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# 海洋汞同位素研究进展

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**摘 要:** 海洋作为地球上最重要的汞储库之一,在调节全球汞循环中起着关键作用.近年来,汞同位素在研究海洋汞生物地球化学循环方面展现出明显优势,不但能示踪现代海洋汞污染来源及转化过程,还可重建古环境、古气候.总结了不同类型海洋样品汞同位素检测方法,系统归纳了其汞同位素数据,并重点阐述了海洋汞同位素分馏机制.总体上,目前海洋汞同位素数据还很有限,海洋汞循环关键过程的同位素分馏效应及潜在机理研究相对缺乏,精确源解析困难,难以对全球汞关键过程和循环通量进行准确验证和制约.未来还需要深入研究汞同位素分馏机理,进一步明确海洋中汞的来源、迁移及转化,为完善全球汞循环及精准防控海洋汞污染提供基础数据和理论支持.

**关键词:** 海水;海洋沉积物;海洋生物;汞稳定同位素;汞浓度;汞形态;海洋学.

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# Progresses in Study of Mercury Isotopic Compositions in the Ocean

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**Abstract:** Ocean, one of the most important reservoirs of mercury (Hg) on earth, plays a critical role in mediating the global Hg cycling. Recently, Hg isotope approach has shown significant advantages in studying the biogeochemical cycling of oceanic Hg, as it could be used not only to trace marine Hg sources and transformation processes, but also to reconstruct the paleoenvironment and paleoclimate. In this paper, it summarizes analytical methods for accurately measuring Hg isotopes in different marine samples, reported Hg isotopic compositions in seawater, marine sediments and biological samples of different regions worldwide, and elaborates the potential migration and transformation processes that fractionate Hg isotopes in the ocean. Overall, due to the fact that limited data are available for Hg isotopes in the ocean, and the studies on the potential mechanisms and processes fractionating Hg isotopes are still relatively scarce, the systematics of Hg in marine environment and thus the global Hg cycling model still could not be accurately established using Hg isotopes. In the future, it is still necessary to well investigate Hg isotope fractionation during potential biogeochemical processes such as the bioaccumulation and sedimentation, and to deeply decipher the source, migration and transformation of marine Hg using stable isotope approach, in order to provide basic data and theoretical support for improving the global Hg cycling and fairly preventing and controlling marine Hg pollution.

**Key words:** seawater; marine sediment; marine biota; Hg stable isotope; Hg concentration; Hg speciation; oceanography.

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## 0　引言

海洋占地球面积的71%,蕴含着丰富的水资源、生物资源、矿物资源以及可再生能源,给人类带来无法估量的价值.除此之外,海洋还是地球气候的"调节器",在调节和稳定地球气候上发挥着决定性作用.随着经济的发展,全球范围内的海洋都面临着包括汞污染在内的一系列环境挑战,引起广泛关注.海洋作为地球上最重要的汞储库之一,总汞储量预估有 1 440 Mmol (Mason and Sheu, 2002),是重要的汞源和汞汇,在调节汞全球循环中起着核心作用.海洋中的甲基汞(Methyl mercury,MeHg)可通过食物链进入到高营养级的食用鱼类,最终对人类健康构成严重威胁(Depew *et al.*, 2012).因此,了解海洋生态系统中汞的迁移转化过程对人类健康、海洋汞污染防治以及生物地球化学基础研究都具有重要意义.

海洋汞生物地球化学循环的研究无论从理论还是实验分析方面都很有限.尤其是海水中汞浓度非常低,加之基质复杂,大大限制了海水汞的准确测定.除此之外,有些海洋生态系统汞循环研究使用的观点并不是基于实际海洋样品或者模拟海洋环境,而是利用了类似的生态系统(如淡水生态系统)相关研究的结论(Masbou *et al.*, 2018; Motta *et al.*, 2020);但是,海洋生态系统是否完全遵守这些规律还不清楚(Zheng *et al.*, 2021),导致海洋汞循环的研究还存在着诸多不确定性.作为近十几年新兴的研究方法,汞稳定同位素已在解析汞的来源和示踪汞的迁移转化过程方面表现出巨大应用潜力.研究表明,汞同位素分馏效应可用来有效示踪海洋水体、沉积物以及食物链中汞的来源(Yin *et al.*, 2018),追踪海洋中汞的转化过程,约束海洋汞的生物地球化学循环(Blum *et al.*, 2013; Sun *et al.*, 2020a),并完善海洋乃至全球汞循环模型(Outridge *et al.*, 2018).

目前海洋汞同位素研究已取得很多重要进展,并有很快拓展之势.尽管目前有不少综述文章刻画了汞同位素地球化学研究进展(Bergquist and Blum, 2009; Yin *et al.*, 2010, 2014; Hintelmann and Zheng, 2011; Blum, 2012; 王柱红等, 2012; Blum *et al.*, 2014; 冯新斌等, 2015; Blum and Johnson, 2017; 李春辉等, 2017; Kwon *et al.*, 2020; Tsui *et al.*, 2020; 郑旺等, 2021),但还没有单独介绍海洋汞同位素的综述文献.本文系统总结30多篇有关实际海洋样品(包括海水、海洋沉积物、海洋生物、海洋悬浮颗粒物)汞同位素研究成果,并分4个部分进行详细论述.第一部分介绍海水汞同位素分析面临的挑战,以及目前比较可行的海水、海洋沉积物和海洋生物样品高精度汞同位素测定方法;第二部分概述了全球海洋不同样品(海水、海洋沉积物、海洋生物)的汞同位素组成数据,并结合其浓度、形态数据分析了汞的可能来源和经历的关键迁移转化过程,初步构建了海洋生态系统汞同位素(包括质量分馏(Mass Dependent Fractionation, MDF)和非质量分馏(Mass Independent Fractionation,MIF))循环框架;第三部分总结了海洋汞的输入输出通量和各储库的汞同位素数据,分析了目前海洋汞及其同位素的收支状况;第四部分结合目前海洋生态系统中汞研究进展,展望了未来海洋汞同位素研究的发展方向.本文旨在全面总结海洋汞同位素的研究现状,分析当前研究面临的问题和难点,为进一步完善基于汞同位素的海洋生态系统及全球汞循环研究提供基础数据.

## 1　海洋样品汞同位素分析方法

### 1.1　海水汞的浓缩提纯

迄今为止,海洋生态系统汞同位素研究主要集中在海洋生物和海洋沉积物,对海水汞同位素的研究报导非常少.这主要是因为海水中汞含量非常低(一般<1 pM,如表1所示,pM表示pmol/L,又等于$10^{-12}$ mol/L),需要大量富集才能达到准确测定汞同位素组成的质量要求(> 5 ng,ng = $10^{-9}$ g);其次是海水基质复杂(主要阴阳离子如碘离子、有机物等),会严重影响汞同位素测试(Zheng *et al.*, 2011; Štrok *et al.*, 2014; Lin *et al.*, 2015; Liu *et al.*, 2021c).要获得精确的海水汞同位素比值,一方面需要去除绝大部分基质干扰,另一方面需要对大量(几升甚至几十升)海水进行浓缩提纯,富集得到足够量汞,然后才能在多接收电感耦合等离子体质谱仪(Multi-Colletor Inductively Coupled Plasma Mass Spectrometer,MC-ICP-MS)上进行精确的同位素测定.因此,需要一个有效的浓缩提纯海水汞并保证高回收率(90%~110%)的前处理方法.以往的海水汞同位素分析采用了两种预富集方法:一种是吹扫捕集法,另一种是色谱法(Štrok *et al.*, 2014; Lin *et al.*, 2015).前者需要较高的汞浓度,不

适用于浓度极低的海水;后者很难去除海水中的复杂基质,影响预富集回收率以及汞同位素测定(Štrok *et al.*, 2014; Liu *et al.*, 2021c).除此之外,这两种预富集方法由于实验条件的限制,一般需将样品运送回实验室进行处理,而无法直接在采样船上原地进行.例如,Štrok *et al.*(2015)对比了船上预富集和运送回实验室预富集海水样品后总汞浓度和汞同位素的检测结果,发现与船上预富集相比,实验室预富集的总汞浓度要低得多,并把此归因于运输和储存样品过程中海水Hg(II)的有机还原,导致汞以Hg(0)形式损失.该推断得到汞同位素数据证实:运送回实验室预富集样品的$\delta^{202}$Hg值偏正,而$\Delta^{199}$Hg值偏负,这与黑暗条件下有机物介导的Hg(II)非生物还原过程的汞同位素分馏结果一致.该研究强调了开展实地、实时预富集的必要性(Štrok *et al.*, 2015).

鉴于上述海水汞同位素前处理方法的局限性,Liu *et al.*(2021c)最近开发了预富集大量海水中低浓度汞的共沉淀法,如图1所示.该方法是基于沉淀平衡理论和溶度积常数建立的,即利用硫酸铜和硫化钠形成的硫化铜粗颗粒将新形成的纳米硫化汞颗粒共沉淀下来,之后将含硫化汞的颗粒过滤到滤膜上并进行消解,对消解液中的汞直接进行同位素测试.具体实验操作如下:在过滤后的海水中(以下试剂添加量是针对10 L海水样品)加入0.2 M BrCl消解至少12 h,将所有形态的汞都转化成Hg(II);共沉淀时首先加入0.5 mL 0.5 M $CuSO_4$溶液,摇匀并静置5 min,使得CuS的形成先于$H_2S$,从而防止先加入$Na_2S$后形成$H_2S$逃逸;接下来加入1 mL 0.5 M $Na_2S$溶液,摇匀并静置10 min,保证HgS和CuS共沉淀;之后进一步加入1 mL 0.5 M $CuSO_4$,摇匀并静置5 min,以沉淀多余的$S^{2-}$;最后用0.1 μm PVDF滤膜过滤并用4 mL反王水消解至少24 h,即可进行同位素检测.实验结果表明,该方法具有较高的回收率(98%±12%, $n$=32)、较低的程序空白(103 pg Hg, $n$=8)以及非常好的重现性和测量精度(NIST 3133, $\delta^{202}$Hg=0.00‰±0.10‰, 2SD, $n$=205).该方法用于天然海水痕量汞的预富集,不但去除了海水基质的影响,可以进行精确的汞同位素测定,还有效解决了船上样品处理不方便和将大量海水运输到实验室分析的难题(Liu *et al.*, 2021c),为长期出海采样及开展远洋汞同位素研究提供了可能.

### 1.2 海洋沉积物和生物样品前处理

海洋沉积物和生物样品,前处理方法相似且较为成熟.常用的前处理方法为消解(Bloom *et al.*, 2003; Meng *et al.*, 2019; Bonsignore *et al.*, 2020)和热解(Biswas *et al.*, 2008; Yang *et al.*, 2022),如图1所示.消解是使用电热板、微波或者高温高压设备从固体样品中提取汞(Foucher and Hintelmann, 2006).沉积物常用的消解溶液为混酸,包括王水($HCl:HNO_3$=3:1)、反王水($HCl:HNO_3$=1:3))以及氢氟酸(HF)、硝酸($HNO_3$)、盐酸(HCl)、硫酸($H_2SO_4$)组合.生物样品常用的消解液为$H_2O_2$/$HNO_3$(Lee *et al.*, 2005)或$HNO_3$/BrCl(Madenjian *et al.*, 2019).热解主要是将沉积物、生物等固体样品在高温下(接近1 000 ℃)加热,使汞主要以单质形态释放并被捕集到吸收液中再进行同位素检测.最常用的吸收液为$KMnO_4$/$H_2SO_4$体系(Biswas *et al.*, 2008)或$HNO_3$/HCl混酸体系(Sun *et al.*, 2013a).消解和热解方法处理样品各有优缺点.总体而言,消解方法耗时较长,样品载入量少,对于低汞浓度样品可能无法通过消解提取足量的汞以满足高精度同位素分析.在某些情况下,消解可能无法从固相中完全提取汞.例如使用王水无法从生物炭或者黑炭等样品中完全提取汞,但生物炭和黑炭广泛分布在海洋沉积物中(Fu *et al.*, 2020),对于耐酸性样品如硅酸盐样品,混酸消解也无法从中完全提取汞(Liang *et al.*, 2003; Sun *et al.*, 2013b).热解方法耗时较短,对于样品汞浓度要求不高,但是热解过程中升温速率和载气流速等因素会显著影响样品汞回收率并可能产生显著的汞同位素分馏(Sun *et al.*, 2013a).此外,当样品有机质含量较高时,热解过程极易产生不完全燃烧的挥发性有机物,干扰吸收液对汞的吸收,导致汞回收率下降.

### 1.3 汞同位素检测

MC-ICP-MS的成功研发使得汞同位素领域的研究取得突破性进展.目前MC-ICP-MS可以开展各类样品(包括但不仅限于水体、沉积物、以及生物等样品)的汞稳定同位素测试.由于汞具有强挥发性,所以冷蒸汽产生法是从样品中提取Hg的最简单的办法.通过配备冷蒸汽发生系统,海洋样品前处理形成的Hg(II)溶液(参考1.1和1.2节)稀释至一定浓度与$SnCl_2$溶液被同时引入进样装置,在线反应产生的Hg(0)蒸汽与雾化器产生的TI气溶胶被同时引入等离子体进行检测,如图1所示.在同位

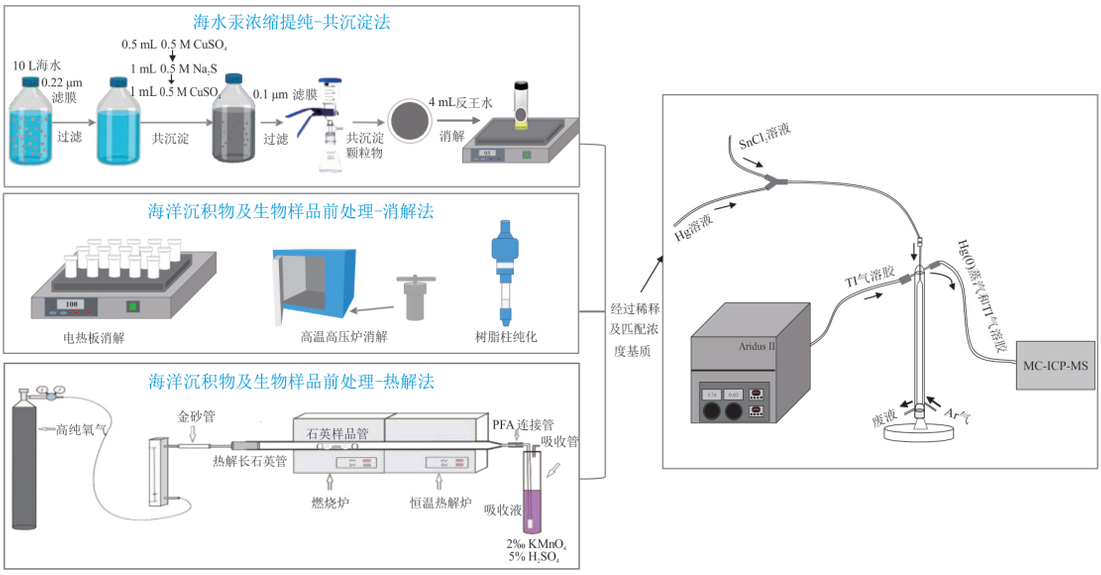


图 1　不同类型海洋样品汞同位素测试装置示意图

Fig.1　Schematic diagram of mercury isotope testing equipments for different marine samples

素测试过程中通过检测与汞质量数相近的 Tl 同位素($^{203}$Tl 和 $^{205}$Tl)来校正仪器的质量歧视效应(质量歧视效应是指同位素分析过程中仪器和分析程序引起的分馏效应);使用标样-样品交叉测定法(Standard-Sample Bracketing,SSB)来检测仪器稳定性;通过插入已知同位素组成的标准物质(例如 NIST SRM 8610)来校正仪器的误差.除此之外,由于汞同位素检测的高精度、高稳定性及高灵敏度,所以对基体、浓度、酸度、空白等具有较高的要求,这就需要在低流程空白的基础上,保证标准溶液的汞浓度、基体和酸度与样品溶液的匹配度在 10% 以内,最大限度地保证样品测试的准确度和精确性.总之,要做好对样品从容器准备、试剂配制、采集、储存、前处理到仪器检测的每一步骤的空白和数据质量控制,确保最终同位素数据的真实性和可靠性.本研究搜集了近几年(2015 年以后)MC-ICP-MS 测试的 1 043 个标样(NIST SRM 3133、NIST SRM 8610 和 NIST SRM 3177)的汞同位素数据,目前汞同位素测试精度平均值如下:$\delta^{202}$Hg、$\Delta^{199}$Hg、$\Delta^{200}$Hg、$\Delta^{201}$Hg 和 $\Delta^{204}$Hg 的测试精度分别为 0.04‰、0.02‰、0.03‰、0.04‰ 和 0.08‰(2SD,其中 $\Delta^{204}$Hg 总结数据为 62 个)(Bonsignore *et al.*, 2015; Yin *et al.*, 2015; Blum and Johnson, 2017; Gleason *et al.*, 2017; Demers *et al.*, 2018; Yin *et al.*, 2018; Meng *et al.*, 2019, 2020, 2021; Sun *et al.*, 2020a, 2020b; Jung *et al.*, 2022).

汞同位素质量分馏通常用 $\delta^{xxx}$Hg(‰)表示,定义如下:

$$\delta^{xxx}\mathrm{Hg}(‰)=[(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg})_{样品}/(^{xxx}\mathrm{Hg}/^{198}\mathrm{Hg})_{标准}-1]\times 1\,000, \quad (1)$$

式中的 $^{xxx}$Hg 代表汞同位素:$^{199}$Hg、$^{200}$Hg、$^{201}$Hg、$^{202}$Hg 和 $^{204}$Hg,标准为 NIST SRM 3133 汞标准溶液,为美国国家标准物质研究所(NIST)认证的国际通用的汞标准物质.汞的非质量分馏用 $\Delta^{xxx}$Hg(‰)表示,并根据 $\delta^{xxx}$Hg 使用以下公式计算:

$$\Delta^{xxx}\mathrm{Hg}(‰)=\delta^{xxx}\mathrm{Hg}-\beta_{xxx}\times\delta^{xxx}\mathrm{Hg}, \quad (2)$$

其中 $\beta_{xxx}$ 是根据质量分馏定律所得的转化系数,对于 $^{199}$Hg、$^{200}$Hg、$^{201}$Hg 和 $^{204}$Hg 的系数分别约为 0.252 0、0.502 4、0.752 0 和 1.493 0.

## 2　海水汞同位素组成

本节详细总结海水中汞的同位素组成,同时结合海水汞的浓度和形态数据,重点分析影响海水汞同位素组成变化的原因以及由此反映出的海水汞的来源和迁移转化信息.图 2 系统展示了自然海洋样品中汞同位素组成的变化范围.

### 2.1　海水汞同位素变化特征

一般而言,海水相对于海洋沉积物和海洋生物的汞同位素可提供更多关于汞来源和转化过程的直接信息.目前海水汞同位素数据报导非常有限,只有 6 项研究报告了海水(多数为高汞含量的近岸海水)的汞同位素组成(Štrok *et al.*, 2014, 2015;

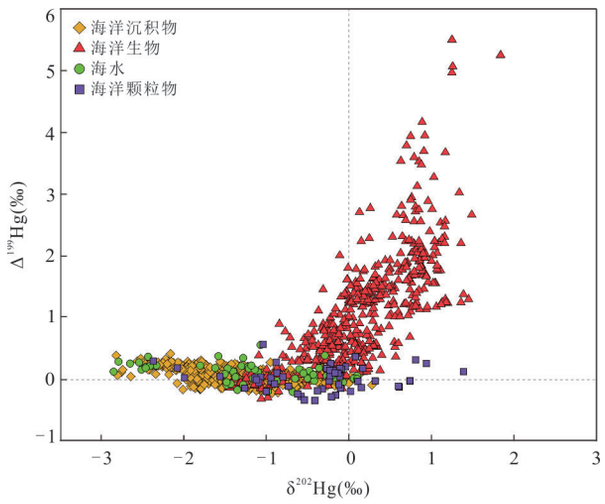


图 2 海水、海洋沉积物、海洋颗粒物以及海洋生物样品的 $\delta^{202}Hg$ vs. $\Delta^{199}Hg$

Fig.2 $\delta^{202}Hg$ versus $\Delta^{199}Hg$ for seawaters, marine sediments, marine particulate matters and marine biotas

海洋沉积物据 Balogh *et al.*(2015), Bonsignore *et al.*(2015, 2020), Yin *et al.*(2015, 2018), Gleason *et al.*(2017), Meng *et al.*(2019, 2020, 2021), Sun *et al.*(2020b), Jung *et al.*(2022);海洋生物据 Gehrke *et al.*(2009), Point *et al.*(2011), Blum *et al.*(2013, 2020), Balogh *et al.*(2015), Masbou *et al.*(2015), Yin *et al.*(2016), Madigan *et al.*(2018), Masbou *et al.*(2018), Motta *et al.*(2019, 2020), Bonsignore *et al.*(2020), Orani *et al.*(2020), Sun *et al.*(2020a), Renedo *et al.*(2021), Jung *et al.*(2022);海水据 Štrok *et al.*(2014, 2015), Meng *et al.*(2020), Jiskra *et al.*(2021), Liu *et al.*(2021c);海洋颗粒物据 Motta *et al.*(2019), Jiskra *et al.*(2021), Qiu *et al.*(2021)

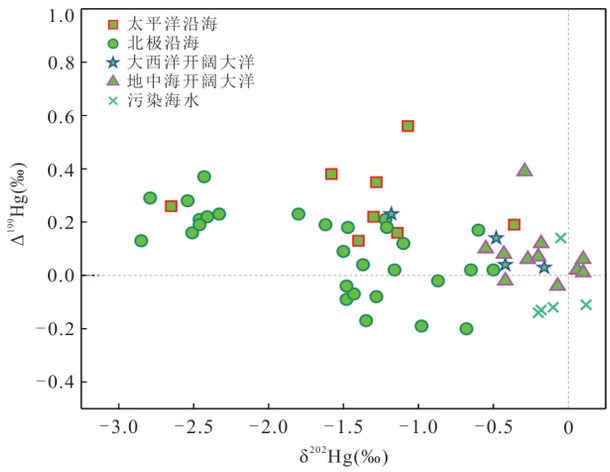


图 3 海水样品的 $\Delta^{199}Hg$ vs. $\delta^{202}Hg$

Fig. 3 $\Delta^{199}Hg$ versus $\delta^{202}Hg$ for seawaters

海水数据与图 2 中的相同

Lin *et al.*, 2015; Meng *et al.*, 2020; Jiskra *et al.*, 2021; Liu *et al.*, 2021c),包括一项是受严重污染的水体(Lin *et al.*, 2015),如图 3 所示.除污染海水外,自然海水展示了较大的 $\delta^{202}Hg$(−2.85‰～+0.10‰, $n$=53)和 $\Delta^{199}Hg$(−0.20‰～+0.56‰, $n$=53)变化范围.相对自然海水,受污染海水 $\delta^{202}Hg$ 值略偏正,为−0.20‰～+0.12‰($n$=5),$\Delta^{199}Hg$ 值变化范围更小,为−0.14‰～+0.14‰($n$=5)(Lin *et al.*, 2015).此外,受污染海水总汞浓度(194 pM, $n$=5)明显远高于其他 5 项研究中的海水浓度(2.29 pM, n=37),其汞同位素值与工业源的汞同位素信号($\delta^{202}Hg$: −0.53±0.51‰, $\Delta^{199}Hg$: −0.02±0.11‰, $n$=481)(Yin *et al.*, 2018)更为接近,表明污染海水中的汞可能来源于工业排放,因此不能反映天然的海水汞同位素组成.除质量分馏(MDF)和奇数汞同位素非质量分馏(odd-MIF)外,Štrok *et al.*(2014, 2015)的两项研究中还观察到明显的偶数汞同位素非质量分馏(even-MIF),$\Delta^{200}Hg$ 甚至高达 0.53‰.迄今为止,even-MIF 主要发现于大气以及受大气沉降影响的陆地和水生环境,但其具体机理还不明确(郑旺等, 2021).主流观点认为 even-MIF 可能产生于对流层顶部大气汞光化学氧化过程(Chen *et al.*, 2012).

### 2.2 海水汞同位素影响因素

海水汞同位素组成可能受赋存形态及来源控制.自然条件下,海水中 THg 和 MeHg 浓度非常低,为 pM 水平,不同海域的海水 THg 和 MeHg 浓度存在显著差异(表 1).近海和开阔大洋海水 THg 浓度对比显示,开阔大洋 THg 浓度(0.59～2.50 pM,平均 1.22 pM, $n$=538)远低于近海地区(2.21～19.65 pM,平均 15.49 pM, $n$=509).河流是海洋汞的重要来源,约有 6% 的河流汞可以到达开阔大洋,其余大部分则沉积到近海沉积物中(Zhang *et al.*, 2019).虽然河口的清除和沉积作用可以减少河流输入海洋的汞通量,但仍然会使近海海水中汞浓度远高于远离陆源影响的开阔大洋,表明人为影响下的陆源输入对海水的汞浓度影响很大(Amos *et al.*, 2014; Buck *et al.*, 2015).大气沉降也是海水中汞的主要来源,地表径流和大气沉降对海洋汞的贡献在近海和开阔大洋之间存在显著差异(Sunderland and Mason, 2007; Amos *et al.*, 2014; Zhang *et al.*, 2015; Zhu *et al.*, 2020),但仅凭汞浓度数据无法准确判断其主要来源,汞同位素信息能提供更直接、更可靠的证据.陆地输入的汞一般具有明显偏负的 $\delta^{202}Hg$,以及负的或者接近零的 $\Delta^{199}Hg$,而大气输入的汞具有略微偏负的 $\delta^{202}Hg$,但 $\Delta^{199}Hg$ 却显著偏正

(Yin *et al.*, 2018). 如图 3 所示,近海和开阔大洋海水汞同位素组成具有显著差异,已报导的近海海水汞同位素绝大部分具有负的 $\delta^{202}$Hg 和正的 $\Delta^{199}$Hg,介于陆地输入和大气输入之间. Jiskra *et al.* (2021)首次报导了开阔大洋海水汞同位素数据,其 $\delta^{202}$Hg 平均值为 −0.27‰±0.21‰($n$=16),$\Delta^{199}$Hg 平均值为 0.08‰±0.01‰($n$=16),并指出其汞主要来源于大气输入. 在此之前,也有一些研究利用降雨中的汞同位素信号预测了开阔大洋海水的汞同位素组成. 例如,Blum *et al.* (2013)提出太平洋海水溶解 Hg(II)同位素组成类似太平洋沿岸雨水($\delta^{202}$Hg: 0.00‰~0.20‰,$\Delta^{199}$Hg: 0.25‰~0.35‰)(Sherman *et al.*, 2012; Donovan *et al.*, 2013),与开阔大洋实际海水样品汞同位素组成存在差异. 未来还需要开展更多海水汞同位素研究,以进一步刻画海洋储库汞同位素特征. 特别是 Liu *et al.* (2021c)建立的可适用于远洋船上的低浓度海水汞同位素分析方法,有望快速拓展开阔大洋海水汞同位素认知.

**表 1　全球不同海域海水中总汞(THg)和甲基汞(MeHg)浓度数据**

Table1　THg and MeHg concentrations in seawaters from different regions of the world

| 海域 | THg(pM) | | | | MeHg(pM) | | | | 参考文献 |
|---|---|---|---|---|---|---|---|---|---|
| | 表层 | 中层 | 深层 | 总体 | 表层 | 中层 | 深层 | 总体 | |
| **开阔大洋** | | | | | | | | | |
| 大西洋 | 0.52±0.11 ($n$=6) | 0.54±0.15 ($n$=7) | 0.68±0.17 ($n$=9) | 0.59±0.17 ($n$=22) | 0.04±0.01 ($n$=6) | 0.19±0.13 ($n$=9) | 0.37±0.07 ($n$=9) | 0.23±0.16 ($n$=22) | Jiskra *et al.*, 2021 |
| 大西洋 | 1.51±0.82 ($n$=26) | | | 1.51±0.82 ($n$=26) | | | | | Soerensen *et al.*, 2013 |
| 热带太平洋 | 0.35±0.30 ($n$=70) | 0.90±0.29 ($n$=74) | 1.12±0.33 ($n$=88) | 0.82±0.44 ($n$=232) | 0.19±0.13 ($n$=56) | 0.41±0.32 ($n$=60) | 0.26±0.27 ($n$=66) | 0.29±0.27 ($n$=182) | Munson *et al.*, 2015 |
| 北冰洋中部 | 1.31±1.34 ($n$=22) | 0.81±0.24 ($n$=29) | 0.85±0.36 ($n$=32) | 0.96±0.76 ($n$=83) | 0.11±0.11 ($n$=22) | 0.17±0.12 ($n$=29) | 0.10±0.09 ($n$=32) | 0.12±0.10 ($n$=83) | Heimbürger *et al.*, 2015 |
| 南大洋 | | 1.15±0.22 ($n$=10) | 1.35±0.39 ($n$=14) | 1.33±0.45 ($n$=71) | | 0.44±0.17 ($n$=31) | 0.52±0.11 ($n$=19) | 0.29±0.21 ($n$=241) | Cossa *et al.*, 2011 |
| 地中海 | 0.86±0.09 ($n$=5) | 1.03±0.06 ($n$=6) | 0.99 ($n$=1) | 0.96±0.11 ($n$=12) | 0.17±0.10 ($n$=5) | 0.4±0.04 ($n$=6) | 0.29 ($n$=1) | 0.29±0.14 ($n$=12) | Jiskra *et al.*, 2021 |
| 地中海西部 | 2.56±1.67 ($n$=43) | 2.45±0.93 ($n$=17) | 2.20±0.17 ($n$=5) | 2.50±1.25 ($n$=65) | | | | | Cossa *et al.*, 1997 |
| 北大西洋 | | | | 2.40±1.60 ($n$=27) | | | | | Mason *et al.*, 1998 |
| 北太平洋 | 0.64±0.26 | | 1.10±0.31 | 1.15±0.86 | | | | | Laurier *et al.*, 2004 |
| **近海** | | | | | | | | | |
| 中国渤海 | | | | 5.80±2.74 ($n$=58) | | | | 0.27±0.03 | Wang *et al.*, 2020 |
| 中国渤海 | | | | 2.21±0.53 ($n$=4) | | | | | Liu *et al.*, 2021c |
| 中国黄海 | | | | 6.63±4.08 ($n$=23) | | | | | Wang *et al.*, 2020 |
| 中国东海 | | | | 19.65±5.11 ($n$=351) | | | | 1.00±0.55 ($n$=351) | Liu *et al.*, 2020 |
| 中国东海 | | | | 7.22±3.08 ($n$=38) | | | | | Wang *et al.*, 2016 |
| 中国南海 | | | | 6.15±1.73 ($n$=35) | | | | 0.58±0.23 ($n$=33) | Fu *et al.*, 2010 |
| 东日本海 | 0.49±0.08 | 1.2±0.20 | 1.10±0.08 | | 0.03±0.02 | 0.44±0.10 | 0.53±0.09 | | Yang *et al.*, 2017 |

注:为便于比较,表中一些数据从原始浓度(ng/L)转换为摩尔单位(pM). 汇总数据中,海洋分层情况为海洋表层(0~200 m)、海洋中层(200~1 000 m)、海洋深层(1 000 m 以下). 表中数据为 THg±1SD 或 MeHg±1SD,$n$ 为样品个数.

海水中汞同位素信号除了受汞输入源的影响外,还受海洋关键生物地球化学过程的影响.但由于目前海洋汞同位素分馏过程研究十分有限,现有的水体汞同位素分馏过程及其机理大多是基于实验室的淡水模拟实验获得的,仅有个别实验模拟了海洋条件(Malinovsky and Vanhaecke, 2011; Jiménez-Moreno *et al.*, 2013),正如图4所总结的,目前发现的淡水水体中改变汞同位素信号的主要过程包括:

(1)氧化还原过程,包括液相Hg(0)氧化(Amyot *et al.*, 1997; Lalonde *et al.*, 2001, 2004; Mason *et al.*, 2001)和Hg(II)还原,二者都具有光化学和非光化学介导的两种反应途径(Lalonde *et al.*, 2001, 2004).对于液相非光化学Hg(0)氧化,目前研究了小分子硫醇有机物和还原性天然有机质参与的Hg(0)氧化过程的汞同位素分馏(Gu *et al.*, 2011; Zheng *et al.*, 2012),研究表明它们存在动力学分馏和平衡分馏两种机制,这两种机制产生的同位素分馏方向相反,即平衡分馏在产物Hg(II)中产生正的MDF以及较小且偏负的odd-MIF,而动力学分馏在产物Hg(II)中产生负的MDF以及较小的正的odd-MIF(Zheng *et al.*, 2019).对于液相光化学Hg(0)氧化,目前还没有相关实验报导其汞同位素分馏效应.非光化学Hg(II)还原目前已确定了可溶性有机质(DOM)和$SnCl_2$对Hg(II)的暗还原以及微生物对Hg(II)的暗还原,前者会在反应物Hg(II)中产生正的MDF和负的odd-MIF(Zheng and Hintelmann, 2010b),后者在反应物Hg(II)中只产生正的MDF,而不产生MIF(Kritee *et al.*, 2007, 2008).Hg(II)光还原的汞同位素分馏研究相对较多,该过程会在反应物Hg(II)中产生正的MDF和不同方向的odd-MIF,MIF的方向不仅受基团类型的影响,也受pH和溶解氧的影响(Bergquist and Blum, 2007; Zheng and Hintelmann, 2009; Rose *et al.*, 2015).

(2)无机汞的甲基化过程,包括生物甲基化和非生物甲基化.这两种途径均在反应物Hg(II)中产生正的MDF,且几乎不产生MIF(Rodríguez-González *et al.*, 2009; Malinovsky and Vanhaecke, 2011; Jiménez-Moreno *et al.*, 2013; Perrot *et al.*, 2015; Janssen *et al.*, 2016).

(3)甲基汞的降解过程,包括光化学降解(Sellers *et al.*, 1996; Chen *et al.*, 2003)和微生物降解(Marvin-Dipasquale *et al.*, 2000; Heyes *et al.*, 2006).光化学降解会在反应物MeHg中产生正的MDF和正的odd-MIF(Bergquist and Blum, 2007; Malinovsky *et al.*, 2010; Chandan *et al.*, 2015; Rose *et al.*, 2015; Kritee *et al.*, 2018),而微生物降解在反应物MeHg中只会产生正的MDF,而几乎不产生MIF(Kritee *et al.*, 2009).

(4)Hg(II)和Hg(0)的非氧化还原过程,包括Hg(II)的吸附、络合、沉淀等和Hg(0)的蒸发、挥发、扩散等.Hg(II)的非氧化还原过程通常只会在反应物Hg(II)中产生正的MDF,而几乎不产生MIF.例如,汞与硫醇官能团结合(Wiederhold *et al.*, 2010)、吸附到针铁矿(Jiskra *et al.*, 2012)、硫化物矿物的沉淀等(Smith *et al.*, 2015).而对于Hg(0)的非氧化还原过程,其中Hg(0)由溶解态向气态的挥发和气态Hg(0)的扩散只会在反应物Hg(0)中产生正的MDF,而Hg(0)由金属液态向气态的蒸发则在反应物Hg(0)中不仅产生正的MDF,还会产生较大的负odd-MIF(Zheng *et al.*, 2007; Estrade *et al.*, 2009; Ghosh *et al.*, 2013; Koster Van Groos *et al.*, 2014; 郑旺等, 2021).

(5)同位素交换过程,即不发生净的汞形态转化的情况下产生的同位素迅速交换,包括Hg(II)与Hg(0)之间的同位素交换以及不同形态Hg(Ⅱ)之间的同位素交换.这些交换过程也会引起汞同位素分馏,且均会产生MDF和MIF(Criss, 1999; Wiederhold *et al.*, 2010; Zheng *et al.*, 2019; 郑旺等, 2021),很可能会在自然海水的汞同位素分馏中产生不容忽视的影响,值得关注.

综上可知,淡水水体汞同位素分馏过程绝大多数都发生于汞的不同形态或不同相态之间的转变,郑旺等(2021)已经详细阐述了以上过程的汞稳定同位素分馏机理.但与淡水不同的是,海水的基质更为复杂,环境因素更为多变,这些都会使得汞在海水中的形态转化和迁移分布显著不同于淡水.海水中的汞主要有3种赋存形态:溶解态零价汞(Hg(0))、二价无机汞(Hg(II))和甲基汞(MeHg)(Mason and Fitzgerald, 1993; Morel *et al.*, 1998; Selin, 2009; Bowman *et al.*, 2015),其形态转化和分布不仅受以上提到的光照和微生物相关转化过程的控制(Barkay and Poulain, 2007; Gionfriddo *et al.*, 2016; Liu *et al.*, 2020),还受其他多种环境因

素的控制,包括温度(Ci *et al.*, 2015)、盐度(Wang and Wang, 2010; Achá *et al.*, 2011; Zhang *et al.*, 2012)、pH(Watras *et al.*, 1995)、DOM(Wang and Wang, 2010; Kim *et al.*, 2014)等.这些环境因素均会通过影响汞循环中的各个关键环节来影响汞的迁移转化进而影响汞同位素分馏,包括氧化/还原、甲基化/去甲基化、吸附/解吸等(Ci *et al.*, 2016),具体表现为:

(1)温度的影响.有研究发现,表层海水中的THg与温度呈负相关关系(Liu *et al.*, 2020),归因于较高的温度可促进Hg(0)的形成以及随后Hg(0)从表层海水向大气的释放(Ci *et al.*, 2015);研究还发现,较高温度有利于汞的甲基化而不利于甲基汞的降解(Ullrich *et al.*, 2001).

(2)盐度和pH的影响.研究已表明这两者是决定海水中汞化学形态最重要的环境因素(Laporte *et al.*, 1997).海水中,Hg(II)的无机形态主要以氯化物$HgCl_3^-$和$HgCl_4^{2-}$为主(Wang and Wang, 2010; Gworek *et al.*, 2016),MeHg则主要以$CH_3HgCl$形态存在(Morel *et al.*, 1998; Wang and Wang, 2010).研究发现,海水中卤化物形态的无机汞比其他形态的无机汞络合物更不容易被还原和甲基化(Gårdfeldt *et al.*, 2003; Whalin *et al.*, 2007),并且氯化物还能有效促进海水中的Hg(0)迅速氧化为Hg(II)(Amyot *et al.*, 1997; Ci *et al.*, 2016);甲基汞降解的速率取决于水体中存在的甲基汞结合配体类型,相对于淡水中与含硫配体和与有机物结合的甲基汞,海洋中以氯化物为主要形态存在的甲基汞更不容易被降解(Zhang and Hsu-Kim, 2010).这些表明,海水的高盐度环境提高了汞在海水中的滞留时间,降低了甲基汞的光降解速率,增加了汞进入食物链的潜力,从而意味着海洋生态系统中汞的转化和迁移显著不同于淡水生态系统,其更容易发生汞污染.关于pH的影响,研究发现,海水pH的降低,比如海洋酸化事件,有利于无机汞的甲基化过程(Xun *et al.*, 1987),使得Hg(II)转化为Hg(0)的速度更快(Chakraborty *et al.*, 2015).

(3)DOM的影响.研究发现,DOM会通过诱导光化学反应(Jeremiason *et al.*, 2015)和控制暗氧化还原反应(Gu *et al.*, 2011)极大地影响水体汞的氧化/还原、甲基化/去甲基化等过程,且其影响程度因DOM的种类和浓度而异(Jiang *et al.*, 2017).

可见,在海水复杂的基质中,发生的汞同位素分馏过程会受到以上这些因素的共同影响,使各个过程的分馏程度变化范围很广(Bergquist and Blum, 2007),并可能使海水汞同位素分馏并不完全遵循基于淡水模拟实验所获得的汞同位素分馏规律.例如,已有研究发现,在接近海水$Cl^-$浓度和弱碱性pH条件下,甲基汞光降解过程产生的MIF几乎为零(Malinovsky *et al.*, 2010; Jiménez-Moreno *et al.*, 2013),而并不是淡水体系中的产生显著MIF.值得指出的是,图4所示的绝大多数过程都趋向于使液相中剩余的汞富集较重的同位素.Jiskra *et al.*(2021)根据海水汞同位素组成,认为海洋接收的大气汞沉降中50%以上都是Hg(0),虽然目前大气Hg(0)在海水中的转化机制还不清楚,但实验研究已证实Hg(0)暗氧化的动力学分馏会导致海水$\delta^{202}$Hg值偏负(Zheng *et al.*, 2019);基于此,笔者猜测沉降到海洋中的Hg(0)暗氧化的动力学分馏可能是导致海水汞同位素$\delta^{202}$Hg偏负的重要原因,但尚需更多关于Hg(0)氧化的实验和机理研究来验证此观点.不仅如此,由于目前海水汞同位素分馏相关研究还非常有限,未来需要大量工作去探究并完善海水汞关键反应过程的同位素分馏机理.

## 3　海洋沉积物和悬浮颗粒物汞同位素组成

进入到海洋中的汞大部分沉降到沉积物中,海洋沉积物既是海洋中汞的重要汇也是重要的二次排放源(Covelli *et al.*, 1999).作为汞汇,经河流输入或大气沉降到海洋中的汞会被埋藏于沿海和深海沉积物中,并在洋流作用下随沉积物进行传输,只有经过更长时间尺度才能再次参与大气-陆地-海洋汞循环(Zhang *et al.*, 2015).而作为汞的二次排放源,沉积物中的汞可在扰动或微生物等作用下再次释放到水相,被生物吸收进入海洋食物链,也可逸散到大气中,从而继续参与汞循环.本节主要汇总了有关海洋沉积物和悬浮颗粒物的汞同位素数据,并结合沉积物中汞浓度和形态数据,重点阐述了影响沉积物中汞同位素组成的可能原因以及由此反映出的汞来源和迁移转化信息.

### 3.1　海洋沉积物汞同位素变化特征

如表2所示,深海沉积物中的THg浓度一般是ng/g(ng = $10^{-9}$ g)水平,但受严重污染的近海沉积物THg浓度会达到μg/g(μg = $10^{-6}$ g)水平.不同海域沉积物的THg浓度存在显著差异,开阔大洋沉

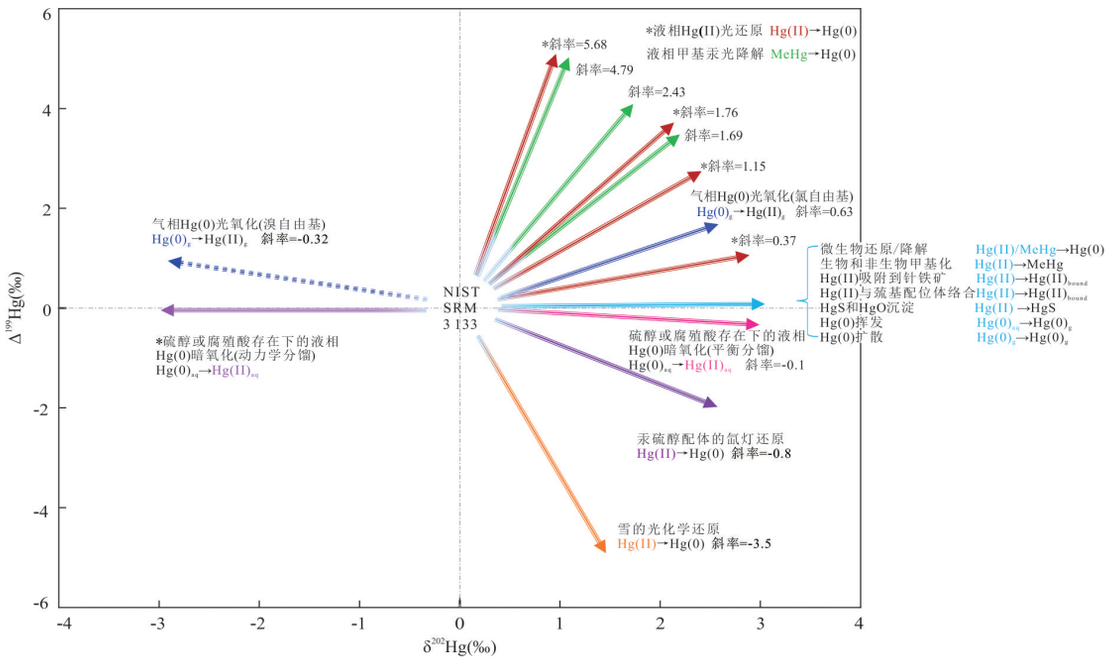


图 4 实验室观察到的汞同位素分馏过程及其特征概述 ($\Delta^{199}$Hg vs. $\delta^{202}$Hg)

Fig. 4 Overview of the general patterns in mercury isotope fractionation that have been observed experimentally ($\Delta^{199}$Hg versus $\delta^{202}$Hg)

箭头的方向指示每个反应中反应物或者产物的同位素分馏方向,箭头的颜色代表不同的反应(其中同种颜色的多个箭头则代表同一种反应在不同实验条件下得到的不同结果),具体如下:红色箭头表示液相 Hg(II)光化学还原反应物的同位素分馏特征(Bergquist and Blum, 2007; Zheng and Hintelmann, 2009; Rose *et al.*, 2015);绿色箭头表示液相甲基汞光化学降解反应物的同位素分馏特征(Bergquist and Blum, 2007; Rose *et al.*, 2015);深蓝色实线箭头表示氯自由基主导的气态 Hg(0)光氧化反应物的同位素分馏特征(Sun *et al.*, 2016);深蓝色虚线箭头表示溴自由基主导的气态 Hg(0)光氧化反应物的同位素分馏特征(Sun *et al.*, 2016);浅蓝色箭头表示微生物介导的 Hg(II)还原或甲基汞降解(Kritee *et al.*, 2007, 2009),生物或者非生物甲基化(Rodríguez-González *et al.*, 2009; Malinovsky and Vanhaecke, 2011; Jiménez-Moreno *et al.*, 2013; Perrot *et al.*, 2015),Hg(II)吸附到针铁矿(Jiskra *et al.*, 2012),Hg(II)与巯基配位体络合(Wiederhold *et al.*, 2010),HgS 和 HgO 沉淀(Smith *et al.*, 2015),Hg(0)挥发(Zheng *et al.*, 2007)和 Hg(0)扩散(Koster Van Groos *et al.*, 2014)等一系列过程中反应物的同位素分馏特征;粉色箭头表示硫醇或腐殖酸存在下的液相 Hg(0)暗氧化平衡分馏中产物的同位素分馏特征(Zheng *et al.*, 2019);深紫色箭头表示汞硫醇配体氙灯还原中反应物的同位素分馏特征(Zheng and Hintelmann, 2010a);橙色箭头表示雪中 Hg(II)光化学还原中反应物的同位素分馏特征(Sherman *et al.*, 2010);浅紫色箭头表示硫醇或腐殖酸存在下的液相 Hg(0)暗氧化动力学分馏中产物的同位素分馏特征(Zheng *et al.*, 2019)

积物的 THg 浓度范围从北大西洋的 1.9 ng/g 到西北太平洋 170 ng/g,平均值为 53.7±20 ng/g ($n$=948);近海沉积物 THg 浓度有的低至 1 ng/g 以下,有的高达 4 μg/g 以上($n$=1 232),变化范围较大,有些区域污染非常严重,表明近海海域可能接收了更多人为源汞的输入.现有研究表明,汞同位素已成为海洋沉积物中汞来源的良好示踪手段.综合已有数据(图 2),海洋沉积物的 $\delta^{202}$Hg 值在 −2.82‰~0.28‰ 之间(平均值为 −1.24‰±0.61‰,$n$=638, 1SD),$\Delta^{199}$Hg 值在 −0.22‰~0.42‰ 之间(平均值为 0.07‰±0.11‰, $n$=638, 1SD), $\Delta^{200}$Hg 值在 −0.11‰~0.20‰ 之间(平均值为 0.02‰±0.04‰, $n$=522, 1SD),大多接近于 0.00‰.其中绝大多数数据是河口和近海沉积物的,而只有少数是深海沉积物的,比较来看,沿海沉积物 $\delta^{202}$Hg 范围为 −2.82‰~+0.61‰,平均值为 −1.23‰±0.61‰ (1SD, $n$=546),$\Delta^{199}$Hg 范围为 −0.22‰~+0.42‰,平均值为 0.06‰±0.11‰(1SD, $n$=546);深海沉积物 $\delta^{202}$Hg 范围为 −0.49‰~ −1.21‰,平均值为 −0.99‰±0.39‰, $\Delta^{199}$Hg 范围为 −0.13‰~+0.45‰,平均值为 0.10‰±0.10‰(1SD, $n$=92).可见,沿海沉积物的 $\delta^{202}$Hg 值相对于深海沉积物更负,表明沿海沉积物更多地接收了陆地汞源输入(尤其是河流输入,流域源汞同位素 $\delta^{202}$Hg: −1.82‰±0.39‰,$\Delta^{199}$Hg: −0.29‰±0.12‰,2SD),而深海沉积物则更多地接收了大气汞源输入(大气源汞同位素 $\delta^{202}$Hg: −1.22±1.08‰,$\Delta^{199}$Hg: 0.38±0.33‰, 2SD).研究还表明,沉积物剖面中的汞同位素组成

**表 2　全球不同海域沉积物中的 THg 和 MeHg 浓度(ng/g)**

Table 2　THg and MeHg concentrations in marine sediments from different regions of the world (ng/g)

| 研究区域 | 样品量 $n$ | THg 范围 | THg 平均值 | MeHg 范围 | MeHg 平均值 | MeHg/THg | 参考文献 |
|---|---|---|---|---|---|---|---|
| **大洋海域** | | | | | | | |
| 西北太平洋 | 50 | 19.0～158.0 | 77.0 | | | | Sattarova and Aksentov, 2018 |
| 西北太平洋深海 | 466 | 8.0～170.0 | 68.8 | | | | Aksentov and Sattarova, 2020 |
| 北大西洋 | 233 | 1.9～112.1 | 18.2 | | | | Kita *et al.*, 2016 |
| 西地中海深海 | 86 | 9.0～100.0 | 47.1 | | | | Cossa *et al.*, 2021 |
| 北冰洋 | 35 | 22.0～169.0 | 72.2 | | | | Gleason *et al.*, 2017 |
| 地中海 | 56 | 12.0～447.3 | 54.1 | 0.09～3.71 | 1.09 | 2% | Ogrinc *et al.*, 2007 |
| 大西洋中部 | 22 | 0.54～78.8 | 42.3 | 0.01～1.24 | 0.62 | 1.1% | Hollweg *et al.*, 2010 |
| **近海** | | | | | | | |
| 中国近海 | 611 | 1.10～398.0 | 35.2 | | | | Meng *et al.*, 2014; Jeong *et al.*, 2021 |
| 韩国近海 | 53 | 12.0～98.0 | 42.4 | | | | Jeong *et al.*, 2021 |
| 东西伯利亚海 | 35 | 13.0～92.0 | 36.0 | | | | Aksentov *et al.*, 2021 |
| 北大西洋边缘海 | 49 | 8.00～1 351 | 106.5 | | | | Vieira *et al.*, 2021 |
| 卡塔尔海岸线 | 11 | 8.00～34.3 | 21.6 | | | | Hassan *et al.*, 2019 |
| 波罗的海 | 91 | 1.20～341.8 | 84.0 | | | | Kwasigroch *et al.*, 2021 |
| 南大洋边缘海 | 188 | 12.6～86.6 | 41.6 | | | | Zaferani *et al.*, 2018 |
| 中国渤海和黄海 | 83 | 4.70～100.6 | 27.3 | 0.01～0.71 | 0.16 | 0.6% | Yu *et al.*, 2021 |
| 中国东海 | 35 | 53.0～157.0 | 79.4 | 0.20～1.10 | 0.72 | 1.1% | 刘畅等, 2018 |
| 东北大西洋比斯开湾 | 24 | 18～973 | 243.2 | 0.07～2.03 | 0.70 | 0.4% | Azaroff *et al.*, 2019 |
| 亚得里亚海 | 22 | 680～9 950 | 4 350 | 0.47～7.85 | 3.48 | 0.08% | Acquavita *et al.*, 2012 |
| 拉普捷夫海 | 18 | 30.9～96.1 | 51.2 | 0.03～3.14 | 0.53 | 0.7% | Liem-Nguyen *et al.*, 2022 |
| 波罗的海 | 47 | 4.0～294.0 | 106.8 | 0.02～2.36 | 0.45 | 0.48% | Siedlewicz *et al.*, 2020 |

有助于揭示主导汞源的历史变化并重建不同汞源输入通量的历史年代表.现有研究发现,大多数沉积物剖面的汞浓度和汞同位素都表现出一致的变化趋势,即在距今 200 年左右的时间内,随着深度的增加总汞浓度总体上呈现先上升后下降的趋势,也就是说沉积物次表层存在汞浓度显著增加的现象,这可能与 19 世纪中叶工业革命造成的人为汞排放大量增加有关(Gobeil *et al.*, 1999; Jin and Liebezeit, 2013; Xu *et al.*, 2013; Gleason *et al.*, 2017; Kim *et al.*, 2019).同样地,汞同位素组成在沉积物次表层也存在显著不同,即与其他层相比具有明显较大的负 $\delta^{202}$Hg 和明显较小的正 $\Delta^{199}$Hg 值,且两者均趋向于 0,这与工业汞源的同位素特征较为接近,进一步证明了工业革命时期工业源等人为汞的大量输入(Ogrinc *et al.*, 2019; Bonsignore *et al.*, 2020).除此之外,沉积物汞的浓度和同位素变化除了源的输入外,还可能与沉积物内部发生的过程有关.

本研究总结的所有海洋沉积物样品产生的 $\Delta^{199}$Hg/$\Delta^{201}$Hg 比值为 1.23,介于已报导的水体 Hg(II)光还原(1.0)和 MeHg 光降解(1.36)的 $\Delta^{199}$Hg/$\Delta^{201}$Hg 比值之间(Bergquist and Blum, 2007),说明在进入沉积物前,海洋中的汞可能经历了 Hg(II)的光还原和 MeHg 的光降解.而海洋悬浮颗粒物则是汞向深海及沉积物迁移的主要途径,它们由透明的外聚物、浮游生物和细菌细胞、碎屑、以及有机物组成,也是汞进入食物网的重要来源(Ortiz *et al.*, 2015).因此,海洋悬浮颗粒物的汞同位素组成既可代表输出到海洋内部的汞同位素组成,也可作为甲基化和随后生物积累的汞的标志物(Lamborg *et al.*, 2016; Motta *et al.*, 2019).这里总结的海洋悬浮颗粒物数据多数在开阔大洋获得,如图 2 所示,海

洋悬浮颗粒物汞的$\delta^{202}$Hg值变化范围较大，为−2.37‰～+1.39‰（平均值为−0.33‰±0.64‰，$n$=84，1SD）；$\Delta^{199}$Hg值变化范围较小，为−0.34‰～+0.57‰（平均值为0.00‰±0.19‰，$n$=84，1SD）.与海水（平均值为−1.16‰±0.84‰，$n$=53，1SD）相比，海洋悬浮颗粒物明显更偏正，可能是由于不同区域汞输入源不同导致，也可能是由于汞甲基化和去甲基化等过程使海洋悬浮颗粒物发生明显汞同位素分馏导致；但沉积物（平均值为−1.24‰±0.61‰，$n$=638，1SD）中的$\delta^{202}$Hg值较海水略偏负，可能是由于海水中的汞经历了更大程度的光化学分馏过程，也可能是海水中的汞吸附到固相上发生了汞同位素质量分馏，导致沉积物汞略偏负.因为现有研究发现，Hg（II）键合到硫醇基团（Wiederhold *et al.*，2010）、吸附到针铁矿（Jiskra *et al.*，2012）、形成硫化汞和氧化汞沉淀（Foucher *et al.*，2013）等过程都可能导致固相的$\delta^{202}$Hg值显著负偏.另一个原因可能与沉积物内部发生的转化过程有关，包括沉积物中不稳定形态的汞向上覆水体的扩散、缺氧条件下不稳定形态的汞转化为硫化汞或多硫化汞、有氧条件下不稳定形态的汞转化为不溶性腐殖质结合态汞等（Beldowski and Pempkowiak，2009），这一系列沉积物埋藏后及成岩过程中的再活化、扩散和清除过程会重新分配汞，并导致汞同位素发生质量分馏.可以说，沉积物中的汞是水体汞经过一系列复杂过程后的最终产物，这些相关过程已在上一节海水汞同位素部分做了详细的介绍.

### 3.2 影响海洋沉积物汞同位素关键过程

正如前面所提到的，沉积物充当了水体汞重要的二次排放源，因此，相比于总汞浓度和总汞同位素数据，更需要关注的是沉积物中汞的化学赋存形态以及形态汞同位素组成，因为它们可以更好地给出沉积物汞的生物可利用性信息以及反演沉积物汞向上覆水体的二次释放过程.根据Bloom *et al.*（2003）提出的五步连续提取法，沉积物中的无机汞可分为以下5种赋存形态：水溶态汞（如$HgCl_2$）、胃酸可溶态汞（如HgO、$HgSO_4$）、有机及其他络合物结合态汞（如与腐殖酸结合的汞、$Hg_2Cl_2$）、强络合态汞（如Fe/Mn氧化物中的汞、无定形有机硫化物中的汞、矿物晶格中的汞）和硫化物结合态汞（如HgS）（Bloom *et al.*，2003）.其中，强络合态汞和有机络合态汞是绝大多数海洋沉积物中汞的主要络合形态，开阔大洋沉积物中大部分汞与硫化物或铁锰氧化物等无机成分络合（Kannan and Falandysz，1998），而河口和近海沉积物中大部分汞与有机物络合并且有机物上有足够的未络合汞的结合位点（Weber，1993；Chakraborty *et al.*，2014）.研究表明，生物可利用性最高的汞是强络合态汞，其次是有机络合态汞（因其迁移性较低）和水溶态/胃酸可溶态汞（因其所占比例较低，<5%），最低的是硫化物结合态汞（因其最为稳定）（Zhong and Wang，2006）.可见，汞化学赋存形态研究对于明确沉积物汞的潜在迁移性和生物有效性至关重要，尤其是针对不同形态汞的同位素组成研究，将有助于进一步厘清沉积物汞的精确来源与迁移转化机制.例如，Crowther *et al.*（2021）通过研究河床沉积物中不同形态汞同位素组成，发现水溶态汞在同位素上更类似于强结合态汞和硫化物结合态汞，可能是由于强结合态汞和硫化物结合态汞作为沉积物汞主要形态会将溶解的汞慢慢释放到孔隙水中，随后又作为水溶态汞吸附到沉积物上.然而目前针对沉积物中单一形态汞同位素分馏的研究还非常少（Stetson *et al.*，2009；Wiederhold *et al.*，2013，2015；Yin *et al.*，2013；Grigg *et al.*，2018；Brocza *et al.*，2019；Crowther *et al.*，2021），未来亟需开展大量相关研究以进一步完善海洋汞同位素分馏理论及其应用.

### 3.3 影响海洋沉积物汞同位素的环境因素

需要指出的是，沉积物中汞的赋存形态及其与上覆水体间的交换受多种地球化学因素影响，主要包括温度、盐度、pH、硫化物浓度、氧化还原条件、总有机碳（TOC）等（Gilmour *et al.*，1992）.

温度和盐度的影响.研究表明，温度升高有利于沉积物中汞的解吸过程和汞向上覆水体的扩散，因为沉积物中的汞向水体释放是一个吸热过程（单长青等，2006；王欣悦等，2015）.盐度，一方面会通过影响汞对甲基化细菌的生物可利用性（Hollweg *et al.*，2009；Schartup *et al.*，2015）而影响沉积物汞的甲基化活性，通常海洋低于淡水（Olson and Cooper，1974；Blum and Bartha，1980；Ullrich *et al.*，2001），因为厌氧沉积物的盐度与Hg（II）甲基化能力呈显著负相关，高盐下的甲基化水平仅为低盐下的40%（Blum and Bartha，1980；Compeau and Bartha，1987）；另一方面会影响汞在水-沉积物界面的迁移转化，例如，高盐度条件会减弱汞对粘土矿物

的吸附,导致沉积物中的汞向近底水中释放(Celo *et al.*, 2006; Green-Ruiz, 2009).

pH和硫化物的影响.pH会影响汞在水相和沉积物相的分配,pH<7时,沉积物中酸溶态和水溶态汞更易溶出,pH>7时,有机结合态汞更易溶出(Lors *et al.*, 2004);同时较高pH下,汞与一些矿物如针铁矿的吸附增强(Jiskra *et al.*, 2012),且高pH和硫化物浓度下,HgS的溶解度明显增大(Ravichandran *et al.*, 1998).

氧化还原条件的影响.由于汞对氧化还原过程的敏感性,氧化还原条件的任何变化都会导致沉积物汞形态的变化.在氧化条件下,汞更容易与有机物结合,而在还原环境下,水体中的氧气含量低,甚至有$H_2S$的出现,硫化条件下汞更倾向于与还原态硫化物结合,目前已有不少古海洋地质样品表现出硫化物结合态汞为汞主要结合形态的特征(Zheng *et al.*, 2018; Shen *et al.*, 2019, 2020; Them *et al.*, 2019).显生宙以来地球经历的5次生物大灭绝都与海洋氧化还原状态的改变密切相关(Anbar and Rouxel, 2007; Whiteside and Grice, 2016; 卢贤志, 2021; 王振飞等, 2021).汞及其同位素在记录海洋氧化还原状态及重建古海洋演化方面具有不可替代的优势(Zheng *et al.*, 2018).

TOC的影响.研究表明,TOC在控制沉积物中汞的赋存发挥着重要作用,因为大部分海洋沉积物中THg与TOC呈现显著相关性(Kita *et al.*, 2016; Aksentov and Sattarova, 2020; Jeong *et al.*, 2021),且中印度海脊沉积物中超过80%的THg为有机物结合态汞(Lim *et al.*, 2020).但也有研究表明Hg与TOC之间没有相关性,这可能是由不同来源的有机质导致的(Aksentov *et al.*, 2021).

可以说,汞在沉积物与上覆水体之间的迁移转化是海洋内部汞循环的关键环节,这一环节受以上多种因素影响,阐明这一环节中各个反应过程的汞同位素分馏规律及其控制因素将有助于反演海洋汞循环历史并预测海洋汞污染变化,同时也是完善海洋汞同位素分馏理论必不可少的,但目前只有极少数相关研究(Wiederhold *et al.*, 2010; Jiskra *et al.*, 2012; Foucher *et al.*, 2013),未来亟待加强.

## 4　海洋生物汞同位素变化特征

本节主要概述全球海洋生物中的汞同位素组成,并结合其汞浓度和形态数据,着重阐述海洋生物汞同位素变化特征及其反映出的汞循环信息尤其是甲基汞的来源和迁移转化过程.

受甲基汞提取与分离技术的限制,目前大多数生物样品的汞同位素测试都是针对THg(Zhang *et al.*, 2021).如图2所示,海洋生物$\delta^{202}$Hg值为$-1.46‰\sim+1.49‰$ ($n$=487),$\Delta^{199}$Hg值为$-0.31‰\sim+5.50‰$ ($n$=487),变化范围均很大,且总体来看均显著高于海水、海洋颗粒物以及海洋沉积物(图2).究其原因,目前已有很多相关研究,有研究发现这是由于汞从海水或沉积物被低营养级生物富集并向高营养级生物传递过程中发生了汞同位素分馏(Perrot *et al.*, 2012).而目前更多的研究表明在营养级传递过程中并不发生汞同位素分馏,海洋生物中较高的汞同位素组成是由于甲基汞随营养级的优先传递所导致的,因为沉积物或大洋水柱产生的甲基汞在被海洋生物摄取前经历了光降解反应,在剩余甲基汞中产生了显著偏正的$\delta^{202}$Hg和$\Delta^{199}$Hg(图4);且由于光降解的程度不同,剩余甲基汞具有的$\delta^{202}$Hg和$\Delta^{199}$Hg值大小也显著不同(Bergquist and Blum, 2009; Gehrke *et al.*, 2011),当甲基汞随食物链营养级优先传递时,沿食物链生物体内的甲基汞占比(MeHg/THg)也越来越高,因此海洋生物表现出显著高于海水和海洋沉积物的汞同位素组成,并展现出较大的$\delta^{202}$Hg和$\Delta^{199}$Hg变化范围(Meng *et al.*, 2020).也正因海洋高营养级生物中的甲基汞占比非常高(MeHg/THg通常高于80%,甚至高达>95%),故其总汞同位素组成可被视为甲基汞的同位素组成,而海水和海洋沉积物因甲基汞占比非常低,其总汞同位素组成则主要代表了无机汞的同位素组成.未来如能提取出海水甲基汞进行同位素测定,与生物样品的甲基汞同位素值进行对比,将有助于准确判断生物样品甲基汞同位素MIF信号是否来自海水中甲基汞的光化学过程,从而能够更好地追溯海洋生物甲基汞的来源与转化.

海洋生物体内的汞主要以$HgCl_2$和$CH_3HgCl$两种化学形态存在,它们是海洋生物对无机汞和有机汞生物利用性最高的形态(Laporte *et al.*, 1997).相比于海水和海洋沉积物,海洋生物体内总汞浓度明显较高,尤其是甲基汞浓度及其占总汞的比例(表3),这是因为甲基汞能够在水生食物网中快速被生物富集,并优先随营养级传递而进行生物放大(Lehnherr *et al.*, 2011; Gilmour *et al.*, 2013; Mun-

son *et al.*, 2018; Rosera *et al.*, 2020),使得食物链顶端生物的MeHg浓度比海水和沉积物高出几个数量级(Braune *et al.*, 2015).但是,目前关于食物网中甲基汞的来源尚不明确,以往研究只依靠浓度信息并不能实现精确的源解析,近期研究采用汞同位素手段初步得到了一些结论.对于近海生物,研究结果表明其食物网中的甲基汞可能主要来自于近海沉积物(Perrot *et al.*, 2010; Meng *et al.*, 2020),因为近海生物主要是底栖生物,生活在沉积物的顶部或者上方,沉积物中产生的甲基汞可有效地转移到近海食物链(Bonsignore *et al.*, 2015; Meng *et al.*, 2020).例如,根据对近海全食物链生物的汞同位素分析,Meng *et al.*(2020)推断得到近海生物所富集的甲基汞在水体发生光降解前的$\delta^{202}$Hg值在很大程度上与沉积物重叠,所富集的无机汞的odd-MIF值也与沉积物非常相似,从而表明近海食物网中甲基汞很有可能来源于近海沉积物.而对于开阔大洋生物,越来越多的证据表明海水相对于海洋沉积物更有可能成为其甲基汞的主要来源(Mason and Fitzgerald, 1990; Cossa *et al.*, 2009, 2011; Sunderland *et al.*, 2009; Kirk *et al.*, 2012; Mason *et al.*, 2012; Lehnherr, 2014),因为开阔大洋甲基汞的深度垂直剖面几乎没有显示出任何沉积源的贡献(Lehnherr, 2014).除此之外,汞同位素证据还显示,深海动物群具有显著偏正的$\Delta^{199}$Hg(1.47‰±0.13‰),表明外海中的甲基汞主要来源于上层海水(Sun *et al.*, 2020a),而不是海底沉积物(具有非常小或者接近0的$\Delta^{199}$Hg),且上层海水中的汞可能通过颗粒物的沉降作用达到深海进而被生物富集.在过去几十年中,海洋生物体内汞浓度有所增加,甚至在海洋最深处的马里亚纳海沟生物群中也发现了高汞浓度(547±230 ng/g)(Sun *et al.*, 2020a);表明人类污染已经蔓延至此,海洋汞污染已成为全球性环境问题,需要更多的研究来厘清其迁移转化机制,以制定有效政策来缓解海洋汞污染.

**表3 全球不同海域海洋生物中的THg和MeHg浓度(ng/g)**

Table 3 THg and MeHg concentrations in marine biotas from different regions of the world (ng/g)

| 区域 | 样品类型 | 样品数 *n* | THg范围 | THg平均值 | MeHg范围 | MeHg平均值 | MeHg/THg | 参考文献 |
|---|---|---|---|---|---|---|---|---|
| 南大洋 | 鱼类 | 83 | 100~1 940 | 500 | | | | Queirós *et al.*, 2020 |
| 南大洋* | 鱼类 | 194/74 | 58~476 | 167 | 33~512 | 144 | 86% | Seco *et al.*, 2020 |
| 西北地中海 | 鱼类 | 48 | 210~4 420 | 1 162 | | | | Koenig *et al.*, 2013 |
| 太平洋 | 鱼类 | 300 | 50~790 | 384 | | | | Meador *et al.*, 2005 |
| 印度洋 | 鱼类 | 187 | 210~3 970 | | | | | Kojadinovic *et al.*, 2007 |
| 大西洋(加纳近海) | 鱼类 | 56 | 4~122 | | | | | Voegborlo and Akagi, 2007 |
| 东北大西洋沿岸 | 鱼类 | 706 | 50~7 473 | 988 | | | | Chouvelon *et al.*, 2012 |
| 东北大西洋 | 鱼类 | 53 | 30~6 350 | 1 609 | 20~4 780 | 1 257 | 76% | Romero-Romero *et al.*, 2022 |
| 大西洋(亚述儿群岛) | 鱼类 | 70 | 190~1 440 | 900 | | | | Afonso *et al.*, 2007 |
| 韩国马山湾 | 底栖生物 | 399/89 | 6~1 290 | 135 | 1~1 290 | 131 | 65% | Hilgendag *et al.*, 2022 |
| 加拿大坎伯兰湾 | 底栖生物 | 71 | 20~3 170 | 763 | | | | McMeans *et al.*, 2015 |
| 大西洋岸 | 哺乳动物 | 344/344 | 50~3 440 | 862 | 50~3 160 | 819 | 94% | Wagemann *et al.*, 1998 |
| 南大洋公海 | 海鸟 | 110 | 180~15 160 | 2 474 | 180~11 570 | 2 220 | 88% | Renedo *et al.*, 2020 |
| 西北冰洋 | 哺乳动物 | 69/19 | 400~119 320 | 21 080 | 570~3 380 | 1 560 | 14% | Masbou *et al.*, 2018 |
| 北太平洋阿拉斯加湾 | 哺乳动物 | 53/18 | 87~13 900 | 2 786 | 30~370 | 134 | 9% | Masbou *et al.*, 2015 |
| 中国南海 | 鱼类 | 166/96 | 11.9~1 772 | 152 | 6.22~358 | 105 | 69% | Liu *et al.*, 2014 |
| 中国渤海 | 鱼类 | 67 | 2.05~344 | 63.8 | | | | Liu *et al.*, 2013 |
| 中国渤海 | 鱼类 | 55 | 9~270 | 60 | 7~131 | 25 | 42% | Qu *et al.*, 2022 |
| 中国东海 | 鱼类 | 148 | 20~660 | 260 | 10~590 | 180 | 74% | Cheng *et al.*, 2009 |

注:*测定的是有机汞浓度,而非甲基汞浓度.

海洋生物汞同位素变化特征不仅能提供生物甲基汞的来源和迁移信息,还能进一步示踪甲基汞的转化过程.通过深入分析生物汞同位素与营养级、海水深度和海域位置(近海 vs. 开阔大洋)之间的关系,可以发现海洋生物的$\delta^{202}$Hg和$\Delta^{199}$Hg随着深度增加而降低,这是由于相比下层海水,上层海水中甲基汞经历了更大程度的光降解,其剩余甲基汞向下输送与下层光降解程度较低甚至未发生光降解的甲基汞混合,导致纵向剖面上呈现出了MDF和odd-MIF随深度而降低的变化趋势(Mason *et al.*, 1996; Blum *et al.*, 2013).与河口和近海生物相比,开阔大洋生物的$\delta^{202}$Hg和$\Delta^{199}$Hg值更高,这也是光化学反应程度的不同所造成的,因为开阔大洋初级生产力较低,能允许更多的光线穿透,因此水体甲基汞光降解程度更高(Bergquist and Blum, 2007; Gantner *et al.*, 2009; Senn *et al.*, 2010; Perrot *et al.*, 2012; Blum *et al.*, 2013; Meng *et al.*, 2020),而近海水域中的甲基汞被认为主要产生于底部沉积物,这些甲基汞既没有大量暴露于阳光下也没有完全混合于水柱中,而是直接被转移到食物网中,所以其汞同位素分馏程度较低(Balogh *et al.*, 2015).不仅如此,海洋生物的$\Delta^{199}$Hg整体上还具有明显的南北梯度变化,即随着纬度升高而降低,这可能反映了光照强度的变化对水体汞光化学反应程度的影响(Point *et al.*, 2011; Masbou *et al.*, 2018).

水体或沉积物中的无机汞可通过硫酸盐还原菌、铁还原菌、产甲烷菌等厌氧微生物的甲基化作用转化为甲基汞,但近期的研究显示,当海洋生物摄入IHg和MeHg后,会在体内发生IHg甲基化和MeHg降解(Yang *et al.*, 2021),转化机制和关键因素尚不清楚.Yang *et al.*(2021)发现海洋鱼类肠道微生物在汞生物转化中起着主导作用,并发现虽然鱼体内的甲基化相当缓慢,且甲基汞降解速率高于甲基化速率,但在长期自然环境下,体内甲基化导致的甲基汞积累也不容忽视.汞一旦被生物吸收,就会进入血液并迅速分布在各种组织和器官(López-Berenguer *et al.*, 2020),尽管暴露于汞的海洋生物也存在一些机制进行“解毒”,且不同物种具有不同的“解毒策略”,比如去甲基化机制(Wintle *et al.*, 2011)、排泄机制(如尿液、粪便、毛发,呼吸作用等)(Nigro *et al.*, 2002; Correa *et al.*, 2014)、汞与金属硫蛋白的结合以及汞与硒的结合机制等(Ikemoto *et al.*, 2004; Burger and Gochfeld, 2013; Romero *et al.*, 2016),但生物体内汞的消除和排泄途径非常缓慢(Chouvelon *et al.*, 2018).目前关于海洋生物体内汞转化和“解毒”过程的同位素分馏规律研究几乎还是空白,未来需要深入研究来探明海洋生物汞的原位迁移转化.

## 5　海洋汞同位素通量模型

全球海洋中的汞主要来源于大气沉降、河流、海底热液和火山等地质活动输入、以及海底地下水输入等(Donovan *et al.*, 2013; Mil-Homens *et al.*, 2013; Štrok *et al.*, 2019; Meng *et al.*, 2020; Liu *et al.*, 2021c),参与海洋内部循环后,则通过逸散回大气、埋藏于沿海/深海沉积物以及海沟等主要途径从海洋内部去除(Cossa *et al.*, 2022).海洋应该是一个动态平衡的系统,希望通过现有的海洋汞输入和输出通量以及同位素信息($\delta^{202}$Hg和$\Delta^{199}$Hg)简单检验全球海洋汞是否处于稳态.从表4和图5可看出,海洋汞的总输入通量(4 800 t/a)与总输出通量(4 894 t/a)较为接近,表明目前海洋汞收支基本平衡.但由于目前通量计算的不确定性较大,因此光靠通量评估是不够准确的,汞同位素特征则可以为汞通量提供强有力的约束,因为不同的储库具有不同的汞同位素特征.考虑到MDF普遍发生在任何过程中,不确定性较大,这里只用$\Delta^{199}$Hg进行约束.通过公式(3)进行简单计算,结果显示,在汞同位素的约束下依然处于平衡状态(表4),再次证明了我们的模型中海洋汞处于收支平衡的结论.

$$F_{输入}\times\Delta^{199}\mathrm{Hg}_{输入}\approx F_{输出}\times\Delta^{199}\mathrm{Hg}_{输出}, \quad (3)$$

其中,$F_{输入}$和$F_{输出}$表示海洋汞输入和输出通量,公式中所用的数据如表4所示.

需要指出的是,由于汞的各输入、输出通量以及汞同位素组成还没有建立完善,因此该模型还有许多不确定因素.特别是海底火山和热液汞输入,由于缺乏数据,它们在海洋汞模型中很少受到约束,但越来越多的证据表明,海底地质活动可能向深海释放大量汞(Cox and McMurtry, 1981; Stoffers *et al.*, 1999; Engle *et al.*, 2006; Sherman *et al.*, 2009).目前海底火山热液的汞同位素研究还非常有限,尚难以将源特征和同位素分馏过程区分开来,因此海底火山热液源的同位素特征还难以确定.根据现有研究,高温条件下的火山热液过程几乎不会导致汞的MDF和MIF,且在热液喷口附近采集

**表4 海洋汞输入源和输出源的通量和同位素组成($\Delta^{199}$Hg和$\delta^{202}$Hg)**

Table 4 Fluxes and isotope compositions ($\Delta^{199}$Hg and $\delta^{202}$Hg) of Hg input sources and output sources in the ocean

| 类别 | 通量 (t/y) | 通量范围 (t/y) | $\Delta^{199}$Hg (‰) | $\Delta^{199}$Hg±1SD (‰) | $\delta^{202}$Hg±1SD (‰) | 数据量 (*n*) |
|---|---|---|---|---|---|---|
| **输入源** | | | | | | |
| 河流输入[1,i] | 1 000 | 893～1224 | −0.29 | −0.29±0.12 | −1.82±0.39 | 156 |
| 热液输入[2,ii] | 100 | ＜600 | 0.00 | 0.00±0.00 | 0.00±0.00 | |
| 大气Hg(II)沉降[2,iii] | 1 500 | 912～1 900 | 0.41 | 0.41±0.34 | −0.43±0.77 | 172 |
| 大气Hg(0)沉降[2,iii] | 2 200 | 1 900～2 888 | −0.19 | −0.19±0.10 | 0.37±0.65 | 220 |
| $F_{输入}$ | 4 800 | $F_{输入}\times\Delta^{199}Hg_{输入}$ | −93 | | | |
| **输出源** | | | | | | |
| 埋藏于沿海沉积物[1,iv] | 730 | 410～1 100 | 0.06 | 0.06±0.11 | −1.19±0.43 | 546 |
| 埋藏于深海沉积物[2,v] | 600 | 200～600 | 0.10 | 0.10±0.10 | −0.99±0.39 | 92 |
| 埋藏于海沟[3,vi] | 164 | 101～227 | 0.24 | 0.24±0.07 | −1.19±0.43 | 19 |
| 海洋Hg(0)逃逸[2,vii] | 3 400 | 2 900～4 000 | −0.07 | −0.07±0.10 | 0.44±0.02 | 61 |
| $F_{输出}$ | 4 894 | $F_{输出}\times\Delta^{199}Hg_{输出}$ | −94.84 | | | |

注：通量数据：[1]据Liu *et al.* (2021b)；[2]据Outridge *et al.* (2018)；[3]据Liu *et al.* (2021a). 同位素数据：[i]据Yin *et al.* (2018)；[ii]据Smith *et al.* (2008), Sherman *et al.* (2009)和Kim *et al.*(2022)；[iii]据Jiskra *et al.* (2021)；[iv]据Balogh *et al.*(2015), Bonsignore *et al.*(2015, 2020), Yin *et al.* (2015, 2018), Gleason *et al.*(2017), Meng *et al.*(2019, 2020, 2021), Sun *et al.*(2020b)和Jung *et al.*(2022)；[v]据Jiskra *et al.*(2021)；[vi]据Liu *et al.* (2021a)；[vii]据Zheng *et al.*(2007).

的沉积物$\delta^{202}$Hg较小，略正(0.16‰±0.47‰)，海洋热液样品在沉积过程中富集较重的汞同位素，由此推测海底火山热液源的$\delta^{202}$Hg和$\Delta^{199}$Hg可能均接近于0‰；而之所以实际检测的火山热液样品中$\delta^{202}$Hg变化范围非常大(−4‰～+1‰)，是因为在热液蒸汽输送和排放过程中发生了MDF(Smith *et al.*, 2005, 2008; Sherman *et al.*, 2009; Gratz *et al.*, 2010; Kim *et al.*, 2022). 此外，以往的全球或者海洋通量模型都没有考虑海沟的埋藏，但最近的研究表明地球的最深处——海沟也会埋藏大量的汞，至少与模型中的热液输入量相当(Liu *et al.*, 2021a)，因此笔者将海沟埋藏也纳入此模型中. 同时，海底地下水也可能将大量汞带入海洋中，已有研究指出，对于沿海海域，海底地下水输入可能是与大气输入同样重要的汞源(Bone *et al.*, 2007; Laurier *et al.*, 2007; Black *et al.*, 2009)，但全球汞模型尚未对此进行解释，在这里也不做过多阐述.

## 6 海洋汞同位素地球化学展望

虽然汞同位素已被广泛应用于地球化学、古环境、生态效应、天体化学等领域，展现出广阔的应用前景，但关于海洋汞同位素的研究还十分缺乏，未来无论是检测分析方法还是同位素分馏过程机理研究都有待加强，特别是以下几个主要方面：

(1)受检测难度高的限制，海水汞同位素研究尚处于起步阶段，这极大限制了汞同位素在海洋汞来源和转化方面的应用，亟需应用并拓展最新建立的海水汞同位素分析方法，开展远洋实时、原位海水汞同位素检测，以补充海水汞同位素数据库，同时要加强基于海水的室内模拟实验研究，以完善海水汞同位素分馏理论.

(2)海洋沉积物中汞的赋存化学形态、沉积过程及汞在沉积物-海水界面间的交换、及其控制因素尚不明晰，需要深入开展针对沉积物不同形态汞的同位素组成及分馏规律研究，同时结合室内模拟实验，以厘清汞在沉积物与上覆水体之间的迁移转化过程. 同样，还要深入研究海水-大气界面交换过程汞同位素分馏，以进一步优化和制约海洋和大气两个重要储库间汞的转化通量.

(3)海洋生物中汞尤其甲基汞的来源与过程解析是全面理解海洋汞生物地球化学循环的关键，也是有效控制海洋汞污染人体健康危害的基础，但目前相关研究尚得不到准确的结论，亟需建立针对甲基汞的同位素分析方法，深入开展海水、海洋沉积物、海洋生物样品中甲基汞的同位素组成研究，以揭示海洋生物甲基汞的准确来源(海水 or 沉积物 or 生物原位甲基化)，追踪其经历的转化过程(水体光降解 or 生物解毒).

(4)海洋汞的重要自然源的同位素信息尚不明

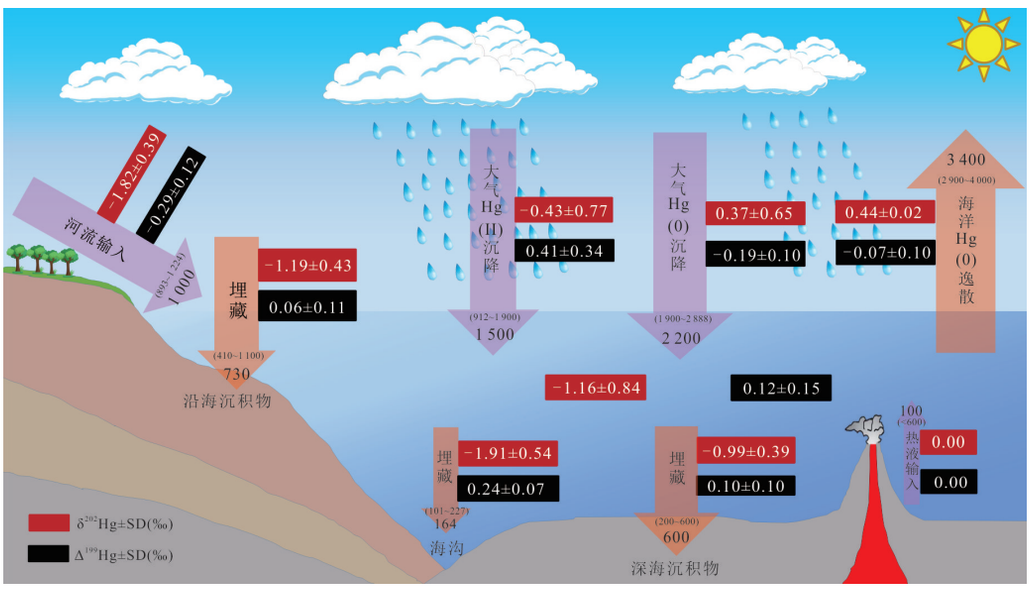


图5　海洋汞通量和同位素模型

Fig. 5　Input and output fluxes and isotope compositions of Hg in the ocean

粉色箭头表示海洋汞的输入,橙色箭头表示海洋汞的输出;箭头里的数字为输入或输出通量,单位为t/a,括号里面的数字表示通量范围,箭头大小表示输入或输出通量的相对大小.海水汞同位素数据及参考文献同图2,其他数据及参考文献同表4

确,未来需要开展特别是海底火山热液系统与地下水输入等潜在来源的汞同位素组成及变化特征研究,以补充海洋汞输入源的同位素数据库,在结合海洋洋流驱动同位素变换研究基础上,进一步完善海洋汞同位素通量模型.

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