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Distribution and behavior of dissolved hydrogen sulfide in hydrothermal plumes

Abstract—Through the deep ocean, hydrothermal plumes disperse high concentrations of key chemical tracers including He-3, CH₄, Mn, Fe, H₂S, etc. This paper focuses on the distribution and behavior of total dissolved sulfide (sulfide hereafter) in hydrothermal plumes to show that its plume concentration decreases to subnanomolar a few kilometers from the vents. We also report on sulfide removal rates determined at in situ conditions; we observe that they are two orders of magnitude greater than for open ocean seawater, consistent with sulfide being detected only in the vicinity of hydrothermal vents. From our observations, we infer that the sole presence of sulfide in hydrothermal plumes locates active venting at the kilometer scale.

An exhaustive review of hydrothermal vent fluid chemistry data confirms that sulfide is vented at all known sites in concentrations from one to several tens of mmol L⁻¹ (Von Damm 1995). Conversely, little is known about hydrothermal plume sulfide concentrations since the few available water column data (i.e., Mottl and McConachy 1990; Radford-Knoery et al. 1998; Mandernack and Tebo 1999) do not constrain the lateral extent of sulfide in the plume. Here, we present two studies; the first one pertains to the distribution of total dissolved sulfide (sulfide hereafter) in the hydrothermal plume of an Atlantic ocean vent site, and the second one examines the kinetics of sulfide removal at conditions of temperature and concentration (nanomolar range) encountered in the plume.

We studied the Rainbow hydrothermal plume because its dispersion is well characterized (German et al. 1998; Thurnherr and Richards in press) and the end member vent fluids have been analyzed (Douville et al. 1997). We report on the data from four vertical hydrocast stations occupied during the Flame cruise (Fig. 1) for which sulfide measurements were performed. Three of these stations are within 2 km of each other, slightly downstream from the vent site (German et al. 1998; Thurnherr and Richards in press). The fourth station (Flame-HYD02) is located 4 km farther downstream.

Water samples collected in trace metal cleaned Niskin-type sampling bottles were subsampled for shipboard (sulfide) and shore-based (manganese, other parameters) analyses. Sulfide analyses were completed less than 40 min after the

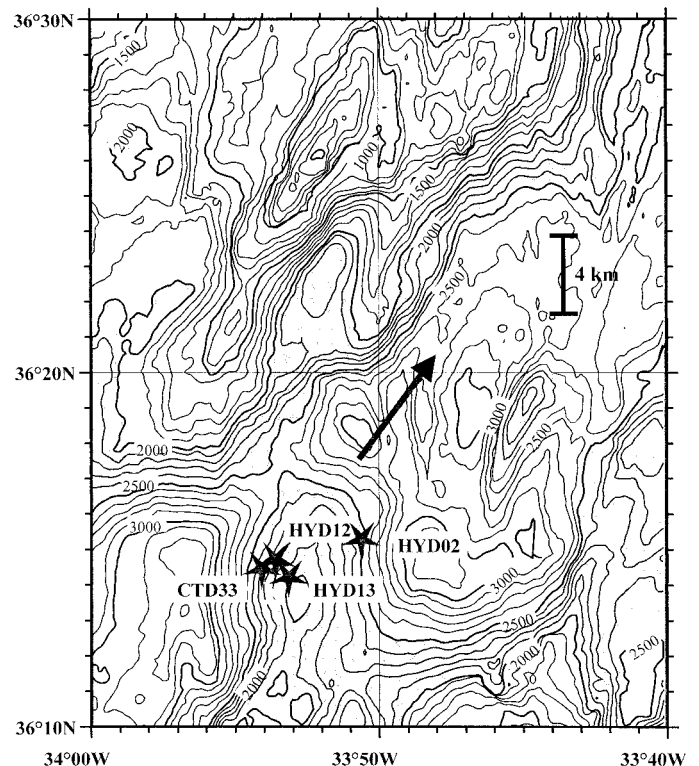


Fig. 1. Bathymetric map with station locations (stars) and the Rainbow hydrothermal vent field (cross). The arrow indicates the prevailing current direction at plume depth in the rift valley, and the scale bar indicates distance. For clarity, the ridge area between 2,500 and 2,000 m depth is grayed; the neutrally buoyant hydrothermal plume disperses between 2,100 and 1,900 m depth.

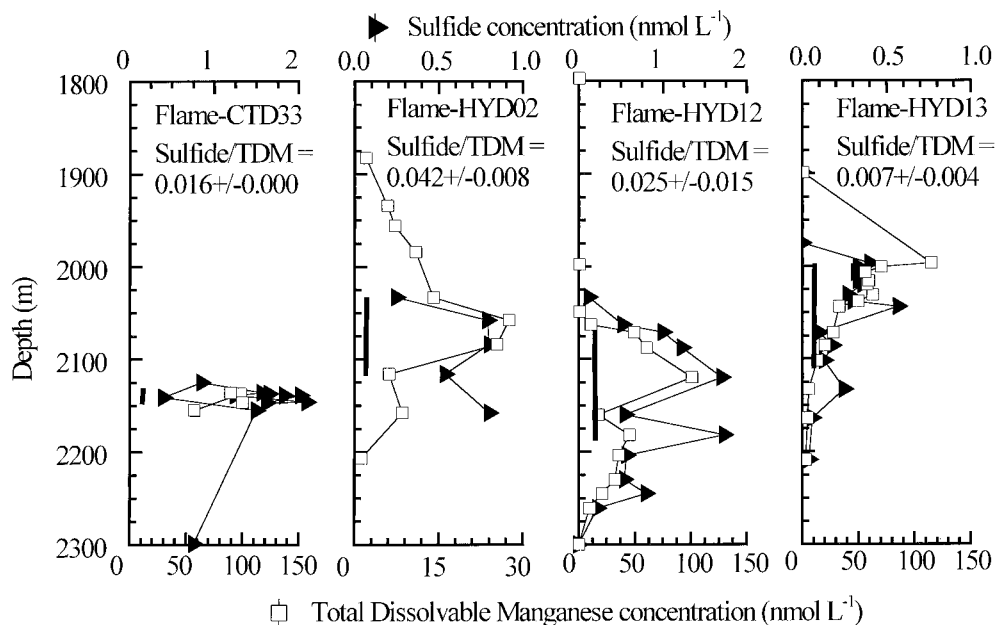


Fig. 2. Concentration depth profiles for sulfide (upper scale, triangles) and total dissolvable manganese (TDM, squares lower scale). Samples were collected and analyzed on board ship for sulfide and at the shore laboratory for TDM. For each panel, note the correspondence between the trends of these hydrothermal tracers. Sulfide/TDM ratios are calculated for the depth layer with highest TDM concentrations (vertical line near the depth axis).

rosette arrived on deck, and hence less than 2 h after closing the Niskin in situ. Because they do not change the interpretation of the data, the reported concentrations are uncorrected for sulfide removal that occurred during that time span. The analytical procedure used to determine sulfide is based on the quenching of fluorescein mercuric acetate (FMA) by dissolved sulfide (Radford-Knoery et al. 1998). Analyses were carried out using a flow injection analysis manifold coupled to a fluorimetric detector. Hermetically collected subsamples were held until analysis in all-polyethylene syringes. Using a peristaltic pump and an injection valve, 250 μL of sample held in the injection loop was repeatedly inserted (about 1 min^{-1}) into a carrier stream consisting of sulfide-free seawater pumped at 1.3 ml min^{-1} . This stream was then mixed with a FMA solution (50 nmol L^{-1} in de-ionized water, pumped at 1.3 ml min^{-1}) in a 50 cm long mixing column and passed through the flow cell of the fluorescence detector (excitation 499 nm, emission 523 nm). The presence of sulfide in the sample quenches FMA fluorescence and generates a peak in the baseline. Peak areas were quantified using a chromatography data acquisition and processing system (Dionex). The entire procedure was calibrated at sea using gravimetric (preweighed Na_2S chips) or volumetric (H_2S_g) standards. Total dissolvable manganese concentration (TDM) was determined following the methods of Resing and Mottl (1992) and Aballéa et al. (1998) on stored, acidified samples.

Profiles from all four stations exhibit similar properties with high concentrations of sulfide (up to 2.1 nmol L^{-1} , Flame-CTD 33) at plume height (2000–2200 m) reducing to below detection levels ($<0.1 \text{ nmol L}^{-1}$) in the water column both above and below this depth horizon (Fig. 2). Corre-

sponding TDM depth profiles are also plotted in Fig. 2 and show similar trends. To predict how far from the venting site sulfide may be advected, we have estimated the rate of sulfide removal from the hydrothermal plume as close as possible to in situ conditions of concentration and temperature.

To this end, we have conducted incubation studies on selected samples as follows and plotted the results in Fig. 3. Subsamples were held at in situ temperatures (2–4°C) in a refrigerator between repeated sulfide determinations. The measured concentration data were then fitted to a pseudo-first-order removal model. The governing equation of such a model is $-dC/dt = k^*C(t)$ whose root is $\log(C_t) = \log(C_{t=0}) - k^*t$, where C_t is the sulfide concentration at time t , t is time elapsed, and k^* is the pseudo-first-order removal rate constant. The plot of the observed concentrations in the form of $\log(C)$ as a function of time yields a straight line with a slope k^* and a $\log C_{t=0}$ Y-intercept (Fig. 3).

The calculated removal rate constants obtained from these two series of experiments fall consistently in the range $0.1 < k^* < 0.7 \text{ h}^{-1}$ and are even more tightly constrained within a given plume. Although these values suggest close agreement for individual hydrothermal plume environments, we note that these rates are two orders of magnitude greater than oxidation of sulfide by dissolved oxygen in Gulf Stream seawater (i.e., $k^* = 0.007 \text{ h}^{-1}$ for seawater at pH 8, 4°C, and air-saturated seawater; Millero et al. 1987). The faster rates observed in our samples are due to a combination of abiotic (e.g., oxidation by dissolved oxygen) and biologically mediated reactions. Abiotic reactions include complexation/precipitation with chalcophile elements and oxidation by dissolved oxygen catalyzed by trace metals (Vazquez et al. 1989). Removal of sulfide can also be mediated by sulfide-

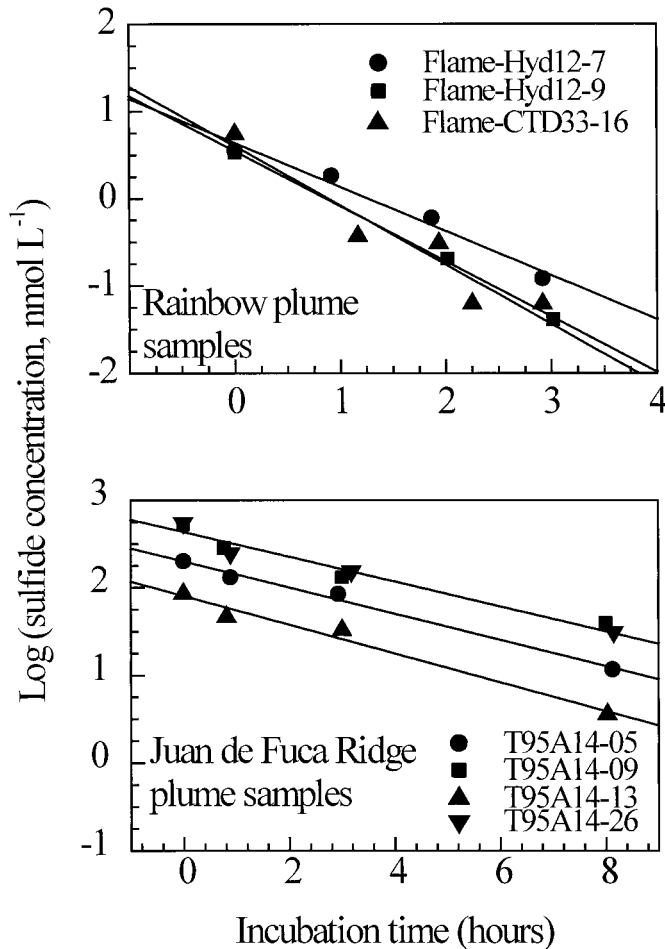


Fig. 3. Pseudo-first-order decay plots of the data used for the experimental determination of the rate of sulfide removal in hydrothermal plume samples. Unspiked samples were analyzed repeatedly at different time points. The natural log of the measured concentrations is plotted versus time.

oxidizing microbes. The internally consistent removal rates observed in this study indicate a considerably faster turnover of sulfide in plume environments than in open ocean surface water. We note that rates that are yet faster were observed by Mandernack and Tebo (1999), albeit on samples with 1,000-fold greater sulfide concentrations. The increased rates are consistent with sulfide complexation/precipitation favored at elevated sulfide and metal concentrations.

To verify that the observed sulfide removal rates are also consistent with the observed sulfide plume distribution, we compute the apparent age of the plume at the stations and compare it to current velocity measurements. Apparent age of the samples is obtained by normalizing sulfide concentration to TDM, which behaves conservatively within the dispersing plume near Rainbow and in the proximal axial valley (Radford-Knøery et al. 1999). In the approximately 100-m thick depth range where the plume is most intense (Fig. 2), the R_{plume} ratio (= sulfide/TDMn, mol/mol) ranges from 0.007 to 0.04. Even the highest of these values already shows pronounced sulfide removal when compared to high-temperature hydrothermal vent fluids ($R_{\text{fluid}} = 0.39$; Douville

et al. 1997). Assuming that sulfide removal follows the average rate for Rainbow of $k^* = 0.61 \text{ h}^{-1}$ (Fig. 3), apparent ages are obtained by substitution of k^* and R values in the expression: $\text{age} = \log(R_{\text{fluid}}/R_{\text{plume}})/k^*$. With apparent ages between 4 and 7 h, we compute an upper bound for plume advection velocity of 4 nmile per 4 h (50 cm s^{-1}) for Sta. Flame-HYD02, the farthest station where sulfide was detected. Similarly, we obtain a lower bound for current at Sta. Flame-CTD33: 1 nmile per 7 h (7 cm s^{-1}). Within the error of our approach, this offers very close agreement with the measurements of high (about 5 to 20 cm s^{-1}) current velocities observed there (German et al. 1998) and independently confirms the robustness of our sulfide removal rates.

At these calculated rates we would then expect sulfide concentrations to decrease to below detection limits ($<0.1 \text{ nmol L}^{-1}$) within less than 4 h downstream from Sta. Flame-HYD 02, or less than 5 h from Sta. Flame-HYD12. Thus sulfide should be undetectable in the water column beyond a distance of at most 10 km from the vent site. This is clearly an upper bound because the latter calculation did not account for plume dilution.

Sulfide is a local (10-km scale or less) water column indicator for venting at the Rainbow hydrothermal site characteristically swept by high-velocity currents (German et al. 1998; Thurnherr and Richards in press). At other sites of the global ridge system, could sulfide be detected farther than 10 km? In more typical midocean ridge settings current velocities are approximately one order of magnitude lower (Cannon and Pashinski 1997), whereas sulfide concentrations in other hydrothermal vents may be an order of magnitude higher than at Rainbow (Von Damm 1995). Consequently, for a common (average = 0.4 h^{-1}) apparent first-order rate constant for both Atlantic and Pacific plumes (Fig. 3), we predict that sulfide concentrations should typically decrease below detection limits within 10 km from any given vent site.

In this work, we have shown that nanomolar sulfide levels occur within neutrally buoyant hydrothermal plumes but only within 10 km of an active hydrothermal field. Given that adult hydrothermal shrimp physiologically respond to millimolar sulfide chemical stimulus (Renninger et al. 1995), it is appropriate to speculate on the possible role of sulfide as a settling cue for dispersing vent fauna. Sulfide could play such a role because its distribution is characterized by extremely sharp lateral gradients due to its rapid removal. Hence if its sole detection by fauna were to trigger settling, the seafloor would then necessarily be reached within 10 km of an active vent site. This would substantially increase chances of finding a suitable environment area over randomly settling to the seafloor.

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