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Mercury and monomethylmercury in fluids from Sea Cliff submarine hydrothermal field, Gorda Ridge

Carl H. Lamborg,[1] Karen L. Von Damm,[2] William F. Fitzgerald,[3] Chad R. Hammerschmidt,[1] and Robert Zierenberg[4]

[1] Submarine hydrothermal systems are hypothesized to be a potentially important source of monomethylmercury (MMHg) to the ocean, yet the amount of MMHg in vent fluids is unknown. Here, we report total Hg and MMHg concentrations in hydrothermal vent fluids sampled from the Sea Cliff site on the Gorda Ridge. MMHg is the dominant Hg species, and levels of total Hg are enhanced slightly compared to seawater. Hg is enriched in deposits surrounding the site, suggesting near-field deposition from fluid plumes, with rapid MMHg demethylation and scavenging of Hg(II) complexes. Assuming the flux of MMHg from Sea Cliff is representative of global submarine hydrothermal inputs, we estimate a flux of $0.1-0.4$ Mmoles y^{-1}, which may be attenuated by scavenging near the vents. However, deep waters are not typically known to be elevated in Hg, and thus we suggest that hydrothermal systems are not significant sources of MMHg to commercial fisheries. **Citation:** Lamborg, C. H., K. L. Von Damm, W. F. Fitzgerald, C. R. Hammerschmidt, and R. Zierenberg (2006), Mercury and monomethylmercury in fluids from Sea Cliff submarine hydrothermal field, Gorda Ridge, *Geophys. Res. Lett.*, *33*, L17606, doi:10.1029/2006GL026321.

1. Introduction

[2] The metalliferous sediments found along the global mid-ocean ridge (MOR) system are a well known testament to the remobilization of metals that occurs as a result of subsurface water-rock reactions, driven by magma emplacement along these tectonic boundaries [*Boström et al.*, 1969]. Mercury (Hg) is among the metals found in these deposits and is generally described as chalcophilic (associated with sulfide minerals [*Ozerova*, 1996]). Of great interest and concern is the potential release of Hg and monomethylmercury (MMHg) from deep-sea hydrothermal systems, which has been hypothesized to be an important source of Hg in marine fish [*Kraepiel et al.*, 2003]. There is some circumstantial evidence for Hg dispersion away from hydrothermal sites. For example, Stoffers and colleagues [*Stoffers et al.*, 1999] observed native elemental Hg

accumulating on rock surfaces in the shallow water, back arc vent system of the Bay of Plenty, New Zealand. They also speculated that these systems might be affecting the concentration of Hg in local fisheries. Here, we report the direct determinations of Hg and, for the first time, MMHg in hydrothermal vent fluids using samples collected at the Sea Cliff site, located on the Gorda Ridge system [*Von Damm et al.*, 2006]. Our results suggest the Hg flux at this site is dominated by MMHg, which raises intriguing questions concerning vent organometallic chemistry as well as the impact of hydrothermal circulation on the global Hg cycle.

2. Setting

[3] The Sea Cliff hydrothermal field is located in the northeast Pacific at the northern end of Gorda Ridge at a depth of $\sim$2730 m [*Von Damm et al.*, 2006]. This hydrothermal field is located on the wall of the axial valley, about 2.6 km east of the axis of spreading. The fluids collected from this site had measured temperatures of up to 308°C (although the data suggests they were >400°C at depth), and were unusually clear, indicating the loss of most of their transition metal content subsurface. All of the fluids had chlorinities significantly less than that of local seawater, indicating they were a vapor that was formed by heat-driven phase separation of seawater, likely at conditions close to its critical point, and later condensed. The relatively high helium concentrations (not shown) for the fluids suggest that magma is present somewhere along the hydrothermal flow path. Fluid compositions and temperatures were the same in 2000, 2002, and 2004; the data reported here are from samples collected in 2002.

3. Methods

[4] Samples were collected from the *ROV Tiburon* into the non-gas tight, Ti major ion collection vessels commonly used on *DSV Alvin*. As Hg can be found in two volatile species in natural waters, Hg° and dimethylHg (DMHg), there is a possibility that some Hg was lost from the samplers due to decompression on return to the surface. Under typical oceanic conditions, Hg° represents a few percent of total Hg, while DMHg is present at trace amounts. Thus, we assume losses of Hg as volatile forms to be modest, but can not confirm this without further study. Following return to the surface, the sample aliquots for Hg analysis were transferred to acid-washed Teflon bottles and acidified to pH < 2 with trace metal grade HCl, and typically amounted to $5-20$ mL. The samples were held in this state under refrigeration for 1 month prior to total Hg analysis, and 4 months for MMHg. These species have been

[1]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.
[2]Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, New Hampshire, USA.
[3]Department of Marine Sciences, University of Connecticut, Groton, Connecticut, USA.
[4]Department of Geology, University of California, Davis, California, USA.

Table 1. Summary of Hg, MMHg and Mg Analyses of Vent Fluids From Sea Cliff, Gorda Ridge[a]

Sample I.D.	Total Hg, pmole kg^{-1}	MMHg, pmole kg^{-1}	Mg, mmole kg^{-1}
Ambient deep water	<15	<1.4	54
T454-4	<15	13 ± 3	1.51
T454-16	<15	16 ± 3	1.31
T454-20	10 ± 2	8 ± 2	2.35
T456-4	4 ± 1	7 ± 1	1.40
T456-14	7 ± 1	8 ± 2	2.34
T456-20	<15	4 ± 1	2.17
Average	7	9.2	1.85
Typical seawater	<1−2	<0.2	54

[a]Also includes an ambient deep water sample for comparison.

shown to be stable under these conditions for long periods of time [*Vandal et al.*, 1991]. The samples were clear and were not filtered prior to analysis. Twenty four hours prior to total Hg analysis, a 1 or 5 mL subsample was acidified/oxidized through addition of 50 μL of 180 mM BrCl. Hg was then determined by purge and trap, cold vapor atomic fluorescence (CVAFS [*Fitzgerald and Gill*, 1979; *Bloom and Crecelius*, 1983; *Bloom and Fitzgerald*, 1988]). The detection limit for total Hg was 7 pmole kg^{-1} for 5 mL samples and 15 pmole kg^{-1} for 1 mL samples. MMHg was isolated from 7−20 mL of vent fluid by steam distillation, and determined by GC-CVAFS [*Horvat et al.*, 1993; *Bloom et al.*, 1997]. Detection limits for MMHg were lower than for total Hg, and estimated to be 1.4 pmole kg^{-1} in this study. Uncertainties for these small sized samples are about 20%. Solid phase sample collection and handling was similar to earlier work [*Zierenberg et al.*, 1995]. Hg concentration of solid samples was measured using atomic vapor Hg analyzer calibrated using USGS GXR-2 reference standard soil [*Gladney and Roelandts*, 1988].

4. Results

[5] In Table 1, we summarize the results of analysis of six samples. Total dissolved Hg concentrations ranged from 4−10 pmole kg^{-1}, with three of the samples below detection Dissolved MMHg ranged from 4 to 16 pmole kg^{-1}, with the sample T456-4 of questionable MMHg analytical quality. For the samples where both total and MMHg are available, the methylated form clearly dominates the speciation. Ambient seawater samples collected at the same time and handled identically were below detection for similarly sized samples, indicating little contamination of the samples occurred. Typical open oceanic dissolved Hg concentrations range from less than 1 to 2 pmole kg^{-1} and typically <10% MMHg [*Fitzgerald and Lamborg*, 2004]. Thus, these fluids were elevated above ambient seawater by ca. 2−30x in total Hg and highly enriched in MMHg. All the samples presented here are very low in their magnesium (Mg) content, indicating they are relatively undiluted samples of hydrothermal fluid, and we therefore have used their average value as an estimate of the Hg concentration in pure vent fluids (9.4 pmole kg^{-1} for MMHg and Hg assuming all is methylated).

[6] While this is a very high concentration of MMHg compared to oceanic water column values, it is similar to the concentrations observed in coastal porewaters [*Hammerschmidt et al.*, 2004]. Sediment porewater MMHg

is generated from inorganic Hg by microorganisms, presumably sulfate reducing bacteria [e.g., *Compeau and Bartha*, 1985]. MMHg in the vent fluids in some situations could conceivably be supplied by production in sediments overlying the regions of seawater intrusion with subsequent transport to the vents. Additionally, a subsurface biosphere located in rock fractures might also methylate Hg [e.g., *Deming and Baross*, 1993]. As this hydrothermal site has no sediment cover, the first of these two possibilities can be ruled out. Without further study, it is impossible to rule out the subsurface biosphere as a source of MMHg. If the presence of high percentages of MMHg in very hot hydrothermal vent fluids are the result of abiological methylation of Hg somewhere within the system, this would be the first observation of hydrothermal organometallic chemistry. Abiotic methylation of Hg has been observed under different conditions [*Bloom et al.*, 1997; *Hammerschmidt and Fitzgerald*, 2001; *Gardfeldt et al.*, 2003] and appears to require relatively high concentrations of a methyl donor. Such conditions may be found in hydrothermal fluids, though more likely on heavily sedimented systems unlike Sea Cliff [*Cruse and Seewald*, 2001]. This is an intriguing finding and is suggestive that the organometallic geochemistry of other metals in these systems should be considered.

[7] We speculate that the prominence of the monomethyl form is furthermore the result of physical processes occurring subsurface. As mentioned, the emerging fluids are a condensed vapor formed during phase separation [*Von Damm et al.*, 2006]. This process is not unlike the steam distillation approach used to isolate MMHg from environmental matrices prior to analysis [*Horvat et al.*, 1993], albeit at a much higher temperature, and would result in a physical isolation of methylated forms from Hg^{2+} in the vapor phase.

[8] Geochemical modeling using the EQ3/6 code [*Wolery*, 1992] suggests that the Sea Cliff fluids are supersaturated with respect to HgS minerals (cinnabar and metacinnabar) at their sampled conditions if total Hg concentrations are used as the model input. This is consistent with bulk samples of hydrothermal crusts from the site having elevated Hg contents (5.8−17.3 ppm; Table 2) relative to typical rock concentrations (10−300 ppb [*McDonough and Sun*, 1995]), particularly for material of low sulfide concentration. Supersaturation of Hg in the fluid phase could also be the result of the prominence of MMHg, however, which is more soluble than Hg^{2+} in the presence of sulfide [*Dyrssen and Wedborg*, 1991]. In order to further constrain the conditions under which Hg accumulates in these rocks, samples were examined using transmitted and reflected light microscopy to determine mineralogy and paragenetic relationships. Areas dominated by a single mineral phase or paragenetic stage were then subsampled by microdrill and analyzed for Hg in order to establish the phases hosting Hg. Contrary to the predictions of the geochemical modeling, anhydrite and saponite samples from the active chimneys have low Hg concentrations in the tens of part per billion range (Table 2). In contrast, the clay rich hydrothermal crust sampled at the base of an active chimney has the highest Hg concentration of the samples measured. The higher concentration of Hg in late-stage, lower T phases is consistent with the known geochemistry of Hg deposits which form at relatively modest temperatures and in the distal portions of hydrothermal systems [*Barnes*

Table 2. Summary of Total Hg Analyses From Solid-Phase Samples Collected Near the Sea Cliff Site

Sample	Description	Hg, ppm
T186-R2	Clay-rich hydrothermal crust	5.8
T186-R3	Clay-rich hydrothermal crust at base of active chimney	17.3
T186-R3C	Anhydrite from active (305°C) chimney	0.07
T186-R3C	Saponite inner lining from active (305°C) chimney	0.02
T186-R6	Barite crust	8.1
T186-R6	Sphalerite (w/ trace galena) drilled from barite crust	12.6
T186-R6	Late-stage, euhedral barite drilled from barite crust	15.5
T454-R3A	Chalcopyrite-rich sulfide clast drilled from siliceous hydrothermal crust	0.9
T456-R3A	Sphalerite-rich sulfide clast drilled from siliceous hydrothermal crust	12.4
T456-R3B	Late-stage pyrite drilled from siliceous hydrothermal crust	15.5
T456-R5	Pyrite vein drilled from basalt clast in siliceous crust	0.3

and Seward, 1997]. Thus, distribution of Hg in these deposits is consistent with release of MMHg, but appears to require relatively rapid demethylation to account for the appearance of Hg near the vents.

[9] The total dissolved Hg (and MMHg) flux due to hydrothermal activity is estimated, on the first order, to be $0.1-0.4$ Mmole y^{-1} (using 9.2 pmole kg^{-1} for Hg concentration in fluids and assuming the amount of seawater passing through high temperature axial systems is $1-4 \times 10^{19}$ g y^{-1} globally [*Mottl*, 2003]). This is an upper limit for the seawater flux through this part of the hydrothermal system and if the true value is less, as several authors have suggested [*German and Von Damm*, 2004], then the hydrothermal input of Hg is likely to be $\ll 0.1$ Mmole y^{-1}. Current models of the global Hg cycle variously estimate the combined river and atmospheric inputs of Hg to the ocean to be $10-16.4$ Mmole y^{-1} [*Lamborg et al.*, 2002; *Mason and Sheu*, 2002]. Therefore, if Sea Cliff inputs of Hg to the ocean are typical of submarine hydrothermal systems world-wide, then this source represents <4% of total Hg inputs to the ocean. As indicated in Table 1, however, this flux appears dominated by MMHg. Rolfhus and Fitzgerald [*Rolfhus and Fitzgerald*, 1995] estimated that a flux of 0.2 Mmole y^{-1} of MMHg was required to sustain the concentration of Hg in ocean fish (on average 0.2 ppm; fish production 0.5% of primary production). Based on these few measurements, it would appear that hydrothermal vents might, at the upper limits of our estimates, supply MMHg on this scale. It must be noted, however, that deep water datasets [e.g., *Fitzgerald et al.*, 1998; *Laurier et al.*, 2004] do not indicate sufficient MMHg concentrations to supply the surface ocean at this rate. It is therefore likely that MMHg is removed from hydrothermal fluid plumes, with eventual deposition in metalliferous sediments or possible decomposition during its long residence in deep water (ca. 1000 yrs). We therefore suggest that our total Hg and MMHg data do not support the hypothesis that hydrothermal vents are a significant source of Hg to commercially important fisheries as has been suggested by Kraepiel and colleagues [*Kraepiel et al.*, 2003].

References

Barnes, H. L., and T. M. Seward (1997), Geothermal systems and mercury deposits, in *Geochemistry of Hydrothermal Ore Deposits*, 3rd ed., John Wiley, Hoboken, N. J.

Bloom, N., and W. F. Fitzgerald (1988), Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold-vapor atomic fluorescence detection, *Anal. Chim. Acta*, *208*, 151–161.

Bloom, N. S., and E. A. Crecelius (1983), Determination of mercury in seawater at sub-nanogram per liter levels, *Mar. Chem.*, *14*, 49–59.

Bloom, N. S., J. A. Colman, and L. Barber (1997), Artifact formation of methyl mercury during aqueous distillation and alternative techniques for the extraction of methyl mercury from environmental samples, *Fresenius J. Anal. Chem.*, *358*, 371–377.

Boström, K., M. N. A. Peterson, O. Joensuu, and D. E. Fisher (1969), Aluminum-poor ferromanganoan sediments on active ocean ridges, *J. Geophys. Res.*, *74*, 3261–3270.

Compeau, G. C., and R. Bartha (1985), Sulfate-reducing bacteria - Principal methylators of mercury in anoxic estuarine sediment, *Appl. Environ. Microbiol.*, *50*, 498–502.

Cruse, A. M., and J. S. Seewald (2001), Metal mobility in sediment-covered ridge-crest hydrothermal systems: Experimental and theoretical constraints, *Geochim. Cosmochim. Acta*, *65*, 3233–3247.

Deming, J. W., and J. A. Baross (1993), Deep-sea smokers: Windows to a subsurface biosphere?, *Geochim. Cosmochim. Acta*, *57*, 3219–3230.

Dyrssen, D., and M. Wedborg (1991), The sulphur-mercury(II) system in natural waters, *Water Air Soil Pollut.*, *56*, 507–509.

Fitzgerald, W. F., and G. A. Gill (1979), Subnanogram determination of mercury by two-stage gold amalgamation applied to atmospheric analysis, *Anal. Chem.*, *51*, 1714–1720.

Fitzgerald, W. F., and C. H. Lamborg (2004), Geochemistry of mercury in the environment, in *Treatise on Geochemistry, Environ. Geochem.*, vol. 9, Elsevier, pp. 107–148, New York.

Fitzgerald, W. F., D. R. Engstrom, R. P. Mason, and E. A. Nater (1998), The case for atmospheric mercury contamination in remote areas, *Environ. Sci. Technol.*, *32*, 1–7.

Gardfeldt, K., J. Munthe, D. Stromberg, and O. Lindqvist (2003), A kinetic study on the abiotic methylation of divalent mercury in the aqueous phase, *Sci. Total Environ.*, *304*, 127–136.

German, C. R., and K. L. Von Damm (2004), Hydrothermal processes, in *Treatise on Geochemistry*, pp. 182–222, Elsevier, New York.

Gladney, E. S., and I. Roelandts (1988), compilation of elemental concentration data for USGS geochemical exploration reference materials GXR-1 to GXR-6, *Geostand. Newsl.*, *14*, 21–118.

Hammerschmidt, C. R., and W. F. Fitzgerald (2001), Formation of artifact methylmercury during extraction from a sediment reference material, *Anal. Chem.*, *73*, 5930–5936.

Hammerschmidt, C. R., W. F. Fitzgerald, C. H. Lamborg, P. H. Balcom, and P. T. Visscher (2004), Biogeochemistry of methylmercury in sediments of Long Island Sound, *Mar. Chem.*, *90*, 31–52.

Horvat, M., L. Liang, and N. S. Bloom (1993), Comparison of distillation with other current isolation methods for the determination of methyl mercury-compounds in low-level environmental-samples. 2. Water, *Anal. Chim. Acta*, *282*, 153–168.

Kraepiel, A. M. L., K. Keller, H. B. Chin, E. G. Malcolm, and F. M. M. Morel (2003), Sources and variations of mercury in tuna, *Environ. Sci. Technol.*, *37*, 5551–5558.

Lamborg, C. H., W. F. Fitzgerald, J. O'Donnell, and T. Torgersen (2002), A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients, *Geochim. Cosmochim. Acta*, *66*, 1105–1118.

Laurier, F. J. G., R. P. Mason, G. A. Gill, and L. Whalin (2004), Mercury distributions in the North Pacific Ocean - 20 years of observations, *Mar. Chem.*, *90*, 3–19.

Mason, R. P., and G. R. Sheu (2002), Role of the ocean in the global mercury cycle, *Global Biogeochem. Cycles*, *16*(4), 1093, doi:10.1029/2001GB001440.

McDonough, W. F., and S.-S. Sun (1995), The composition of the Earth, *Chem. Geol.*, *120*, 223–253.

Mottl, M. J. (2003), Partitioning of energy and mass fluxes between mid-Ocean ridge axes and flanks at high and low temperature, in *Energy and Mass Transfer in Marine Hydrothermal Systems*, pp. 271–286, Dahlem University Press, Berlin.

Ozerova, N. A. (1996), Mercury in geological systems, in *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances*, Springer, New York.

Rolfhus, K. R., and W. F. Fitzgerald (1995), Linkages between Atmospheric Mercury Deposition and the Methylmercury Content of Marine Fish, *Water Air Soil Pollut.*, *80*, 291–297.

Stoffers, P., M. Hannington, I. Wright, P. Herzig, C. de Ronde, and S. S. Party (1999), Elemental mercury at submarine hydrothermal vents in the Bay of Plenty, Taupo volcanic zone, New Zealand, *Geology*, *27*, 931–934.

Vandal, G., R. Mason, and W. Fitzgerald (1991), Cycling of volatile mercury in temperate lakes, *Water Air Soil Pollut.*, *56*, 791–803.

Von Damm, K. L., C. R. Parker, M. D. Lilley, D. A. Clague, R. A. Zierenberg, E. J. Olson, and J. S. McClain (2006), Chemistry of vent fluids and their implications for subsurface conditions at Sea Cliff hydro-thermal field, Gorda Ridge, *Geochem. Geophys. Geosyst.*, *7*, Q05005, doi:10.1029/2005GC001034.

Wolery, T. J. (1992), EQ3/6, A software package for geochemical modeling of aqueous systems: Package overview and installation guide (version 7. 0), *Rep. UCRL-MA-110662–PT-I*, Lawrence Livermore Natl. Lab., Livermore, Calif.

Zierenberg, R. A., P. Schiffman, I. R. Jonasson, R. Tosdal, W. Pickthorn, and J. McClain (1995), Alteration of basalt hyaloclastite at the off-axis Sea Cliff hydrothermal field, Gorda Ridge, *Chem. Geol.*, *126*, 77–99.

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W. F. Fitzgerald, Department of Marine Sciences, University of Connecticut, 1080 Shennecossett Road, Groton, CT 06540, USA.

C. R. Hammerschmidt and C. H. Lamborg, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, MS 25, Woods Hole, MA 02543, USA. (clamborg@whoi.edu)

K. L. Von Damm, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, 39 College Road, Durham, NH 03825-3525, USA.

R. Zierenberg, Department of Geology, University of California, 1 Shields Avenue, Davis, CA 95616-8605, USA.