

Native Hg_{liq} in the metalliferous sediments of the East Pacific Rise (21°S)

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Abstract

Native Hg droplets, documented here for the first time in mid-ocean ridge metalliferous sediments, were found in the surface sediment of a magmatically robust and ultra-fast spreading mid-ocean ridge, the East Pacific Rise. The surface sediment and Fe–Mn micromnodules in it are enriched in Hg. Two different processes can produce Hg_{liq}^0 in this environment: hydrothermal and biogenic. Bio-transfer of ionic Hg dissolved in the hydrothermal fluids into Hg^0 in the sediment can account for the eventual native Hg occurrences in the close vicinity of the hydrothermal vents. The Hg_{liq}^0 occurrences in the distal metalliferous sediments most probably have originated directly from the hydrothermal fluids and been transported by hydrothermal plumes away from the vents. Condensation of Hg_{liq}^0 from Hg_{vap}^0 in the vent fluids subjected to near critical phase separation seems the most plausible mode of origin of the native Hg occurrences. The high-temperature vents at the global spreading ridge chain introduce an assessed amount of $1.62\text{--}4.86 \times 10^3$ t/yr Hg_{liq}^0 into the ocean. With time, the deposited Hg_{liq}^0 will likely be dissolved in the overlaying seawater and will not survive in the geologic record.

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1. Introduction

Since the dawn of the extensive investigations of the metalliferous sediments in the 1960s it has been established that these sediments are highly enriched in Hg (Boström and Fisher, 1969). Vertical variations of Hg content in these sediments are supposed to mirror the fluctuations of the submarine hydrothermal activity (Cox and McMurtry, 1981). The anomalously large Hg concentrations that exist in near-bottom water of the mid-ocean rift valleys are interpreted to support the suggestion that Hg is injected into the seawater by active hydrothermal springs (Carr et al., 1974, 1975). Overall, the reports on Hg presence in the hydrothermal sediments

are few and the speciation of Hg in them is still poorly known. Indeed, HgS (Pracejus and Halbach, 1996; Stoffers et al., 1999; Prol-Ledesma et al., 2002) and an unusual occurrence of Hg^0 (Stoffers et al., 1999) have been described in submarine massive sulfides from arc settings, but nothing is known of the Hg form of presence in the mid-ocean ridge metalliferous sediments.

In the course of a mineralogical study of metalliferous sediment from the East Pacific Rise (EPR) I came across several soft gray droplets, which appeared to be Hg^0 . Here I report on these occurrences and discuss their possible origin.

2. Geological setting

The southern part of the EPR (Fig. 1A) around 21°S is characterized by an asymmetric and ultra-fast seafloor

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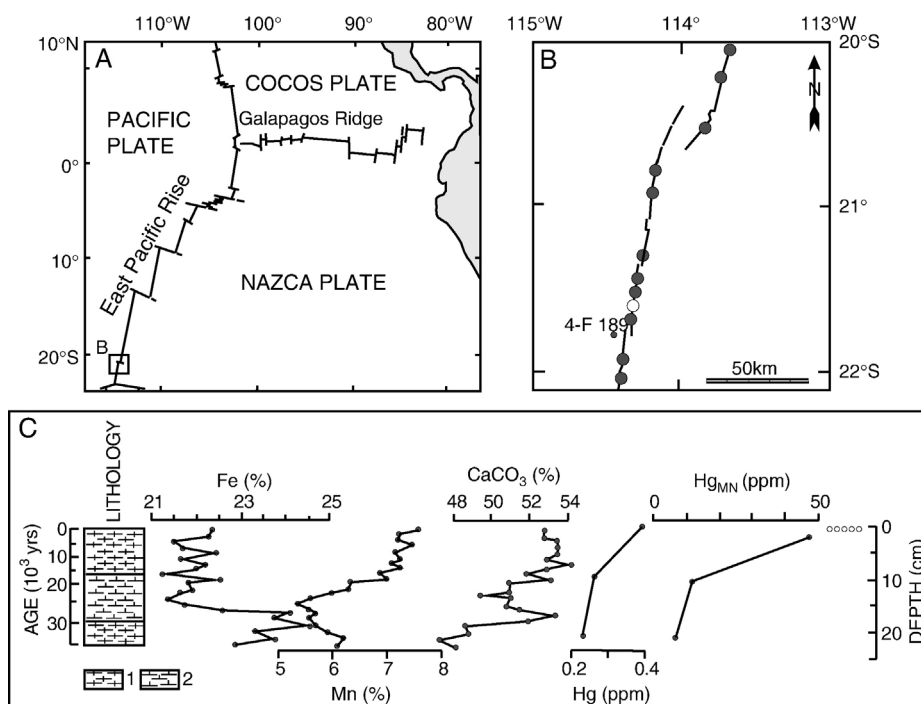


Fig. 1. A: Sketch map of the southeastern part of the Pacific Ocean. B: Diagram of the survey area. Closed circles = vent fields in the EPR rift zone (after Bäcker et al., 1985; Renard et al., 1985; Macdonald et al., 1986; Marchig et al., 1988; Krasnov et al., 1997; Von Damm et al., 2000); open circle = Rapa Nui vent field with Brandon vent (Von Damm et al., 2003); dot = studied site location. C: Stratigraphic section (based on Dekov, 1994) of the studied core showing the lithology; age span; vertical distribution of Fe, Mn, Hg (all on carbonate free basis), CaCO₃; and native Hg occurrences (small open circles) in the studied core. 1 = nanno-foram and foram-nanno oozes; 2 = nanofossil ooze; Hg_{MN} = Hg content in Fe–Mn micronodules.

spreading (Rea, 1978; Naar and Hey, 1989). Most of the ridge crest at 21°S is rifted with a well-defined 50 m deep, 1000 m wide axial graben with vertical walls (Bäcker et al., 1985; Renard et al., 1985; Krasnov et al., 1997). The axial trough is tectonically controlled (Von Damm et al., 2003) and furnished by fresh basalt flows and talus. A large number of active and inactive hydrothermal fields have been revealed in it (Fig. 1B) and an extraordinary near critical phase separation in the vent fluids jetting from one of them (Rapa Nui vent field, Brandon vent: 405 °C, 287 bar) have been documented (Von Damm et al., 2003). The sediment of this area consists of calcareous metalliferous oozes composed of biogenic calcite, hydrothermal precipitates, poorly sorted hyaloclastic material, authigenic clay minerals and a very small percentage of allogenic aeolian material (Dekov, 1994).

3. Material and methods

I studied a short (22 cm) sediment core (4-F 189, 21°47.1'S, 114°26.8'W, 3140 m, gravity corer) taken at a distance of 10 km west from the EPR axis (Fig. 1B) during the 4th cruise of *R/V Geolog Fersman* (1987/88,

VNIIOkeangeologiya, St. Petersburg). The core was sectioned at each centimeter; sample splits were stored in plastic vials and kept at ~2 °C. It consisted of 3 thin lithologic units of strongly oxidized reddish-brown, horizontally bedded metalliferous oozes (Fig. 1C), which were made up of biogenic (foraminiferal and coccolith tests; ~80%), hydrothermal (Fe-oxyhydroxides, Mn-oxides and clays; ~20%), volcanoclastic (volcanic glass, plagioclases, olivines; <1%), and terrigenous (aeolian quartz; <0.1%) material (Dekov, 1994). Fe and Mn were measured by atomic absorption spectroscopy (AAS), Hg by cold-vapor AAS (Perkin Elmer Z-5000; precision <5%; standards GSPN-3, Nod-P-1), the carbonate content by the method of the carbonate bomb (Müller and Gastner, 1971). Subsamples of selected Fe–Mn micronodules were analyzed for Hg. Scanning electron microscope (SEM) observations were made on C-coated specimens using a JEOL JSM-5410LV electron microscope coupled with EDS ($V=15$ kV; $I=10$ nA; electron beam diameter of 2 μ m). X-ray diffraction (XRD) examinations on air-dried mounts of finely ground bulk sample powders were made using Phillips X-ray diffractometer PW 1710 with monochromatic Cu K α radiation, $V=40$ kV,

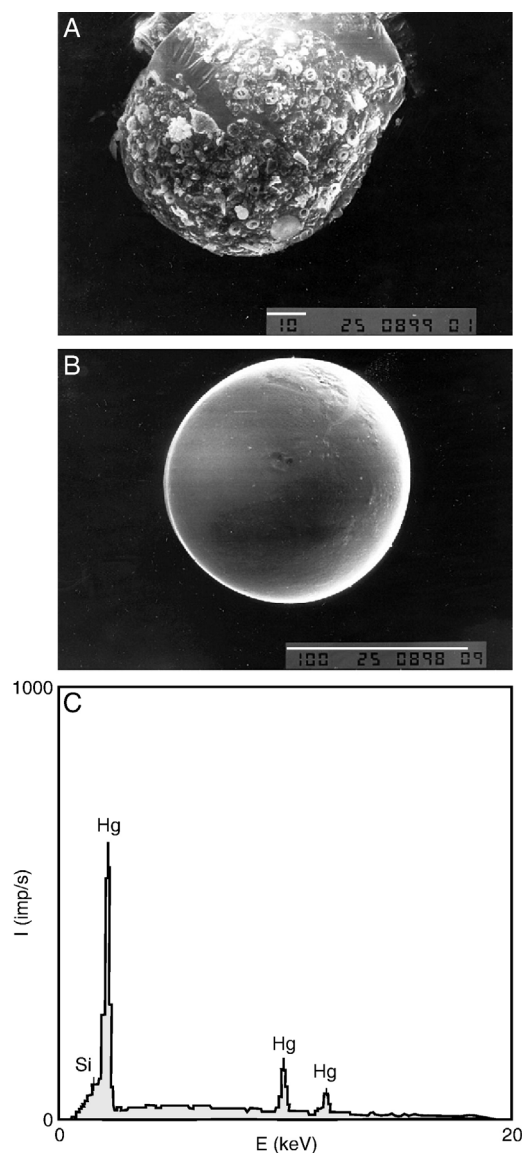


Fig. 2. A: SEM micrograph [Secondary Electron Image (SEI)] of a native Hg droplet (H11.S1); B: SEM micrograph (SEI) of a native Hg droplet (H11.S4) after removal of the thin surface film of coccoliths and mineral grains; C: EDS spectrum of native Hg droplet. Scale bars equal to: 10 μm (A); 100 μm (B).

$I=30$ mA: scans from 2 to $65^\circ 2\theta$, with steps of $0.04^\circ 2\theta$, at 1 s/step.

4. Results

In the course of a stereomicroscope investigation of the uppermost horizon (0–2 cm) of the studied core I found 5 soft gray droplets coated by coccoliths and fine-grained particles (Fig. 2A). Removal of this envelope by a fine steel needle revealed the droplets were silver-

white with very strong metallic luster (Fig. 2B). EDS examinations showed the droplets were almost pure Hg with traces of Si (Fig. 2C). Si might be attributed to very fine clay flakes stuck to the droplet surface. Some fine-crystal aggregates on the droplet surface with Hg–S composition suggested they were Hg-sulfides. My attempt to find other Hg droplets in the rest of the

Table 1

Mean Hg content in seafloor hydrothermal sediments and fluids

Object and area of investigation	Content (ppm)	Reference
Metalliferous sediment, 21°S EPR	0.29	This study
Fe–Mn micronodules, metalliferous sediment, 21°S EPR	22.2	This study
Metalliferous sediment, SE Pacific Ocean	0.46 (A.B.) ^a	Gurvich, (2006)
Metalliferous sediment, North EPR	2.12 (A.B.)	Gurvich, (2006)
Metalliferous sediment, Atlantis II Deep, Red Sea	1.87 (A.B.)	Gurvich, (2006)
Metalliferous sediment, Tethys Deep, Red Sea	0.19 (A.B.)	Gurvich, (2006)
J ₃ –Q ₁ metalliferous sediment, Pacific Ocean	0.5 (A.B.)	Gurvich, (2006)
J ₃ –Q ₁ metalliferous sediment, Atlantic Ocean	0.15 (A.B.)	Gurvich, (2006)
Pg ₁ –N ₁ metalliferous sediment, Back-arc basins, Pacific Ocean	1.2 (A.B.)	Gurvich, (2006)
Metalliferous sediment, 45°N Mid-Atlantic Ridge	0.41	Cronan, (1972)
Hydrothermal precipitate, Punta Mita, Pacific margin of Mexico	130.2	Prol-Ledesma et al. (2002)
Hydrothermal Mn-oxides, La Victoria Knoll, California continental borderland	1.34	Hein et al. (2005)
Hydrothermal Fe–Mn crusts, TAG area, Mid-Atlantic Ridge	1.04	Toth (1980)
Hydrothermal Fe–Mn crusts, FAMOUS area, Mid-Atlantic Ridge	0.15	Toth (1980)
Hydrothermal Fe–Mn crusts, Galapagos Ridge	0.15	Toth (1980)
Hydrothermal Fe–Mn crusts, Juan de Fuca Ridge	0.13	Toth (1980)
Hydrothermal fluids, Bahía Concepción, Gulf of California	0.54	Prol-Ledesma et al. (2004)
Bottom seawater, FAMOUS area, Mid-Atlantic Ridge	$0.07\text{--}1.10 \times 10^{-3}$	Carr et al. (1975)
Mid-ocean ridge basalts	0.02	Taylor and McLennan (1985)

^a A.B. = calculated on abiogenic basis.

core failed. Bulk XRD studies found no Hg minerals, or other minerals with high Hg content.

The Hg content of the studied bulk sediment is of the same order of magnitude as of those in the other recent and ancient metalliferous sediments, hydrothermal Fe–Mn crusts and the only submarine hydrothermal fluid that has been studied for Hg (Table 1). It is an order of magnitude higher than that of the average mid-ocean ridge basalt. Only the recent hydrothermal precipitate of the shallow coastal submarine springs off Mexico is 3 orders of magnitude richer in Hg than the studied sediment (Table 1). Fe–Mn micronodules in this study exhibit 2 orders of magnitude more Hg than the parent sediment. This suggests either a primary Hg enrichment of the hydrothermal precipitate (the precursor of the micronodules) in the hydrothermal plume, or a diagenetic enrichment of the buried precipitates. The vertical distribution of Hg correlates well with that of Mn and is roughly inverse to that of Fe (Fig. 1C). Since the studied sediment is thin, young, strongly oxidized, and low in C_{org} , it is not supposed that the Mn enrichment of the surface sediment is fully a result of diagenetic remobilization (Dekov, 1994). Mostly, this is a mere effect of Mn dilution by Fe, the main hydrothermal component. The same holds true for the Hg concentration in the bulk sediment, but not for the Hg content of the Fe–Mn micronodules. The micronodules from the surface horizon are 5 times richer in Hg than the micronodules from the lower part of the core (Fig. 1C). Additionally, the occurrence of native Hg droplets in the surface sediment supports the possibility that the recent hydrothermal emanations from the axial zone are enriched in Hg relative to the previous ones.

5. Discussion

Although it may seem far-fetched to base a paper on five Hg^0 droplets from a single sediment sample, the mode of occurrence and the locality suggest that a contamination is highly unlikely and the material is indeed natural. Thus, possible precipitation processes were examined to identify the formation mechanism for these droplets. Obviously, the precipitation must be closely related to the hydrothermal activity of the nearby spreading center. Two types of processes might be responsible for the native Hg_{liq} formation at the studied setting: hydrothermal and biogenic.

In seawater, microorganisms are able to produce Hg^0 through the reduction of ionic Hg (Mason et al., 1995). They employ a plasmid-specified detoxification mechanism that reduces Hg^{2+} species. Hg^{2+} enters the microbial cell, where a reduction to Hg^0 could occur.

Hg^0 is less toxic and more volatile than Hg^{2+} and part of it vaporizes and leaves the cell (Pracejus and Halbach, 1996). The background seawater does contain ionic Hg species, but their content is so low (within the femtomolar range; Mason and Fitzgerald, 1993) that the biogenic reduction can hardly produce observable amounts of Hg^0_{liq} . Hydrothermal solutions introduce dissolved Hg in the form of Hg^{2+} into the seawater. Thus, the submarine hydrothermal fields, densely populated by bacterial mats, can be expected to be an arena for the bio-transfer of ionic Hg from the hydrothermal fluids into the Hg^0 of the sediment. This process, however, would be localized in the close vicinity of the hydrothermal vents and the transport of the Hg^0_{liq} droplets away (~ 10 km) to the distal metalliferous sediments is unlikely.

In a hydrothermal system, native Hg may be formed following 4 main different chemical paths (Barnes and Seward, 1997): oxidation of HgS , precipitation from $Hg(H_2O)_6$, deposition from Hg_{gas} carried in steam, and condensation of Hg^0_{vap} by cooling. In the hydrothermal systems, Hg is thought to be transported mainly as Hg–S complexes. However, at temperatures above $200^\circ C$ and even under rather oxidizing conditions, Hg^0_{aq} is dominant relative to the other Hg species (Varekamp and Buseck, 1984).

The only investigation of the vent fluids from the studied area is that of the Brandon vent structure (Rapa Nui vent field; Fig. 1B) (Von Damm et al., 2003). Here, vigorous near critical phase separation and segregation in the vent fluids has been observed at the Brandon. The gases (e.g., CO_2 , H_2S , H_2) and volatiles (e.g., Hg, As, Sb, Pb) would be expected to fractionate preferentially into the vapor phase during such a process. When a vapor phase develops from the hydrothermal fluid, Hg partitions strongly into the vapor as Hg^0_{vap} (Varekamp and Buseck, 1984). Data from many hydrothermal systems suggest that $>80\%$ of the Hg in the gas phase occurs as Hg^0_{vap} (Robertson et al., 1977). Although the Hg content and speciation has not been studied in the Rapa Nui vent fluids, it seems likely that the vapor transport of Hg is an important process in the studied area. In highly saline brine phase (3.26% NaCl; Von Damm et al., 2003), Hg would occur mainly as Hg–Cl complexes (Varekamp and Buseck, 1984).

Hg^0_{aq} is stable at high temperatures, if the pressure is sufficient to prevent vaporization (at $400^\circ C$ at least 2.1 bar; Barnes and Seward, 1997). The physical conditions of the Brandon fluids ($405^\circ C$ and 287 bar; Von Damm et al., 2003) suggest Hg^0_{aq} is stable in them before the boiling. At such high temperatures ($>250^\circ C$), the concentration of Hg in the hydrothermal

fluids is controlled by the solubility of Hg^0 (Barnes and Seward, 1997).

I suppose that some Hg_{liq}^0 may have condensed directly from Hg_{vap}^0 in the vapor phase emitted by the hydrothermal vents in the studied area (e.g., Barnes and Seward, 1997). Mixing of the hot, reduced hydrothermal fluids with cool, oxygenated seawater in the area (Boström, 1973) can cause precipitation of Hg_{liq}^0 as a result of increased $p\text{O}_2$ and decreased temperature (e.g., Varekamp and Buseck, 1984). Indeed, quenched high-temperature (250 °C) solutions are reported to contain Hg_{liq}^0 droplets (Dickson, 1964). Thus quenching of the hydrothermal fluid and Hg_{aq}^0 precipitation as native Hg_{liq}^0 is another possible origin of the studied occurrences.

Introduced by the vigorous hydrothermal fluids into the bottom seawater, the tiny Hg_{liq}^0 droplets could be entrained in the hydrothermal plume. The oxidation of the metals dissolved in the hydrothermal fluid (Fe, Mn, etc.) and their transfer into suspension causes depletion of dissolved O_2 in the hydrothermal plume relative to the ambient seawater (e.g., Campbell et al., 1988). In the less oxic plume Hg_{aq} will exist as Hg^0 or HgS^{2-}_2 (e.g., Siegel and Siegel, 1979). Thus, the emitted Hg_{aq}^0 can be preserved in this reduced state in huge and dense hydrothermal plumes like those reported for the Rapa Nui vent field (Von Damm et al., 2003). Along with the Fe–Mn oxyhydroxide suspension, Hg^0 rains from the plume upon the seafloor and is transferred into the metalliferous sediments. However, another question remains open: is the hydrothermal plume capable to carry the droplets 10 km off the ridge crest? The studied section of the southern EPR has the most extensive complex of intense hydrothermal plumes observed so far on the global mid-ocean ridge system (Krasnov et al., 1992; Feely et al., 1996; Baker et al., 2002). The bottom-current system crossing the EPR crest at the studied latitude transports the hydrothermal effluents westward, normal to the ridge axis (Boström, 1973; Gurvich, 2006). These conditions are favorable for the Hg^0 transport in a hydrothermal plume west from the EPR crest, but the high density of Hg (13.6 g/cm³) and the size of the studied Hg^0 droplets (diameter ~ 100 µm; weight 7.12 µg) leave debatable the possibility of this mechanism. Theoretically, there are two alternative ways of Hg^0 transport in a plume. First, although there are still no reports of megaplumes along the southern EPR, the Hg^0 transport through such a cataclysmic discharge of hydrothermal fluids resulting in an extraordinarily large plume (~1 km high, 20 km diameter; Baker et al., 1989) is likely. Megaplume discharge could easily advect Hg^0 droplets like the ones

under discussion. The rotation in its top gravity current (Palmer and Ernst, 1998) may cause retardation in settling of the Hg^0 droplets long enough over time and transport them away from the ridge crest. Second, the emitted Hg^0 droplets had been smaller than those found in the sediment. They gradually grew by coalescence with each other over the transport time of a usual plume. Thus their settling rate may be very low, so that they could be transported away from the ridge crest, aggregate/coalesce then fall prematurely as a result of aggregation/coalescence. Another possibility is in-situ Hg^0 precipitation due to local hydrothermal activity. There is no observation of hydrothermal vents nearby the sampling site, but we cannot fully rule out this way of transport.

Eventually, Hg_{liq}^0 reacts with seawater species and sediment components and is partly transferred to the seawater, while the other part remains in the sediment. This might explain its small retention potential in sediments and occurrence in the most recent surface sediment only.

I am aware of only one report of Hg concentration in submarine hydrothermal fluids (Prol-Ledesma et al., 2004; Table 1). Although it corresponds to shallow coastal water rather than to a spreading ridge hydrothermal field, it can be used for the following assessment. From the annual global production of axial high-temperature hydrothermal fluid of 3×10^{10} t (Elderfield and Schultz, 1996), we can estimate a global flux of Hg associated with high-temperature venting at the ridge axis of 16,200 t/yr. In a study of the vertical distribution of Hg species in the equatorial Pacific, Mason and Fitzgerald (1993) estimated that 10 to 30% of the dissolved Hg in the seawater column is Hg^0 . Although several processes govern the Hg species transformations in seawater, we can employ this proportion for the high-temperature vent fluids injected in bottom seawater as a first approach. Thus the high-temperature vents at the global spreading ridge system are assessed to introduce 1620–4860 t/yr of Hg_{liq}^0 into the ocean.

6. Conclusions

The recent high hydrothermal activity in the rift zone of the spreading center at 21°N EPR produces an enhanced Hg content in the surface metalliferous sediment and native Hg_{liq} droplets spread in it. Most probably, the native Hg_{liq} condenses from Hg_{vap}^0 in the vapor phase of the local hydrothermal fluids subjected to near critical phase separation and segregation. Quenching of the hydrothermal fluids also can spawn

native Hg_{liq} droplets as a result of Hg_{aq}^0 precipitation. Low-oxygen hydrothermal plumes can preserve native Hg_{liq} droplets, transport them away from the hydrothermal fields and deposit them in the distal metalliferous sediments. Hg_{liq}^0 will slowly disappear from the sediment with time dissolved in the overlaying seawater.

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