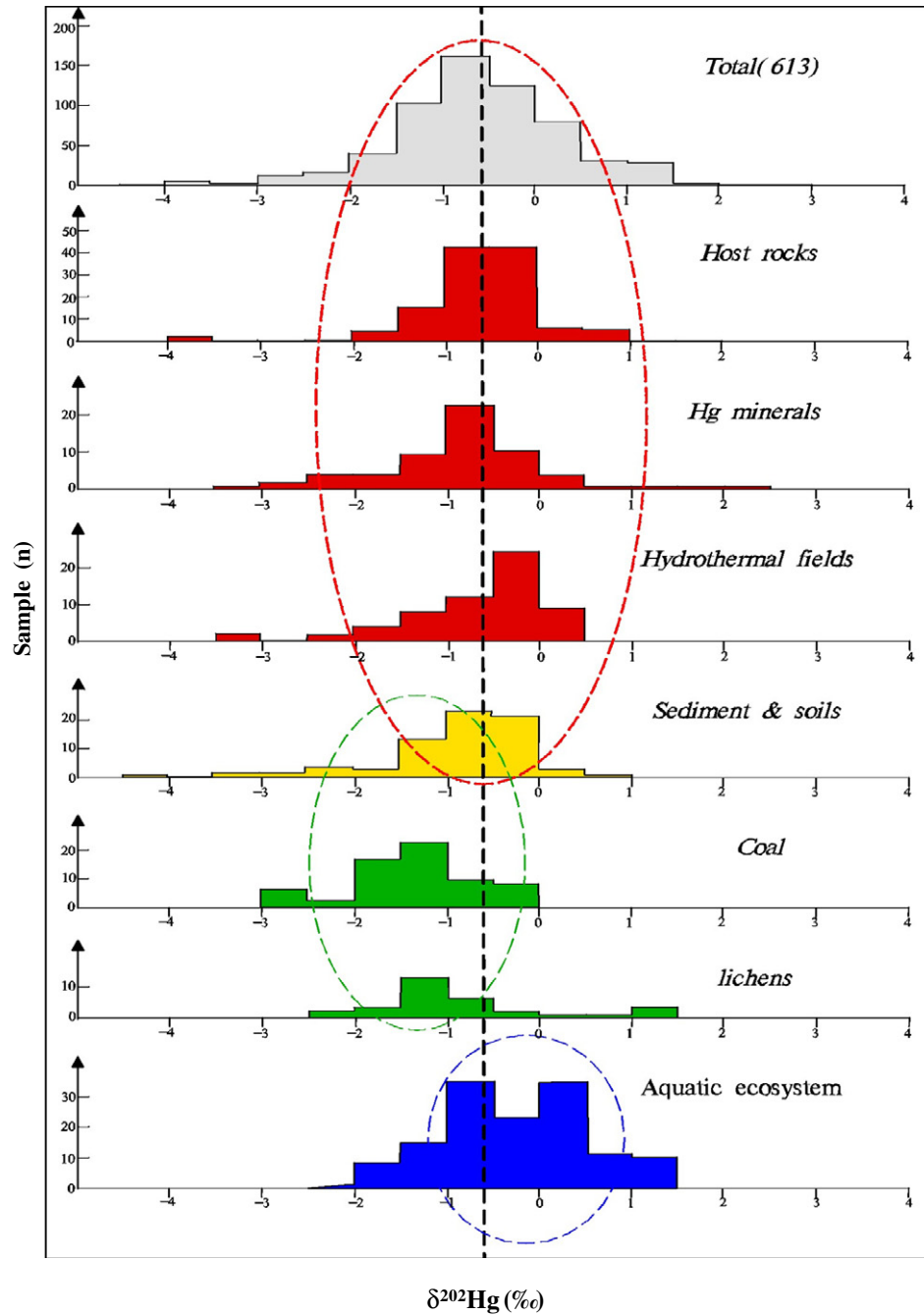
Sherman et al. (2009) found that magmatic processes such as partial melting and magma cooling should fractionate Hg to a lesser degree than lower temperature processes. Smith et al. (2005, 2008) demonstrated that boiling due to decompression and/or fluid mixing produces isotopic fractionation between sinter deposited at the surface and subsurface mineralized veins. These combined effects are postulated to produce a vapor containing isotopically light Hg and a residual liquid at depth containing isotopically heavy Hg (Marumo et al., 2008).

5.2. Aquatic ecosystems

Bergquist and Blum (2007) demonstrated that natural samples from aquatic ecosystems preserve both MDF and MIF signatures of Hg isotopes. They measured fish samples from several lakes and observed that MDF increases with the size and Hg concentration of the fish. Fish from different lakes also display a large range in MIF (4‰) with MIF always having positive values. Fish populations from different locations have different MIF values, but mostly display similar MIF within a location. Additionally, the relationship between the MIF of the two odd isotopes in fish has a similar slope to that found for photo-reduction of CH_3Hg^+. To evaluate the possibility that MIF might be produced within the fish, Das et al. (2009) analyzed food chains at different trophic levels from a single lake with respect to Hg isotopic compositions. Among the food chains there is a striking correspondence between trophic level and $\Delta^{199}Hg$ and $\Delta^{201}Hg$ values for primary, secondary, and tertiary consumers. These observations indicate that the MIF can occur during metabolic processes as well. Similar to other isotopic systems used to study food web dynamics and structure (i.e., C and N) (Fig. 6), both MDF and MIF of Hg isotopes hold a promise for quantifying and understanding Hg pathways and bioaccumulation in the environment (Jackson et al., 2004, 2008a,b; Das et al., 2009; Gantner et al., 2009; Laffont et al., 2009).

5.3. Direct and indirect air samples

Lichens are "filters" of atmospheric particulate and gaseous matter and well-known passive bio-monitors of air quality. Concentrations of Hg and isotopic ratios contained in lichens have been widely used to quantify, discriminate and monitor atmospheric Hg emissions or depositions. Carignan et al. (2009) measured atmospheric Hg in lichens from North America and Europe, which is characterized by negative $\Delta^{199,201}Hg$ (−0.4‰ to −1‰). All the measured samples showing MIF display $\Delta^{199}Hg$ and $\Delta^{201}Hg$ having a 1:1 relationship, essentially due to the MIF of global photo-reaction. Meanwhile, atmospheric Hg depletion events (AMDEs) in snowpack have also been shown to be a good approach to detect the isotopic composition of atmospheric Hg in polar areas. Sherman et al. (2010) successfully measured the Hg isotopic composition of snow samples collected during an atmospheric Hg depletion event in Barrow, Alaska. They report large negative mass-independent fractionation of Hg isotopes in the Arctic snow, developed a refined procedure for promp, precise isotopic analysis of atmospheric Hg vapor and showed that photochemical reactions

Fig. 5. Observed $\delta^{202}Hg$ (relative to NIST-3133) in natural systems (based on published data). The $\delta^{202}Hg$ are similar in host rocks ($n = 133$) (Smith et al., 2005, 2008), Hg minerals ($n = 61$) (Hintelmann and Lu, 2003; Foucher et al., 2009; Smith et al., 2005; Blum and Bergquist, 2007; Epov et al., 2008), hydrothermal emissions ($n = 61$) (Sherman et al., 2009; Smith et al., 2008; Zambardi et al., 2009) and sediments ($n = 74$) (Gehrke et al., 2009; Foucher and Hintelmann, 2006; Foucher et al., 2009; Biswas et al., 2008; Gantner et al., 2009), which suggests that magmatic processes such as partial melting and magma cooling should fractionate Hg to a lesser degree than lower temperature processes. While a significant lower $\delta^{202}Hg$ in coals ($n = 69$) (Biswas et al., 2008) and lichens ($n = 30$) (Carignan et al., 2009) together with a comparable higher $\delta^{202}Hg$ in aquatic organisms ($n = 135$) (Laffont et al., 2009; Bergquist and Blum, 2007; Gantner et al., 2009; Epov et al., 2008) may be the results of multiple isotope fractionation pathways during different biogeochemical processes (Table 1).

triggered the release of a significant portion of the Hg deposited during this atmospheric Hg depletion event.

5.4. Soils and sediments

Several groups have investigated a series of sediments subjected to various Hg sources from different locations worldwide (Jackson et al., 2004, 2008a,b; Foucher and Hintelmann, 2006; Ghosh et al., 2008; Gehrke et al., 2009; Foucher et al., 2009; Feng et al., 2010). Distinct Hg isotopic fingerprints were observed among

geographically well separated locations as well as among neighbouring sites. The $\delta^{202}Hg$ (relative to NIST-1641d or NIST-3133) displayed total differences of approximately 5‰. Only a small degree of MIF was detected in these sediments (Jackson et al., 2004, 2008a,b; Ghosh et al., 2008; Gehrke et al., 2009; Feng et al., 2010).

5.5. Coals and organic soils

Evans (2001) made a comparison of coal and fly ash samples using MC-ICP–MS. Qualitatively, fly ash consistently produced iso-
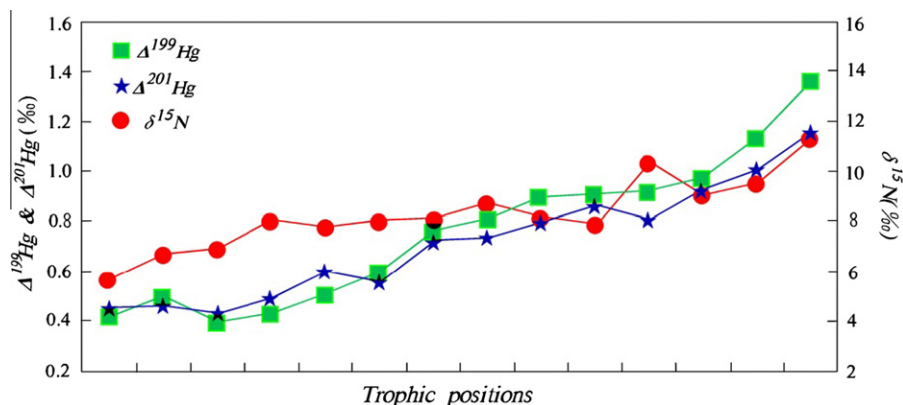
Fig. 6. MIF records in different trophic levels (Das et al., 2009).

topically lighter values. Xie et al. (2005) analyzed a sub-bituminous coal standard (NIST-2682b) in which $\delta^{202}Hg$ was approximately $-4‰$, which demonstrated that the isotope systematics are inconsistent with mass-dependent fractionation.

Biswas et al. (2008) investigated the Hg isotopic composition of modern organic soil horizons distant from point sources of Hg in North America and coal deposits within the USA, China and Russia–Kazakhstan, which are 3 of the 5 greatest coal-producing regions. Mercury stored in organic soil and coal deposits displays a wide range of both MDF and MIF. $\delta^{202}Hg$ varies in coals by $3‰$ and $\Delta^{201}Hg$ varies within a $0.9‰$ interval. A combination of these two Hg isotope signals results in what may be a unique isotopic "fingerprint" for many coal deposits, which offers a new tool for characterizing Hg inputs from natural and anthropogenic sources to the atmosphere and provides new insights into the geochemistry of Hg in coal and soils. In a distinctive way, the study also demonstrated that Hg found in most coal deposits and modern organic soils is subjected to photochemical reduction near the Earth's surface prior to deposition.

6. Applications of mercury stable isotopes

6.1. Tracing mercury pollution history

Unconsolidated and semi-consolidated sediments potentially provide a historic record of loads and rates of Hg deposition. Jackson (2001) measured the isotopic fractionation of Hg in sediment cores from Arctic lake sediments to establish historical records. The core demonstrated an overall $\delta^{202}Hg$ variation becoming gradually heavier from 1899 to 1997 (Fig. 7). This trend is positively correlated with total Hg concentration, and superimposed on both parameters are the oscillatory patterns of smaller variation. Similarly, Hg isotope ratios have been determined in two sediment cores in Guizhou, China (Feng et al., 2010). They demonstrated that processes in lakes/reservoirs related to internal Hg cycling (likely associated with organic matter cycling and degradation) do not appear to destroy or confound the Hg isotopic composition of a given Hg input, and thus, sediment cores might provide the opportunity to trace the sources of Hg contamination in history.

6.2. Tracing sources

Source tracing employing non-traditional isotope systematics is promising for Hg as well as a quantitative approach to establish Hg fluxes within different sources. Distinct isotopic differences can occur between different sources, and these can be exploited to study pollution sources and calculate the contribution of each source using an end-member mixing model (Weiss et al., 2008).
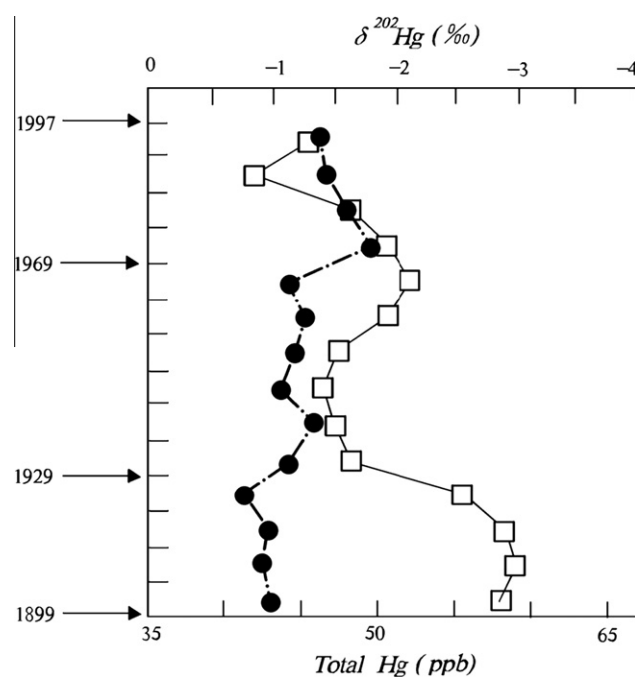

Fig. 7. Historic record of Hg^T and $\delta^{202}Hg$ in Arctic lake sediments. The broken line indicates Hg^T and solid line indicates $\delta^{202}Hg$ (Jackson et al., 2004).

$$\delta_t = f_A\delta_A + (1 - f_A)\delta_B$$

where δ_t is the total δ value, δ_A and δ_B are the isotope values of the sources A and B, respectively, and f_A is the fraction of the total contributed by source A. Foucher et al. (2009) gave the first evidence that tracking of Hg sources in natural systems using Hg stable isotope ratios is feasible. They reported a remarkable isotope difference of Hg between the Hg mining region near Idrija, Slovenia and the river flowing into the Gulf of Trieste, Italy. Finally, these authors used a simple binary mixing-model, and demonstrated that all samples investigated were a result of variable proportions of Hg originating from the Idrija region and from the above-mentioned gulf.

7. Conclusions

Utilization of the stable-isotope system of Hg in order to identify and quantify sources and biogeochemical processes (especially simple redox and biologically mediated reactions) in the environment provides a potent new tool to solve issues that cannot be

studied with conventional techniques. MC-ICP–MS provides an opportunity to measure the isotopic composition of Hg with sufficient precision (<0.2‰) to evaluate natural fractionation processes. Studies published to date suggest that the magnitude of isotope fractionation of Hg is as large as 7‰ for δ^{202}Hg. A common analytical protocol has eventually been accepted by the majority of researchers involved. However, future work ought to calibrate fractionation processes against the variables of interest. Better precision of isotope-ratio determinations will improve the signal-to-noise ratios and allow a detailed study of the physical–chemical nature of fractionation processes. Moreover, this is a fundamental requirement for being able to expand isotope research to various Hg species (Epov et al., 2008; Malinovsky et al., 2008; Dzurko et al., 2009). Measurement Hg isotopes is becoming more and more useful in the study of sources and fate of Hg in the environment. Given the recent findings concerning Hg isotope systems in nature, application of this knowledge to environmental problems is a promising prospect.

Acknowledgement

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