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Distribution and behavior of dissolved hydrogen sulfide in hydrothermal plumes

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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 thekilometer scale.

Keywords: Hydrothermal activity, Plumes, Hydrogen sulphide, Tracers, Methane, Helium isotopes, Metals, Mid-ocean ridges, Chemical oceanography

Distribution and behavior of dissolved hydrogen sulfide in hydrothermal plumes.

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Abstract

Through the deep ocean, hydrothermal plumes disperse high concentrations of key chemical tracers including He-3, CH_4*, Mn, Fe,* H_2S*, etc… (Lilley et al. 1995). 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 sub-nanomolar a few km 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 km 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., (Mandernack and Tebo 1999); (Mottl and Mc Conachy 1990); (Radford-Knoery et al. 1998)) 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 2000) and the end-member vent fluids have been analyzed (Douville et al. 1997). We report on the data from 4 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 down-stream from the vent site (German et al. 1998; Thurnherr and Richards 2000). The fourth station (Flame-HYD02) is located 4km further down-stream. Water samples collected in trace metal-cleaned Niskin-type sampling bottles were sub-sampled for shipboard (sulfide) and shore-based (manganese, other parameters) analyses. Sulfide analyses were completed less than 40 minutes after the rosette arrived on deck, and hence less than 2 hours after closing the Niskin in situ. Because it does not change the interpretation of the data, the reported concentrations are uncorrected for sulfide removal which occurred during in 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 sub-samples were held until analysis in all-polyethylene syringes. Using a peristaltic pump and an injection valve, 250μL of sample held in the injection loop was repeatedly inserted (ca. 1 min-1) into a carrier stream consisting of sulfide-free seawater pumped at 1.3ml min-1. This stream was then mixed with a FMA solution (50nmol L-1 in deionized water, pumped at 1.3ml min-1) in a 50cm-long mixing column, and passed through the flow cell of the fluorescence detector (excitation 499nm, emission 523nm). 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 (pre-weighed Na2S chips) or volumetric (H2S(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 4 stations exhibit similar properties with high concentrations of sulfide (up to 2.1nmol L-1, Flame-CTD 33) at plume-height (2000-2200m) reducing to below detection levels (<0.1nmol L-1) in the water column both above and below this depth horizon (Fig.2). Corresponding 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. Sub-samples 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 (t)) 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 $0.1<k^*<0.7$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*=0.007h-1 for seawater at pH8, 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-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 1000-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 them 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-Knoery et al. 1999). In the ca. 100m-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_{fluid} = 0.39; (Douville et al. 1997)). Assuming that sulfide removal follows the average rate for Rainbow of k*=0.61h-1; Fig.3), apparent ages are obtained by substitution of k* and R values in the expression: age=Log (R_{fluid}/R_{plume}) /k*. With apparent ages between 4 and 7 hours, we compute an upper bound for plume advection velocity of 4 nmile per 4 hours (50cm s-1) for Stn. Flame-HYD02, the farthest station where sulfide was detected. Similarly, we obtain a lower bound for current at Stn. Flame-CTD33 : 1nmile per 7 hours (7 cm s-1). Within the error of our approach this offers very close agreement with the measurements of high (ca. 5 to 20cm 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 (<0.1nmol L-1) within less than 4 hours downstream from Stn. Flame-HYD 02, or less than 5 hours from Stn. Flame-HYD12. Thus sulfide should be undetectable in the water column beyond a distance of at most 10km from the vent site. This is clearly an upper bound because the latter calculation did not account for plume dilution.

Sulfide is a local (10km-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 2000). At other sites of the global ridge system, could sulfide be detected further than 10km? In more typical mid-ocean ridge settings current velocities are approximately one order of magnitude lower (Cannon and Pashinski 1997), while sulfide concentrations in other hydrothermal vents may be an order of magnitude higher than at Rainbow (Von Damm 1995). Consequently, for a common (average=0.4h-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 10km of an active hydrothermal field. Given that adult hydrothermal shrimp physiologically respond to milimolar 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 10km 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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Figure legends

Figure 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 2500 and 2000m depth is grayed; the neutrally buoyant hydrothermal plume disperses between 2100 and 1900 m depth.

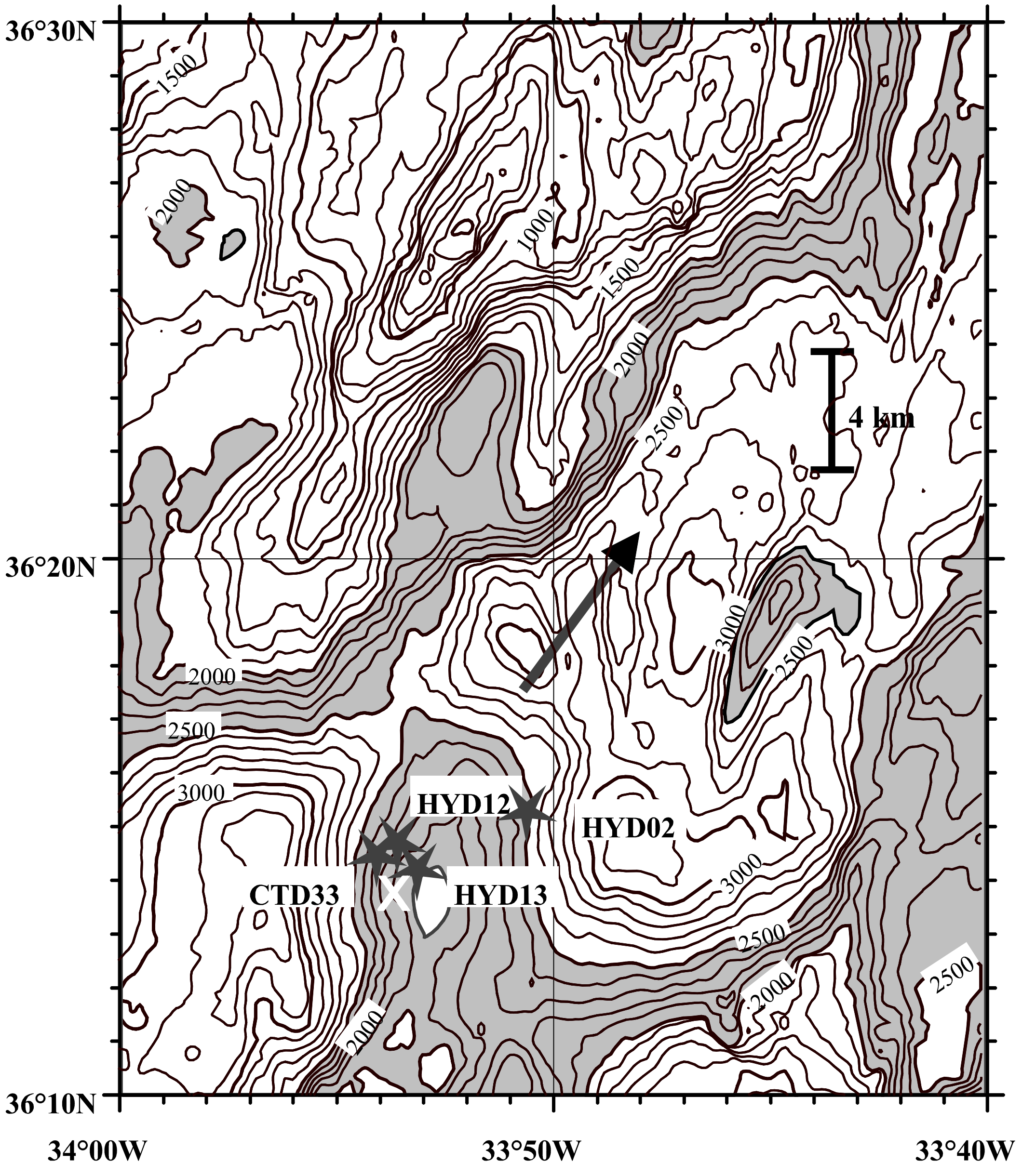

Figure 1
Radford-Knoery et al., 2000

Figure 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).

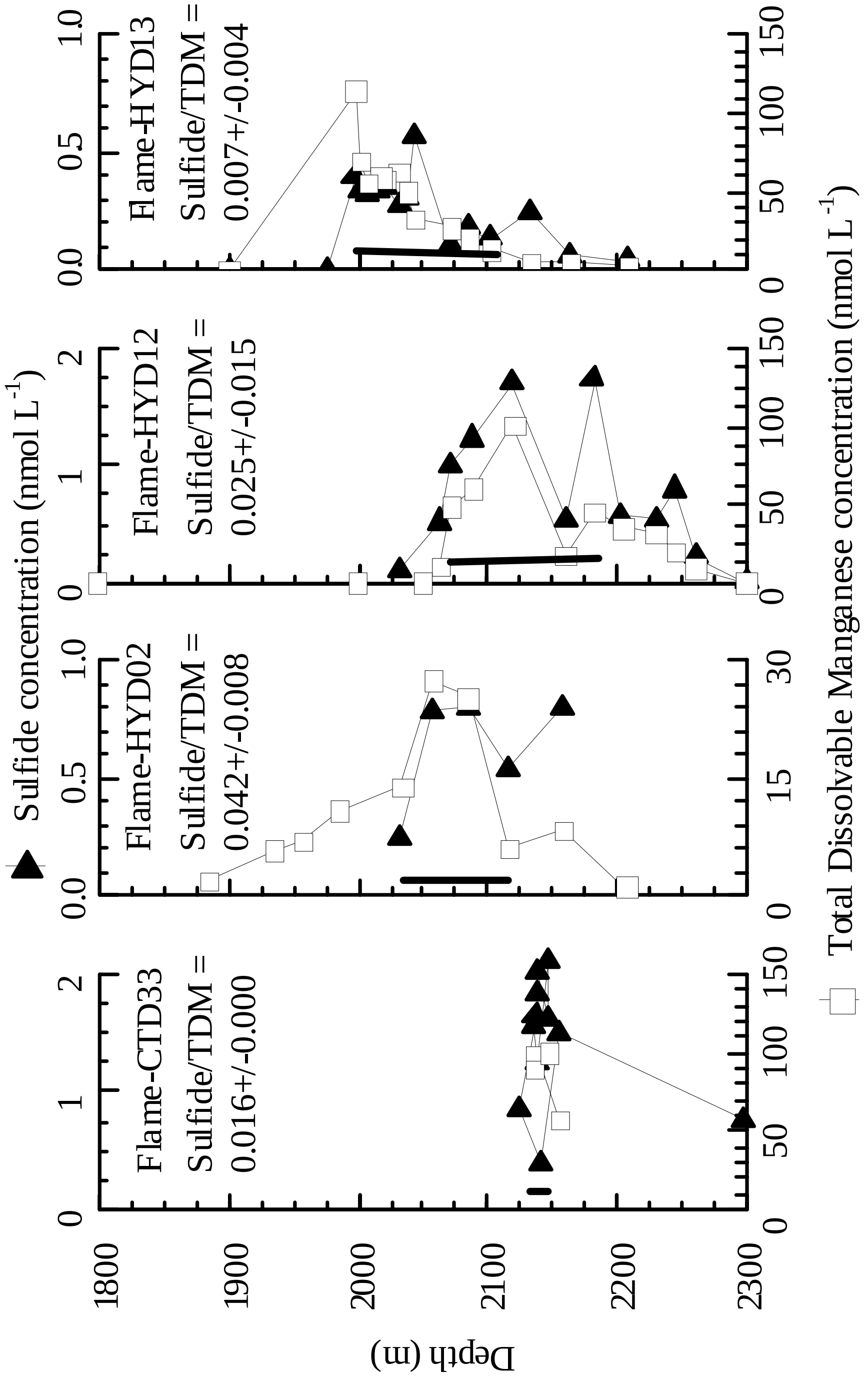

Figure 2 : Radford-Knoery et al., 2000

Figure 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 *vs*. time.

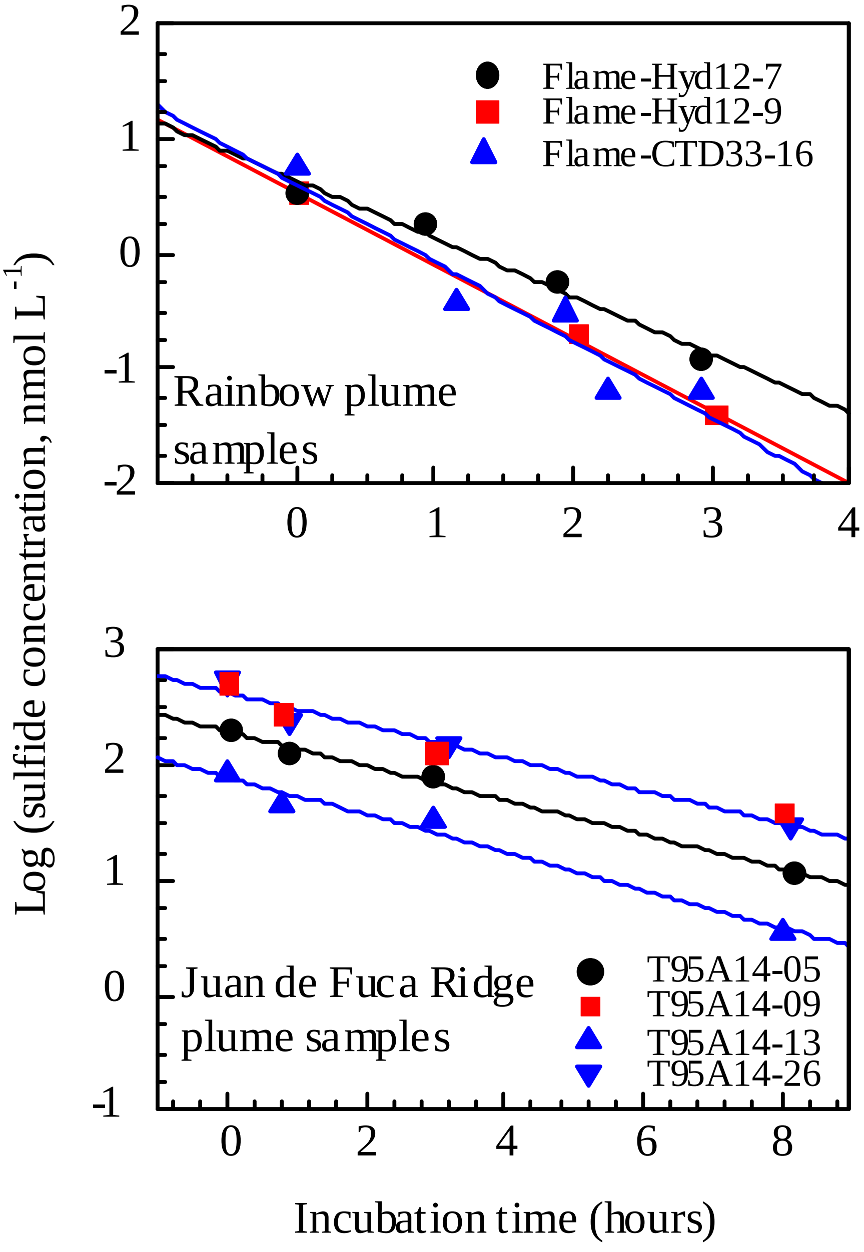

Figure 3
Radford-Knoery et al., 2000