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The geochemistry of Atlantic hydrothermal particles

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Abstract. Particles were collected from the dilute portion of neutrally buoyant hydrothermal plumes from four Mid-Atlantic Ridge sites (MARK, 23°N; TAG, 26°N; Broken Spur, 29°N; Lucky Strike, 37°N). Comparison of data from proximal portions of the TAG (Atlantic) [*German et al.*, 1991; this study] and North Cleft (Pacific) [*Feely et al.*, 1994] plumes show that oxyanion (e.g., V) scavenging is more efficient at TAG, possibly due to a higher proportion of Fe removed as sulfides at North Cleft and/or the more vigorous mixing in the high energy TAG buoyant plume. Chalcophile elements (e.g., Cu) show two stage removal. They are precipitated as sulfides during initial mixing of vent fluids with seawater and are sedimented from the buoyant plume. In the dilute plume they are scavenged from seawater by Fe oxyhydroxides. The REE show continued scavenging in the neutrally buoyant plume and lower levels in 1993 samples, compared to 1988 samples [German et al., 1990] suggesting that the amount of scavenging is related to particle recycling.

Introduction

The impact of vent fluids on seawater chemistry is modified by reactions within hydrothermal plumes during mixing with seawater [e.g., *Trocine and Trefry,* 1988; *Feely et al.*, 1990; *German et al.*, 1990, 1991] Hence, an understanding of processes operating within plumes is needed to assess the impact of hydrothermal activity on the oceans. Vent fluids have been sampled from TAG (26°N), MARK (23°N), Lucky Strike (37°N) and Broken Spur (29°N) [*Edmond et al.*, 1995; *Colodner et al.*, 1993; *James et al.*,1995], but studies of particles from the associated plumes have been confined to TAG [e.g., *Trocine and Trefry*, 1988; *German et al.*, 1990, 1991]. In this study we report the first particulate data from Broken Spur, MARK and Lucky Strike, and present new data from the more dilute portions of the TAG plume, which have allowed for a more detailed understanding of processes operating within hydrothermal plumes.

Sampling and Methods

Particles were collected from the neutrally buoyant plumes using Stand Alone Pumps (SAPS) equipped with 1μm pore-size filters. SAPS were suspended from the ship, on moorings, or mounted on the OSU ZAPS sled [*Klinkhammer et al.*, 1995]. Lucky Strike was sampled during the 1992 FAZAR program [*Langmuir et al.*, 1993]. Broken Spur, TAG and MARK were sampled in 1993 during RRS *Charles Darwin* cruise 77 [*Elderfield,* 1993]. After recovery, the filter housings were rinsed with clean water, sealed in polythene bags and frozen.

On return to Bristol, the filters were refluxed with conc. HNO_3 and then diluted to 5% solutions. Semi-quantitative analyses by ICP-MS were used to set standard concentrations for calibration of analyses (±5%) by standard additions for V, Mn, and Cu, with 100 ppb Ga internal standard, also by ICP-MS. Rare earth elements (REE) were determined by ICP-MS (±10%) at OSU. Al and P were measured (±5%) by ICP-AES. Fe was measured (±5%) by AAS. The data and sample locations are listed in Table 1. Data are expressed as moles of particulate metal per litre of filtered seawater, allowing direct comparison with vent-fluid and seawater concentrations.

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Discussion

During initial mixing of vent fluids with seawater, sulfide and sulfate minerals form and most drop out of the plume close to the vent. Further dilution results in precipitation of Fe oxyhydroxides, together with scavenging and coprecipitation of elements from the vent fluids and entrained seawater. Fine-grained oxides have slow settling velocities and can remain in the neutrally buoyant plume for long periods. Fe is the dominant element in hydrothermal particles and so is used to indicate the hydrothermal input and degree of dilution [e.g., *German et al.*, 1991]. As the plume ages, remaining sulfide and sulfate minerals dissolve. The level of Fe decreases with distance from the vent site and so may be used to infer the age of particles, although low Fe levels are also observed at the upper and lower edges of the laterally dispersed particle plume.

Trocine and Trefry [1988] and *German et al.* [1991] observed uniform particulate Mn levels in the TAG plume, in the range 100-200 nM/l, although *German et al.* [1991] observed increasing Mn (200-300 nM/l) at high (>100 nM/l) particulate Fe levels. Most samples in this study show similar behavior (Fig 1a). A few have much higher Mn levels, typically at low Fe concentrations. Figure 1b shows mixing between high Fe and low Mn/Fe and low Fe and high Mn/Fe, consistent with mixing between the Fe-rich plume and Mn-rich background material [cf.*Trocine and Trefry,* 1988]. The mixing line passes above the average Mn/Fe of background particulates from the deep North Atlantic [*Sherrell and Boyle,* 1992] indicating an additional source of particulate Mn. This may be due to the rift valley topography preventing dispersal of the plume. Our data are consistent with uptake of dissolved

Table 1. Elemental concentrations in plume particulates from MARK (23°N), TAG (26°N) and Lucky Strike (37°N).

	Depth m	Latitude °N	Longitude °W	Fe nM/l	Al nM/l	Mn pM/l	V pM/l	Cu pM/l	*Ce pM/l	Nd pM/l	Eu pM/l	Gd pM/l	Er pM/l
Snakepit													
317T	3304	23°22.13'	44°57.06'	6	-	210	8.6	-	2.49	0.91	0.034	0.13	0.040
317B	3093	23°22.13'	44°57.06'	3	0.89	112	13	30	2.18	0.80	0.026	0.11	0.021
323T	3366	23°22.09'	44°57.12'	5	1.53	127	4.1	257	1.74	0.59	0.017	0.08	0.015
323B	3409	23°22.09'	44°57.12'	9	2.99	182	31	631	1.97	0.69	0.023	0.09	0.016
329T	3407	23°22.12'	44°57.19'	3	2.01	530	25	42	1.08	0.30	0.011	0.03	0.003
329B	3444	23°22.12'	44°57.19'	-	-	172	5.7	10	-	0.09	-	-	-
TAG													
403T	3340	26°08.24'	44°49.58'	50	0.52	189	239	1405	0.98	0.89	0.046	0.18	0.070
403B	3440	26°08.24'	44°49.58'	38	0.62	193	174	647	1.36	1.04	0.050	0.20	0.078
409T	3081	26°08.24'	44°49.59'	4	1.06	190	32	40	1.43	0.60	0.020	0.10	0.025
409B	3231	26°08.24'	44°49.59'	5	0.30	339	27	20	2.54	0.91	0.024	0.11	0.027
Broken Spur													
106B	2728	29°10.11'	43°10.34'	3	0.19	150	5.9	101	1.54	0.48	0.019	0.09	0.022
502T	2890	29°10.04'	43°10.50'	4	1.14	173	38	368	1.73	0.70	0.027	0.09	0.023
502B	2953	29°10.04'	43°10.50'	4	1.34	882	21	466	1.72	0.58	0.021	0.08	0.020
509T	2727	29°09.73'	43°10.46'	2	1.00	165	11	267	1.60	0.51	0.020	0.08	0.013
509B	2827	29°09.73'	43°10.46'	9	0.94	215	13	899	1.66	0.59	0.025	0.10	0.033
520T	2688	29°09.85'	43°10.54'	2	0.88	182	19	38	1.73	0.55	0.025	0.08	0.026
520B	2888	29°09.85'	43°10.54'	14	1.88	3780	27	769	1.30	0.58	0.021	0.10	0.035
526T	2840	29°09.24'	43°10.57'	9	0.93	150	259	480	1.89	0.73	0.030	0.13	0.045
526B	2940	29°09.24'	43°10.57'	9	0.63	209	225	435	1.12	0.41	0.015	0.06	0.016
528T	2763	29°09.17'	43°10.51'	10	1.11	130	10	102	1.80	0.75	0.032	0.13	0.048
528B	2863	29°09.17'	43°10.51'	7	0.97	152	4.9	61	1.25	0.44	0.018	0.07	0.016
FAZAR													
SL-25	1780	37°16.92'	32°14.64'	10	0.79	260	50	50	0.81	0.57	0.024	0.16	0.054
SL-31	1000	37°16.81'	32°14.65'	1.4	1.37	150	10	30	1.23	0.37	0.004	0.11	0.023
SL-39	2270	36°27.82'	33°37.16'	34	1.56	1810	520	930	2.32	1.51	0.066	0.46	0.18
Seawater				1		1000		7000	5.44	21.4	1.06	6.2	5.5
29°N Fluid				2.0e6		2.5e8		4.3e7	4720	2350	1720	510	99
26°N Fluid				5.6e6		6.8e8		1.5e8	9540	6120	3540	1100	290
23°N Fluid				2.6e6		4.5e8		1.8e7	4940	2320	2480	400	68

Broken Spur fluid data from James et al. (1995), TAG and MARK from Edmond et al. (1995) and Mitra et al. (1994).
*A complete set of REE data are available from the authors.

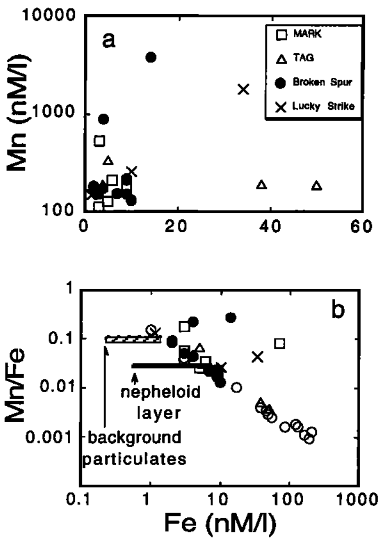

Figure 1. Particulate data from Atlantic plumes a) Mn vs Fe concentrations b) Mn/Fe ratio vs Fe concentrations (symbols as in Fig. 1a, open circles = TAG 1988 [*German et al.*, 1991].

Mn by Fe-rich particles, but at a rate which is slow, such that mixing with background material obscures correlation with hydrothermal Fe.

Trace element versus Fe plots show three types of behavior in neutrally buoyant hydrothermal plumes [*Trocine and Trefry*, 1988; *Feely et al.*, 1990; *German et al.*, 1990, 1991], 1) linear correlation, characteristic of conservative mixing (e.g., V); 2) negative deviation from mixing, indicating removal with respect to Fe (e.g., Cu); 3) positive deviation from mixing, indicative of continued scavenging beyond initial coprecipitation (e.g., REE).

Linear relationships are seen for elements occuring as oxyanions in seawater, e.g., V [*Middleburg et al.*, 1988; *Feely et al.*, 1990] (Fig. 2). This probably reflects changes in the surface charge of Fe oxyhydroxides. At pH <6.7, in the buoyant plume where acidic vent fluids are concentrated, α-FeOOH has a positive surface charge [*Stumm and Morgan*, 1981] and is an effective anion scavenger. As the vent fluids are diluted by seawater, the pH increases and the surface charge becomes negative so the Fe oxyhydroxides become more efficient cation scavengers. The V/Fe ratio is lower (2.76) in plume particles from the North Cleft site, Juan de Fuca Ridge, North Pacific [*Feely et al.*, 1994] than at TAG (4.54) (Fig. 2). V is an oxyanion in seawater and largely conservative, although Atlantic levels are slightly lower (23 nM/kg) than in the Pacific (30-35 nM/kg) [*Middleburg et al.*, 1988]. The

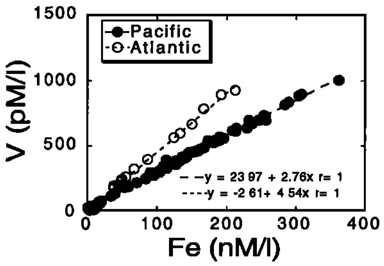

Figure 2. V vs Fe particulate concentrations in plumes from the Pacific (North Cleft [*Feely et al.*, 1994] and the Atlantic (TAG [*German et al.*, 1991; and this study]).

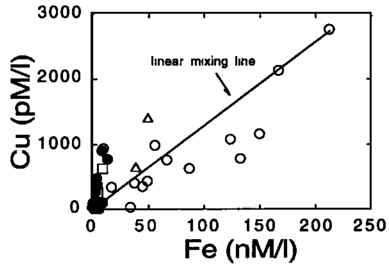

Figure 3. Particulate Cu vs Fe concentrations in the Atlantic plumes (symbols as in Fig. 1a).

higher V/Fe ratio in Atlantic particles, suggests the TAG particles are more efficient oxyanion scavengers than those from North Cleft. Hence, scavenging may not be an equilibrium process with a constant distribution coefficient between dissolved and adsorbed oxyanions. This may reflect limitation by the number of scavenging sites on particles or kinetic controls. Site limitation implies differences in particle composition at the two sites; if a higher proportion of particulate Fe present as sulfides rather than oxyhydroxides would reduce the scavenging efficiency of particles at a given Fe level. The H_2S/Fe ratio of North Cleft vent fluids are higher than at TAG [*Butterfield and Massoth*, 1994; *Edmond et al.*, 1995] favoring formation of Fe sulfides, although most sulfides drop out close to the vent site [*Feely et al.*, 1994]. The TAG hydrothermal site is one of the largest, with the plume rising up to 400 m [*Rudnicki and Elderfield*, 1993], but the North Cleft field is smaller (plume only rises 150 m above its source) [*Baker et al.*, 1993]. Hence, particles in the TAG buoyant plume may undergo more vigorous mixing (and more efficient scavenging) with entrained seawater during the interval the Fe oxyhydroxides maintain a positive charge.

Speer and Helfrich, [1995] suggest that plumes grow for up to a month before becoming unstable and shedding from their source. Rotation of parcels of fluid due to rotation of the Earth is thought to result in a barocyclinic vortex pair, an anticyclonic vortex of plume fluid at the spreading level and a cyclonic vortex of ambient fluid around the rising plume. This is thought to limit entrainment of ambient fluid into the rising plume, resulting in recycling of plume fluid from above, consistent with recycling of particles [*German and Sparks*, 1993]. Laboratory experiments [*Helfrich and Battisti*, 1991] show that as a plume grows it becomes unstable, parcels of fluid are shed off axis and the process begins again. The timescale of this process is ~2 weeks. During recycling, the particles pass through the buoyant plume and may become positively charged and continue to scavenge oxyanions. Hence, extensive recycling at TAG, may also explain the more efficient scavenging of V compared to North Cleft.

Chalcophile elements, e.g. Cu, show negative deviations from a mixing line with Fe, indicating preferential removal from the buoyant plume due to settling of dense sulfides during initial mixing of seawater with vent fluids [*German et al.*, 1991] or dissolution of suspended sulfides with reprecipitation of Fe oxides and release of dissolved Cu [*Metz and Trefry*, 1993]. Maximum particulate Cu/Fe ratios in the TAG (0.028) and MARK (0.07) plumes occur at high Fe levels. Decreasing particulate Cu/Fe ratios at higher dilution are consistent with removal of Cu in the dilute plume. At Broken Spur maximum particulate Cu/Fe ratios are at low Fe levels (2-4 nM/l). This may indicate that Cu is reprecipitated with oxyhydroxides in the more dilute plume. At low Fe levels (≤50 nM/l) at Broken Spur, Cu shows a positive deviation from linear mixing (Fig. 3) and increasing Cu/Fe ratios with decreasing Fe (Fig. 4a). Similar patterns are seen at North Cleft [*Feely et al.*, 1994] (Fig. 4b). Hence, Cu shows two-stage behavior; precipitation and removal by settling-dissolution during early plume evolution, removing most of the dissolved Cu from the vent fluids [*German et al.*, 1991; *Metz and Trefry* 1993], followed by scavenging of Cu from seawater in the dilute plume.

REE exhibit positive deviations from a linear mixing trend with particulate Fe, indicative of continued scavenging in the neutrally buoyant plume [*German et al.*, 1990]. The REE/Fe ratios in fluids from MARK, TAG and Broken Spur are similar ($1.06\text{-}1.09\times10^{-6}$) [*Mitra et al.*, 1994; *Klinkhammer et al.*, 1994; *James et al.*, 1995]. The minumum REE/Fe ratios in particles [e.g., Nd/$Fe_{(min)}$ TAG 1.8×10^{-5}] are higher than in fluids, indicating that the REE are derived from seawater in addition to vent fluids [*German et al.*, 1990].

Particulate REE concentrations in the TAG particles are half those in the 1988 data set [*German et al.*, 1990], e.g., 32B, [Fe] 49 nM/l, [Nd] 2.0 pM/l [*German et al.*, 1990]; 403T, [Fe] 50 nM/l, [Nd] 0.89 pM/l. Extensive particle recycling at TAG [*German and Sparks*, 1993] may also explain the difference in REE between 1988 and 1993, and may reflect different residence times of Fe oxyhydroxides in the recycling plumes at the different sampling times.

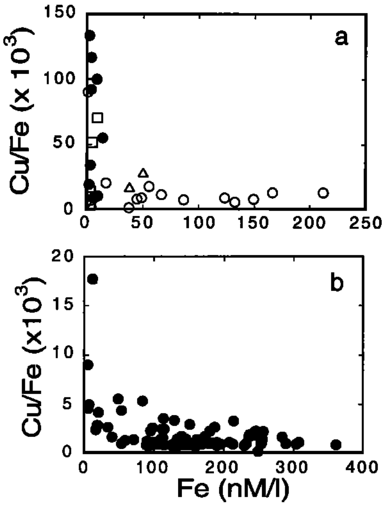

Figure 4. a) Particulate Cu/Fe vs Fe concentrations in Atlantic plumes (symbols as in Fig. 1a). b) Particulate Cu/Fe ratios vs Fe concentrations in North Cleft site, Juan de Fuca Ridge [*Feely et al.*, 1994] plume.

Conclusions

Particles were collected from the dilute plumes at the MARK (23°N), TAG (26°N), Broken Spur (29°N) and Lucky Strike (37°N) vent sites on the Mid-Atlantic Ridge. Comparison of the TAG data with those from the North Cleft field, Pacific [*Feely et al.*, 1994] show that the oxyanion scavenging efficiency at TAG is greater. This may be due to a limited number of scavenging sites on the Pacific particles (due to a higher proportion of Fe sulfides), more turbulent mixing in the higher energy TAG site, leading to more effective scavenging, or more extensive recycling of particles in the buoyant plume. Comparison of data from this study with samples collected from proximal portions of the TAG plume [*German et al.*, 1990, 1991] show chalcophile elements undergo two-stage reaction. Cu is preferentially removed from the buoyant plume as sulfides, leading to negative deviations from a linear mixing line with particulate Fe levels [*German et al.*, 1991]. At greater dilution there is scavenging of Cu from seawater by Fe oxyhydroxides, leading to elevated Cu/Fe ratios in the dilute plume. The REE show continued reaction with particles, with higher REE/Fe ratios in the dilute plume. Continual scavenging of REE from seawater in the neutrally buoyant plume confirms that hydrothermal systems are a net sink for REE. The different REE levels in the TAG particles, between 1988 [*German et al.*, 1990] and this data set, may be due to different residence times of Fe oxyhydroxides in recycling plumes [*Speer and Helfrich*, 1995].

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