

IRON AND COPPER ENRICHMENT OF SUSPENDED PARTICLES
IN DISPERSED HYDROTHERMAL PLUMES ALONG THE MID-ATLANTIC RIDGE

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Abstract. Particulate Fe and Cu concentrations are used in conjunction with dissolved Mn values to identify hydrothermal venting at several sites along the Mid-Atlantic Ridge (MAR). In dispersed hydrothermal plumes, as defined by dissolved Mn anomalies, suspended matter Fe and Cu values were as high as 15.8% and 1100 $\mu\text{g/g}$ respectively, relative to Al at 1.7%. Suspended matter Fe and Cu values correlate well with dissolved Mn concentrations, tracing the intensity of dispersed plumes. In contrast with Fe and Cu, particulate Mn values in vent plumes were low at 700-1200 $\mu\text{g/g}$. Calculated $(\text{Al} + \text{Fe} + \text{Mn})/\text{Al}$ ratios for MAR particles increase with increasing dissolved Mn concentrations. This ratio is used to estimate the percent hydrothermal component of the suspended matter. These sensitive tracers identify a 2-20% hydrothermal contribution to the $10 \pm 2 \mu\text{g}$ of total suspended matter/l found along the rift valley.

Introduction

The discovery and study of hydrothermal vents along seafloor spreading centers during the past decade has revolutionized classical conceptions of the ocean and ocean processes [Corliss et al., 1979; RISE Project Group, 1980]. One outgrowth of these studies is the realization that vents serve as important sources and sinks for several elements in the sea [Edmond et al., 1979]. Presently available data support vents as major sources of Mn, Li, Rb, Si and Ba and sinks for Mg and sulfate [Edmond et al., 1979]. To date, water column chemistry and global mass balance calculations have focused on data from fast-spreading centers in the Pacific and on the dissolved phase. Recent work along slow-spreading areas of the Mid-Atlantic Ridge [Scott et al., 1978; Rona et al., 1984] supports venting at several sites.

The 1984 NOAA VENTS program was designed as a reconnaissance to identify the frequency of hydrothermal plumes along a 1700 km stretch of the Mid-Atlantic Ridge (MAR). The MAR stations were pre-selected on the basis of various indicators of ongoing or previous venting activity including helium-3 in the water column, hydrothermal

mineralization on the seafloor, and a magnetic signature characteristic of hydrothermal alteration of oceanic basalt [Rona, 1978; Rona et al., 1984].

Sampling and Analysis

Water samples were collected from the NOAA Ship Researcher at 12 stations between 26°N and 11°N along the MAR (Figure 1). To achieve optimal conditions for suspended matter trace metal work, the ship was equipped with a portable, fiberglass shell clean laboratory. The double chambered unit consists of an inner Class 1000 clean room with a Class 100 laminar-flow bench and an outer room for garment changing, sampler preparation and sample transfer.

Water for suspended matter collection was obtained with Teflon-lined, 30-liter GO-FLO Niskin bottles mounted on a rosette sampler. These samplers were carefully washed with 1N HCl, rinsed with distilled, deionized water, and flushed with open North Atlantic seawater. The GO-FLO bottles were prepared in the outer chamber of the clean laboratory and remained closed until 10 m below the sea surface. The rosette system was continuously cleaned and maintained during the cruise.

Sampling was guided by a Neil-Brown CTD and a SeaMarTec nephelometer. Water samples were pressure-

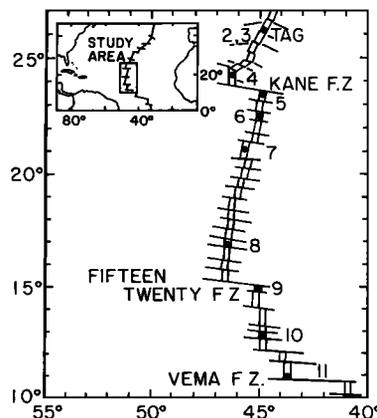


Fig. 1. Map showing section of Mid-Atlantic Ridge with sample stations. Inset map shows study area in central North Atlantic Ocean.

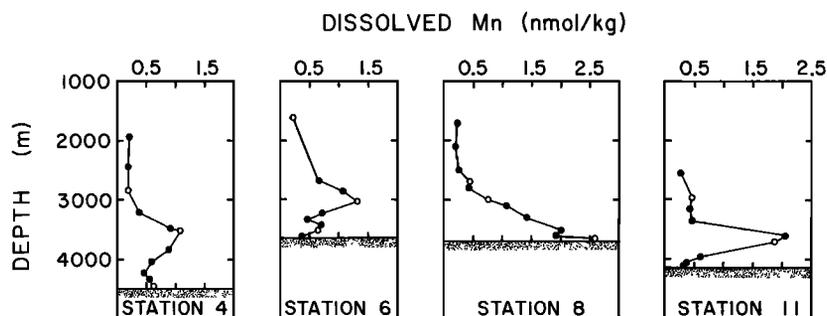


Fig. 2. Vertical profiles of total reactive (dissolved) Mn (using an 8-hydroxyquinoline extraction of unacidified, unfiltered seawater) from four locations along the Mid-Atlantic Ridge (Figure 1). Open circles denote depths at which suspended matter samples were collected. Data from Klinkhammer et al., [1985].

filtered through acid-washed $0.4 \mu\text{m}$ Nuclepore filters following precautions outlined by Trocine and Trefry [1983], including post-filtration rinses of each filter with pH-adjusted (pH 8), distilled, deionized water. All filter manipulations were carried out in the laminar flow hood using nontalced gloves.

Particulate matter weighing and complete acid digestion followed the methods of Eggimann and Betzer [1976] as modified by Trocine and Trefry [1983]. Elemental analysis was by flame and flameless atomic absorption spectrophotometry using a Perkin-Elmer 4000 instrument equipped with deuterium background correction, an HGA-400 graphite atomizer, and an AS-40 auto-sampler. Average precision for all elements analyzed was better than 3%. NBS standard reference sediment 1646 was analyzed several times using 1 mg quantities and all values agree well with established levels. Reagent blanks were typically < 5% of total sample signals.

Dissolved Manganese

Dissolved Mn concentrations served as the shipboard indicator of dispersed hydrothermal plumes during the August 1984 cruise [Klinkhammer et al., 1985]. Water samples were analyzed aboard ship for total reactive Mn (TRM) following 8-hydroxyquinoline extraction of unfiltered, unacidified samples. TRM values are considered to be the dissolved Mn component.

Normal deep-water TRM values were 0.26 ± 0.08 nmol/kg throughout the study area (Figure 2). The terms "Mn-enriched" and "background" are used in this paper to differentiate samples with and without a detectable hydrothermal contribution based on dissolved Mn anomalies. The boundary for this distinction is 0.50 nmol/kg, 3 standard deviations above average bottom water TRM values.

Dissolved Mn anomalies were observed at discrete depths at the TAG area and all other stations. The maximum dissolved Mn concentration was 2.6 nmol/kg at station 8. The Mn anomalies were typically at 3000-3700 m (Figure 2) which is consistent with venting from the walls of the rift valley, but does not preclude venting from the seafloor.

Suspended Particles

Total suspended matter (TSM) concentrations for the MAR samples, all collected at depths of 1600-4500 m, ranged from 7 to $15 \mu\text{g/l}$ and averaged $10 \pm 2 \mu\text{g/l}$. These values

are comparable with concentrations of 6 to $14 \mu\text{g/l}$ reported for deep waters of the North Atlantic [Brewer et al., 1976; Lambert et al., 1984]. No significant differences in average TSM values were observed for samples from Mn-rich waters ($10 \pm 2 \mu\text{g/l}$) relative to normal deep waters ($9 \pm 2 \mu\text{g/l}$).

The composition of the suspended particulate matter was calculated at $17 \pm 5\%$ aluminosilicate detritus, assuming the aluminosilicate component to be 10 times the particulate Al concentration [Lambert et al., 1984]. The Si/Al ratio for all MAR suspended matter collected was 3.7 ± 1.0 , in close agreement with that for average continental crust [Taylor, 1964]. Based on Ca values, the average carbonate content of the MAR particles is about 10%, in contrast with 75% carbonate in the sediments. The bulk of the suspended matter collected is thus biogenic. Such composition is consistent with previously reported data for deep North Atlantic waters wherein no nepheloid layer is observed [Lambert et al., 1984].

Particulate Metals

Suspended matter concentrations of Fe, Cu and Mn are potentially useful tracers of dispersed hydrothermal plumes because of their greatly elevated levels in hydrothermal

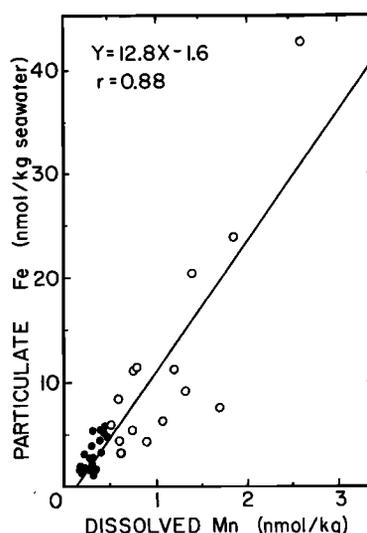


Fig. 3. Scatter plot of particulate Fe vs dissolved Mn concentrations. Open circles denote samples from Mn-enriched waters and solid circles are for background samples.

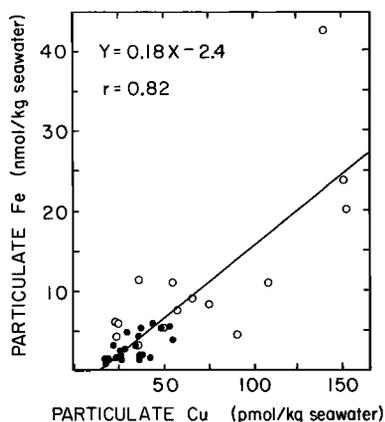


Fig. 4. Scatter plot of particulate Fe vs particulate Cu concentrations. Open circles denote samples from Mn-enriched waters and solid circles are for background samples.

mineral deposits [Scott et al., 1978; Francheteau et al., 1979]. Our 1984 MAR data show that suspended matter Fe values increase from an average of $1.9 \pm 0.9\%$ at non-plume sites to a mean of 6.0% and a maximum of 15.8% of the total suspended matter in Mn-enriched waters. A plot of dissolved Mn vs particulate Fe concentrations for all MAR samples (Figure 3) shows a linear relationship in support of a vent source for these metals. Stations 4, 6, 8 and 11, which gave especially good dissolved Mn signals (Figure 2), also show high particulate Fe values. The same linear trend is found when suspended matter Fe/Al ratios are plotted vs dissolved Mn because Al concentrations are relatively uniform at $1.7 \pm 0.5\%$ for all samples collected.

Particulate Cu concentrations follow the trend observed for Fe (Figure 4). Copper values as high as $1100 \mu\text{g Cu/g}$ suspended matter were observed with an average of $>400 \mu\text{g/g}$ for particles in Mn-rich waters. Observed scatter in the Cu/Fe relationship for samples along the entire cruise track (Figure 4) is consistent with a range of different Fe and Cu contents for metalliferous sediments and metal sulfides [Francheteau et al., 1979; Hekinian et al., 1980].

Waters with a vent component show little or no enrichment in concentrations of particulate Mn relative to Fe and Cu. Manganese values in dispersed plumes average $980 \pm 170 \mu\text{g/g}$ relative to $750 \pm 220 \mu\text{g/g}$ in non-plume waters. Average Mn/Al ratios for dissolved Mn-rich waters are about 40% greater than at other MAR sites; however the plume samples have Cu/Al and Fe/Al ratios which average 100% and 300% greater than background levels. This observation is consistent with a metal sulfide or primary hydrous iron oxide phase as the bulk of the hydrothermal component in samples from the 1984 MAR sites. Manganese is generally a trace component of polymetallic sulfides [Francheteau et al., 1979].

More than 80% of the water column Mn is in the dissolved phase in dispersed plumes. However, if the 2.6 nmol/kg of dissolved Mn at station 8, for example, were to adsorb onto the $15.1 \mu\text{g particles/l}$ at that site, solid phase Mn concentrations would be 1.03% rather than the 0.08% observed.

Boström et al. [1969] used Al, Fe, and Mn concentrations to identify hydrothermal sediments on the East Pacific Rise. They found that most deepsea sediments have

$(\text{Al} + \text{Fe} + \text{Mn})/\text{Al}$ ratios <2.5 and that values >10 were found for sediments with a significant hydrothermal component. A ratio of ~ 1.7 is typical for average continental crust. When our MAR suspended matter data are treated similarly, particles with a suspected plume component based on dissolved Mn data have much higher ratios than background MAR particles (Figure 5). This higher ratio is a function of an increase in particulate Fe values. The $(\text{Al} + \text{Fe} + \text{Mn})/\text{Al}$ ratios increase with increasing dissolved Mn concentrations (Figure 5).

Figure 5 can be used to estimate the % hydrothermal fraction of suspended matter samples. The point of zero hydrothermal contribution is set using a ratio of 2.1 which was derived from Al, Fe and Mn concentrations for background MAR particles $\{(1.8 + 1.9 + 0.07)/1.8\}$. Aluminum concentrations decrease slightly and Fe concentrations increase greatly as the hydrothermal component increases. This trend contrasts with that found by Bolger et al. [1978] along the Galapagos Spreading Center where they observed Mn-rich, but not Fe-rich particles. This difference could reflect geographical differences in vent composition and/or physical separation of solid phase hydrothermal products in time and space.

The maximum hydrothermal contribution to the suspended matter load was found at station 8, where particles contained 15.8% Fe and the $(\text{Al} + \text{Fe} + \text{Mn})/\text{Al}$ ratio was $13.3 \{(1.29 + 15.8 + 0.08)/1.29\}$. To convert this ratio to a percent hydrothermal component: (1) 65% Fe was chosen as a 100% hydrothermal end-member, based on the average percent Fe in Fe hydrous oxides or an oxidized Fe sulfide phase and the lack of quantitatively significant enrichment of any other element in the plume samples, (2) detrital Fe concentrations were calculated using the Fe/Al ratio for non-plume MAR particulates, and (3) a ratio value of 2.1 was set as the 0% hydrothermal component. For station 8, after correcting for detrital Fe (1.3% from $\text{Fe}/\text{Al} = 1.04$), the hydrothermal contribution is 14.5% Fe, which yields

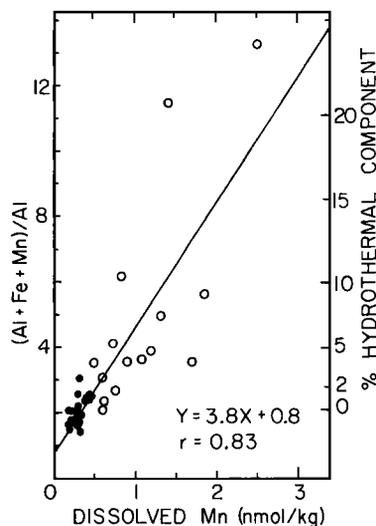


Fig. 5. Plot of $\{(Al + Fe + Mn)/Al\}$ for suspended particles vs dissolved Mn concentrations. The % hydrothermal component of the suspended matter is shown on the right-hand axis. Open circles denote samples from Mn-enriched waters and solid circles are for background samples.

a value of 22% for the hydrothermal contribution to the particulate fraction. This station 8 sample also had the highest suspended matter concentration of 15.1 $\mu\text{g}/\text{l}$. Based on the above calculations, 3.3 $\mu\text{g}/\text{l}$ of the station 8 particles were vent derived.

Combined use of dissolved Mn concentrations and particulate Fe and Cu values provide a powerful tool for identifying dispersed hydrothermal plumes and tracing the transport and separation of particulate phases. Most of the samples collected from Mn-rich waters during the 1984 VENTS cruise had a 2-20% hydrothermal component which is equivalent to 0.2-2 μg of particles/l. The evidence presented here for ongoing hydrothermal activity along the MAR supports indications of venting shown in previous studies [Rona et al., 1984] and shows the importance of continued study of slow-spreading centers.

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