Concentration and stable isotope composition of Hg in deep-sea sediment from the Nankai Trough

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Abstract

Concentrations ($n = 60$) and stable isotope compositions ($n = 10$) of mercury (Hg) were determined for sediments as deep as 2300 m below the seafloor at ODP (Ocean Drilling Program) and IODP (International Ocean Discovery Program) Site 0002C in the forearc Kumano Basin, Nankai Trough. Concentrations of Hg varied within the range of 30–240 µg/kg, except for three samples of trench-fill sediment from the accretionary prism in which Hg concentrations were 330–820 µg/kg. Range of the studied Hg concentration is similar to those of modern subareal and marine sediments. Stable isotope values were close to those of volcanogenic and hydrothermal materials: –0.26 to –0.83‰ for $\delta^{202}$Hg. No mass-independent fractionation was observed, as $\Delta^{199}$Hg was almost zero (range within 0.03 to 0.1). These results suggest that the Hg originated from volcanogenic or hydrothermal detrital materials and is being accreted and/or subducted with the oceanic plate.
INTRODUCTION

The toxic trace element mercury (Hg) is one of the most active elements in the shallow parts of the Earth, including the atmosphere, hydrosphere, and lithosphere. It is a siderophile or chalcophile element in the solid Earth that behaves as a volatile with a strong tendency to accumulate in the biosphere. For that reason, the biogeochemical cycle of this element is well documented, and its stable isotopes have been used effectively to document the Hg cycle (e.g., Yin et al., 2010). The distribution of Hg in soil and sediment is mapped in the land and sea territories of Japan (e.g., AIST, 2022), where high concentrations appear in the present volcanic zone of Northeast Japan and fossil (Neogene) volcanic zone of Southwest Japan. Documented as geological cycle of Hg (e.g., UNEP, 2013), it is clear that Hg is emitted from volcanic and hydrothermal activities to the Earth’s surface; however, its reentry into the Earth’s interior is poorly constrained by observations. In this study, we documented the vertical profile of Hg concentration and the stable isotope composition of actively subducting seafloor sediments to better understand the complete geologic cycle of Hg.

SAMPLES AND ANALYTICAL METHODS

Sediment samples were collected by deep-sea drilling vessel Chikyu from Site C0002 in the Kumano Basin (Fig. 1) during ODP (Ocean Drilling Program) Leg 315 and IODP (International Ocean Discovery Program) Legs 338 and 348. The Kumano Basin is a forearc basin along the Nankai Trough, where the Philippine Sea plate is subducting beneath the Eurasia plate. The lithology of the site is documented in Fig. 2. All samples in this study were squeezed cakes of silty claystone, from which porewater had been extracted, that were preserved in a freezer. The 60 samples were selected from those reported by Masuda et al. (2019) that were used for arsenic (As) analyses. Of these samples, 43 consisted of forearc basin sediments (Units I and II) and forearc or trench-fill deposits (Unit III), and 4 samples were from the uppermost layer of older accretionary sediments (Unit IV). Below a gap of more than 1100 m, where samples were not taken, 13 samples were taken from accreted trench-fill or hemipelagic sediments of the Shikoku Basin, a back-arc basin comprising Philippine Sea Plate (Unit V).

Although the samples had been freeze-dried before the As analysis, frozen samples were used for Hg analyses to inhibit loss of volatile Hg during drying. Water content was determined from the loss of frozen sample weights after heating overnight at 105 °C. Final Hg concentrations are expressed as dry weight. The detailed analytical
procedures of concentrations and stable isotopes are described in the Supplementary Information.

Total Hg concentration was determined for 60 samples using cold vapor atomic absorption spectrophotometry. Results were checked for accuracy by Hg measurements of standard rock sample JSd-3, distributed by AIST (riverbed sediment), for which we determined an average concentration of 250 ± 42 µg/kg (recommended value 254 µg/kg).

Of the 60 samples, 10 were selected for Hg stable isotope analysis using multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) after collecting the Hg in a KMnO₄ solution by cold vaporization. Isotope ratios are expressed as δ notation with respect to ¹⁹⁸Hg values of international standard material NIST SRM 3133:

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

Results were checked by duplicate determinations of standard sample ERM-CC580 (river mouth sediment) distributed by the Institute for Reference Materials and Measurements, Belgium (δ²⁰²Hg = −0.48 ± 0.12‰, Janssen et al., 2016), for which we determined δ²⁰²Hg of −0.43‰ and −0.40‰ with an analytical error of ±0.09‰.

Mass-independent fractionation (MIF) of the Hg isotopes can be quantified as Δ notation using the following equation:

$$\Delta^{xxx}\text{Hg} (\text{‰}) = \delta^{xxx}\text{Hg} - f_{xxx} \times \delta^{202}\text{Hg}$$

$$f_{xxx}$$ is the mass dependent scaling factor; i.e., $$f_{199} = 0.252$$, $$f_{200} = 0.502$$, $$f_{201} = 0.752$$, and $$f_{204} = 1.493$$ (Blum and Bergquist, 2007).

Major mineral compositions of the samples were determined by powder X-ray diffraction photometry using Ni targeted CuKα radiation at 40 kV and 15 mA (Rigaku, Mini-Flex 600).

**RESULTS**

**Hg concentrations**

The Hg concentrations of the samples studied here are listed in Supplementary Table S1 and plotted against depth in Fig. 2b. Concentrations ranged from 30 to 240
µg/kg, except for three deep samples, and the average and standard deviation for all samples but the outliers were 140 ± 42 µg/kg. These values are a close match to those of ocean bottom sediments in and near the Kumano Basin (n = 94, range: 37–290 µg/kg; average and standard deviation: 143 ± 50 µg/kg; AIST, 2022). The three exceptional samples, consisting of Unit V sediment from 2173 to 2213 m below the seafloor, had Hg concentrations of 837, 332, and 357 µg/kg. These are discussed below.

Hg isotope characteristics

Sets of Hg isotopes (δ^{199}\text{Hg}, δ^{200}\text{Hg}, δ^{201}\text{Hg}, δ^{202}\text{Hg} and δ^{204}\text{Hg}, Δ^{199}\text{Hg}, Δ^{200}\text{Hg}, Δ^{201}\text{Hg} and Δ^{204}\text{Hg}) are listed in Supplementary Table S2. Ranges and 2σ errors of δ^{202}\text{Hg} of the 10 samples were −0.83 to −0.18‰ (±0.09‰), and the Hg isotope ratios giving as δ values gave linear relations to δ^{202}\text{Hg} and was explained by simple mass-dependent fractionation. Figure 3 shows the relations between δ^{202}\text{Hg} vs. Δ^{199}\text{Hg} and Δ^{201}\text{Hg} and Δ^{199}\text{Hg}. The values of Δ^{199}\text{Hg} and Δ^{201}\text{Hg} are close to zero and no systematic variation was observed. Combining δ and Δ values of Hg isotopes, MIF is negligible in the studied sediment column. Probable source of the studied Hg will be discussed later.

Mineralogical compositions

Most abundant minerals are quartz, clay minerals (illite and smectite) and feldspars (Supplementary Table S3). Much of quartz and illite demonstrated dominant subareal source. It is notable that the sample containing the highest Hg (837 µg/kg) comprised less amount of these minerals but abundant amorphous materials, plausibly volcanic glass.

DISCUSSION

The sediment samples represented turbiditic silty deposits of Units I, II, and III and upper accretionary prism deposits of Unit IV consisting mainly of silty claystone (Figure 2-a). The Hg concentrations in these units were all overlapped. The variation of Hg isotope compositions in our samples was consistent with mass-dependent fractionation. The stable isotope values corresponded to those from volcanogenic and hydrothermal sources as shown in Figure 3-a (δ^{202}\text{Hg}: -0.26 to -0.83; Δ^{199}\text{Hg}: +0.03 to +0.10). As noted above, prominent mass-independent fractionation was not observed, implying less photogenic alteration or biogenic contribution as a source. The characteristic of Hg concentration and isotope ratios indicate that the Hg came from a single or widely distributed common source throughout the sediment column.
The sediments of Units I, II, and III are forearc slope sediments derived from the Kii Peninsula, where no active volcanism is present; however, Hg mines and riverbed sediments with high Hg concentrations distributed along the Median Tectonic Line are related to Neogene volcanism and subsequent hydrothermal activity (AIST, 2022). Coincidental similar range of Hg concentration of the ocean bottom sediments in the Kumano-nada (in and around the studied site, 37-290 µg/kg, average 143±50 µg/kg, n=95, AIST, 2022) to that of studied sediments is indicative of subareal detrital materials as the source of Hg of the sediments from the Units I, II, III, and probably IV.

Higher Hg concentrations were found in three samples from the deepest part of the sediment column. These represented Unit V, accretionary prism deposits that originated as hemipelagic trench-fill or Shikoku Basin sediments. X-ray diffraction analysis revealed that the sample with the highest Hg concentration (820 µg/kg) contained a large proportion of volcanic glass. Hg concentration >200 µg/Kg of ocean bottom sediments appear along Suruga Trough and Tenryu submarine canyon toward the Nanakai Trough (AIST, 2022), indicating that the Hg has been transported with subareal detrital materials via turbiditic current and deposited along the trench axis. Such a detrital material is one of the possible sources of Hg in the trench-fill deposits of Unit V. Atmospheric deposition of volcanic ash would be another source for Hg, however, photogenic alteration can be negligible as noted above.

Thus, geogenic materials related to the subareal volcanic/hydrothermal activities appear to be the dominant and common Hg source in the studied sediment column, although we did not establish the host phase(s) of Hg in this study.

CONCLUSION

We documented the concentrations and isotope compositions of Hg in subseafloor sediments down to 2200 m below the seafloor. The results indicate that volcanogenic or hydrothermal Hg originated detrital materials is the predominant source of the Hg in these sediments. Our findings suggest that geogenic Hg emitted by magmatic activity is the most important source of Hg in the sediments of subducting slab.

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References


Figure captions

214 Figure 1 Location of IODP Cite C0002.

216 Figure 2 Lithology and Hg concentration of the sediment with depth at IODP Site C0002. a) Lithology of the sediments (Summarized from Strasser et al., 2014; Expedition 348 Scientists and Scientific Participants, 2014); b) Changes of Hg concentration with depth.

221 Figure 3 Relations between $\delta^{202}$Hg vs. $\Delta^{199}$Hg (a) and $\Delta^{201}$Hg vs. $\Delta^{199}$Hg (b) of the sediments from IODP Site C0002 at Nankai Trough. The squares showing the isotopic values in (a) are quartile of each geogenic materials compiled by Sun et al. (2016). Numbers 1, 2, and 3 in (b) gives the linear relations of $\Delta^{201}$Hg vs. $\Delta^{199}$Hg via photochemical reduction experiments (1: methyl Hg, 3: Hg$^+$) and fish tissues (Bergquist and Blum, 2007).
Fig. 1

Kumano-nada Basin

C0002

Nankai Trough

Google Earth

100 km
Fig. 3

Masuda et al., Figure 3