Trace metal concentration and partitioning in the first 1.5 meters of hydrothermal vent plumes along the Mid-Atlantic Ridge: TAG, Snakepit, and Rainbow

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Abstract

To determine the significance of metal fluxes from hydrothermal vents, understanding the speciation, reactivity, and possible transformations of metals and metal sulfides within the hydrothermal plume is critical. In this study, we measure the concentration and partitioning of trace metals (Fe, Mn, Cu, Cd, Co, Pb, Ni) and sulfide phases within the first 1.5 meters of the rising plume at three vent fields (TAG, Snakepit, and Rainbow) along the Mid-Atlantic Ridge. A combination HCl/HNO₃ leaching method was used to differentiate metals present in metal mono-sulfides from those in pyrite and chalcopyrite. At all three vent sites, Mn and Fe are primarily in the < 0.2 µm (filtered) portion, whereas Cu, Co, Cd, and Pb are mainly in the unfiltered fraction. Significant concentrations of HNO₃-extractable metals were found in the < 0.2 µm fraction at all three vent sites, indicating that they likely exist in a recalcitrant nanoparticulate phase such as pyrite or chalcopyrite. At TAG and Snakepit, Cu is correlated with Co, as Co enters into chalcopyrite and other CuFeS phases and Zn is correlated with Cd and Pb as they form discrete metal sulfide phases. At Rainbow, Zn, Cd, and Pb are correlated, but Cu and Co are not correlated. The Rainbow data are consistent with the higher metal to sulfide ratio found at Rainbow. These speciation differences are significant as both mineral type and size will affect the amount of metal transported from the vent site and its availability for biogeochemical processes.

Keywords

Trace metals, metal sulfide, nanoparticles, hydrothermal vent, Mid-Atlantic Ridge

Abbreviations

MAR, Mid-Atlantic Ridge; TAG, Trans-Atlantic Geotraverse; ROV, Remotely Operated

24 Vehicle; AVS, Acid Volatile Sulfide; CRS, Chromium Reducible Sulfide.

25 **1 Introduction**

26 Hydrothermal activity, widespread along plate boundaries and other volcanic hot-
27 spots, results in large fluxes of metals emitted from vents to the surrounding seawater.
28 These metals have potential impact on both the local and global scales and could
29 influence the trace metal budget of the oceans (Butterfield et al., 2003; Tagliabue et al.,
30 2010). The trace metal content of end-member vent fluid varies between vents, dependent
31 on the composition of the rock in which the hydrothermal circulation occurred, as well as
32 the temperature, redox condition, pH, and concentration of inorganic ligands such as
33 sulfide and chloride (Metz and Trefry, 2000).

34 Particles form when this metal-rich, hot, and highly reduced vent water mixes
35 with cold, partially oxygenated ocean bottom water (Haymon, 1983). Previous research
36 has demonstrated that there are two main phases of metal precipitation within the
37 hydrothermal plume. Initially, metal sulfides form, and later, as the plume becomes more
38 oxidic, iron oxides precipitate, scavenging metals and oxyanions onto their surfaces. Within
39 the rising plume, decreasing temperature and increased mixing of seawater with vent
40 fluid are instrumental in controlling the distribution of metal sulfides and trace metals.
41 The temperature change affects the solubility of many minerals (Seyfried and Ding,
42 1995), and mixing alters the pH of the solution. The higher pH induces the precipitation
43 of metal sulfide minerals (Rickard, 1995).

44 Until recently, the predominant assumption has been that most metals emitted
45 from vents thus precipitate either as sulfide or oxide minerals, settling out in a radius of a
46 few kilometers surrounding the hydrothermal vent site (Feely et al., 1987; Mottl et al.,

1990), which led to the conclusion that vents do not contribute significant quantities of transition metals to the oceans. More recent research, however, suggests that metals, specifically iron, may be stabilized either as complexes with organic molecules (Bennett et al., 2008; Sander and Koschinsky, 2011) or as nanoparticulate metal sulfides such as pyrite, which may incorporate other metals into its structure (Yücel et al, 2011) and is a common component of hydrothermal emissions (Gartman et al., 2014). Nano-scale particles would settle from the water column at rates of only a meter or two per year, giving them the opportunity to escape the area immediately surrounding the vent field (Yücel et al, 2011). Additionally, nanoparticulate metal sulfides do not oxidize rapidly under standard conditions (Rozan et al., 2000; Luther and Rickard, 2005), and at typical ocean bottom water temperatures of 2-4 °C oxidative processes would be approximately four times slower. Pyrite in particular oxidizes very slowly due to the stable low spin electronic configuration of ferrous iron when bound to the S_2^{2-} ligand (Luther, 1990; Gartman and Luther, 2014). Iron has been the focus of the majority of investigations due to its importance as a micronutrient in the world ocean; however, other transition metals are also critical components of oceanic cycles and may be incorporated into organics and nanoparticles (Sander and Koschinsky, 2011; Gartman et al., 2014)

To understand the potential impact of hydrothermal venting as a source of trace metals to the greater oceans, the size distribution and mineral speciation of trace metals in the rising plume must be considered. Previous studies at the Mid-Atlantic Ridge (MAR) have characterized trace metal distribution and mineralogy in end-member fluid (Charlou et al., 2002; Douville et al., 2002), in the rising plume 10-150 meters from the top of the TAG mound (Rudnicki and Elderfield, 1993) and into the neutrally buoyant plume (>

300 m above the vent site) (Trefry et al 1985; German 1991; Ludford et al., 1996; Edmonds and German, 2004). These studies are fundamental to determining the chemical composition of the vent fluid, and the types of particles that are dispersed from the immediate vicinity of venting. However, there is a paucity of information about an integral component: processes that occur in the initial stages of seawater mixing in the rising plume, within the first few hundred centimeters from the vent orifice.

The initial stage of the buoyant plume, characterized by very steep physical and chemical gradients between vent and seawater, is of particular importance because the formation of most minerals will occur near the vent source, with 50-60 % seawater mixed with the vent fluid (Klevenz et al., 2011). In Gartman et al. (2014) the geochemistry of the $< 0.2 \mu\text{m}$ fraction of iron in hydrothermal fluid and within the first meter of the orifice was investigated, including SEM-EDS and XRD data. Nanoparticulate pyrite was found to be a significant component of $< 0.2 \mu\text{m}$ iron at the Rainbow, TAG, and Snakepit vent sites (up to 5 % of $< 0.2 \mu\text{m}$ iron). In the study presented here, we present measurements of trace metal and sulfide concentration and speciation in unfiltered and $< 0.2 \mu\text{m}$ filtered samples taken from the vent fluid and within the first 1.5 meters of the rising plume at those same three vent sites along the Mid-Atlantic Ridge. We consider the separation of metals into four different fractions: unfiltered and $< 0.2 \mu\text{m}$ HCl-extractable metals (consisting of dissolved metals, metal chloride complexes, and soluble metal sulfides); and unfiltered and $< 0.2 \mu\text{m}$ HNO_3 -extractable metals (consisting of metals present in pyrite and chalcopyrite, in addition to dissolved metals and soluble metal sulfides), and evaluate differences in metal partitioning between Rainbow, TAG, and Snakepit.

1.1 Study sites

The Trans-Atlantic Geotraverse (TAG), Snakepit, and Rainbow vent sites (Figure 1) were sampled along the Mid-Atlantic Ridge, a slow spreading plate boundary moving at rates less than 3 cm/year (Schmidt et al., 2007). The vent fluid at these three sites has the highest trace metal content of vent fields along the MAR (Douville et al., 2002).

The TAG vent field (26° 8' N, 44° 50' W) lies at a depth of 3620 m on a mound 200 meters wide by 50 m high, and contains high temperature (360-364 °C) black smokers (Hannington et al., 1995) that are clustered together. The lower temperature (265-300 °C) white smokers observed previously have since become extinct (Gartman et al., 2014). The heat source at TAG is approximately 1000 m deeper than that of other MAR vent fields (Crawford et al., 2010). At TAG, movement of the neutrally buoyant plume is primarily influenced by the tides (Edmonds and German, 2004). All samples were taken from the top of the mound, except for one sample that was taken from a diffuse flow zone that was venting black smoke (Table 1).

The Snakepit vent field (23° 22' N, 44° 57' W), at 3460 m depth, is a massive sulfide deposit comprised of black smokers (Crawford et al., 2010). TAG and Snakepit represent basalt hosted vent fields of deeper water depths and higher pressures where phase separation does not occur. The black smokers at Snakepit have been named previously (Lalou et al., 1993), and samples were taken from the Moose (23 22.14 N, 44 57.07 W) and Beehive (23° 22 N, 44 57.13 W) vents (Table 1).

The Rainbow vent field (36° 14' N, 33° 54' W), located 2310 m deep, is comprised of serpentinized peridotite and contains high temperature vents (up to 365 °C) that are characterized by low shipboard pH (2.8), low sulfide, and Fe concentrations an

order of magnitude higher than those at TAG and Snakepit (Douville et al., 2002; Gartman et al., 2014; this work). Vent fluid from Rainbow has a uniform composition, indicating that it comes from a single source (Charlou et al., 2002). Chloride concentrations are elevated as a result of phase separation, which concentrates the fluid to brine and increases metal solubility (Desbruyeres et al., 2001). The vent fluid at Rainbow is high in organics, which is significant because in addition to complexing metals, organic molecules may bond to the surface of nanoparticles, potentially resulting in their stabilization (Lau and Kim, 2008; Wang et al., 2009; Mullaugh and Luther, 2010). Bulk pyrite deposits at Rainbow show high degrees of trace metal substitution for Fe, and contain large quantities of Cu, Zn, and Co (Marques et al., 2006). Dispersion of the neutrally buoyant plume, and further transport of hydrothermally emitted species at Rainbow is primarily driven by bottom water currents (Edmonds and German, 2004). Samples at Rainbow were taken from five different vents: Regner, Ennuyer, Jean Luc, Guillarme (e.g. Seyfried et al., 2011), and Trident, a six meter tall vent (Table 1).

2 Methodology

2.1 Sample collection

Field studies along the Mid-Atlantic Ridge were conducted aboard the R/V *Knorr* from 16 October until 9 November 2012. All end-member vent and rising plume samples at the Mid-Atlantic Ridge were taken by the Remotely Operated Vehicle (ROV) Jason II using Titanium Major Samplers. To obtain samples, the pilots of the ROV Jason II placed the nozzle of the sampler into the vent orifice. Depending upon where in the plume the sample was collected, once either shimmering fluid or black smoke was observed emitting from the sampler, the sample was taken. For samples within the chimney orifice,

sample collection was conducted directly after taking the temperature of the vent fluid within the orifice using the high temperature probe supplied by Jason. For rising plume samples, the Jason pilot held the Major in one manipulator and the temperature probe in the other.

Upon recovery of the samples on board the ship, the pH of the fluid was measured, and subsamples were taken from the Major Sampler to preserve for analysis of metals and sulfur species in both unfiltered and filtered (through a 0.2 μm filter) fractions. Throughout this paper, the partitions are referred to as the ' $< 0.2 \mu\text{m}$ ' and 'unfiltered' fractions, where the unfiltered fraction contains particles, nanoparticles, and dissolved species; and the $< 0.2 \mu\text{m}$ filtered fraction contains (nano)particles $< 0.2 \mu\text{m}$ and dissolved species.

2.1.1 Potential sampling artifacts

Sample recovery occurred between 2 – 12 hours after sample collection. Due to the lag between sample collection and processing, samples cool to ambient bottom water temperature (2-4 $^{\circ}\text{C}$), and also potentially experience changes in pressure and pH that could affect the solubility of the metal phases in the samples.

Trefry et al. (1994) determined that in half of their collected vent fluid samples, up to 20 % of the initial Zn, Cd, and Pb; up to 50 % of initial Cu; and up to 5 % of Co could precipitate in the Major Samplers; however, these percentages were based upon the assumption that all metals were dissolved when the sample was taken. They did not observe precipitation of Fe or Mn in the Major Samplers. Cooling would decrease the rates of many reactions, such as the formation of chalcopyrite, or pyrite, slowing the rate of pyrite or chalcopyrite precipitation by an order of magnitude or greater (cooling from

360 – 2°C would decrease the rate up to 36 fold), thus helping to preserve the sample speciation (Yücel et al., 2011; Gartman and Luther, 2014). Yücel et al. (2011) calculated that < 2 % of the pyrite measured in that study could have formed in the Major Samplers during recovery. Although metal monosulfides such as FeS and ZnS form more rapidly than pyrite and chalcopyrite, (Luther and Rickard 2005) and may have formed in the sampler due to cooling, or dissolved in the sampler due to the decrease in pH, both monosulfides and dissolved metals are extracted in the HCl fraction. Therefore, although precipitation or dissolution of these species in the Major samplers is likely, it would not affect our results.

In addition to cooling, depressurization may occur during sample recovery. A drop in pressure may increase metal sulfide solubility (Reed and Palandri 2006); however, solubility is weakly dependent on pressure relative to cooling (Hsu-Kim et al., 2008). Furthermore, the solubility of metal sulfides is strongly dependent on pH. Klevenz et al. (2011) found that the pH increase due to mixing of vent fluid and sea water led to greater precipitation of metal sulfides than cooling; however, the pH measured shipboard is likely 0.5 – 2 pH units lower than the *in situ* pH (Ding and Seyfried, 2007), which would prevent further precipitation of metal sulfides.

For buoyant plume samples, if particles were predominantly precipitating in the major samplers during sample collection and cooling, rather than in the plume, we would expect the percentage of each metal in the particulate fraction to increase with seawater mixing, as the higher pH should induce greater precipitation of metal sulfides. This was not observed (section 3.2). Although the decrease in mineral formation rates with decreased temperature does not preclude the growth of existing minerals, any potential

particle formation in the Majors would mean that the quantity of metals in the $< 0.2 \mu\text{m}$ fraction presented here is underestimated. Although it is possible that some of the particles measured were formed in the Major Samplers, we do not expect this to significantly change the results reported here.

2.2 Metals analysis

2.2.1 Leaching procedure

Metals in soluble metal sulfides were differentiated from metals associated with pyrite using the HCl/HNO₃ acid leach method of Huerta-Diaz and Morse (1992) as detailed in Yücel et al. (2011) and Gartman et al. (2014). Both filtered ($0.2 \mu\text{m}$) and unfiltered sub-samples were taken from the Major Samplers and each sample was split into two and put in clean centrifuge tubes (polypropylene). One portion was fixed with concentrated trace metal clean HCl (Optima, 35 %) to extract metals from soluble metal sulfides (e.g., FeS, ZnS, CdS, PbS), and the other with HNO₃ (Optima, 70 %) to extract metals from pyrite and chalcopyrite, in addition to soluble metal sulfides. Both fractions were allowed to equilibrate for at least eight hours prior to analysis. HNO₃ is an oxidizing acid capable of dissolving minerals with a pyritic structure (pyrite or chalcopyrite), which are not soluble in HCl. Fe-measurements were conducted shipboard, and the remaining sample was frozen for analysis of other trace metals upon return to shore.

2.2.2 Fe measurements

Iron measurements of both unfiltered and filtered HCl and HNO₃ treated samples were taken shipboard using a UV-Vis absorbance at 562 nm and the ferrozine method of Stookey (1970). Samples were buffered in 2.5 M ammonium acetate prior to addition of the ferrozine reagent. After the initial analysis, the samples were treated with

hydroxylamine hydrochloride as a reducing agent to measure total iron. Fe^{3+} was determined by the difference between these numbers; however, no Fe^{3+} was detectable in any of our samples. The detection limit of this method is 100 nM.

2.2.3 Trace metals

Magnesium (Mg), manganese (Mn), copper (Cu), cobalt (Co), zinc (Zn), cadmium (Cd), lead (Pb), and nickel (Ni) were measured in samples using a Thermo Electron Corporation Finnigan Element XR Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at low resolution. Prior to analysis, samples that had been acidified, leached and frozen shipboard were allowed to settle for a minimum of 8 hours to separate refractory phases (particles not dissolved by acid leaches) prior to subsampling for analysis. Subsamples were diluted 100 times in a solution of 5.2 nM iridium in 2 % Ultrex® nitric acid and 18 megaohm water (Barnstead™, Nanopure). Preparation of the dilutions and analysis with the mass spectrometer were conducted under trace metal clean conditions. Samples were calibrated using an internal standard based on instrument response for replicate mixed standards. The response was normalized using the ratio between the counts for each metal and those for the internal standard of iridium in which the samples were diluted.

2.3 Si measurements

Silicon was analyzed on a Thermo Intrepid II XSP Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) at 212 nm. The detection limit was 1.67 μM silicon. A standard curve was prepared with NIST traceable commercial stock in a 2 % HNO_3 matrix (same as the diluted samples). Yttrium (0.51 mM) was used as an internal

standard. Samples were allowed to defrost for 3 days to eliminate polymerization (Kobayashi, 1967) before making dilutions in 18 megaohm water (MilliQ).

2.4 Sulfide measurements

Acid volatile sulfide (AVS) and chromium reducible sulfide (CRS) were measured using the method of Fossing and Jørgensen (1989) after shipboard fixation and storage. To prepare the samples, 2 mL of 0.5 M NaOH and 5 mL of 0.1 M zinc acetate were added to 5 mL of sample to fix free sulfide and FeS sulfide as ZnS. Both unfiltered and 0.2 μm filtered samples were fixed, and the samples were immediately frozen and stored at -20 °C. Prior to analysis onshore, samples were thawed and added to deoxygenated glass reaction vessels. Then, five mL of 3 M HCl were added to liberate the fixed sulfide as H_2S gas. After 1.5 hours of purge and trap, sulfide gas from the AVS portion was trapped as HS^- in 10 mL of anoxic 0.1 M trace metal clean NaOH (Wu and Boyle, 1998) in a glass test tube, and the NaOH solution was analyzed on a hanging mercury drop electrode (HMDE) controlled by an AIS DLK-100A potentiostat. Sulfide was monitored via cyclic voltammetry at a potential of -0.6 V versus a saturated calomel electrode (Yücel et al, 2011). To extract the CRS fraction, fresh NaOH was added to new test tubes, purged, then 4 mL acidified Cr(II) were injected into the reaction vessels. Cr(II) was prepared by reducing a Cr(III) solution on an amalgamated zinc column. After the addition of Cr(II), the mixture was allowed to purge and trap H_2S for an hour, then the NaOH containing trapped sulfide was again analyzed on the HMDE.

3 Results

3.1 Composition of end-member vent fluid

The concentration of Mg in the 0.2 μm filtered samples is used as a proxy to measure the extent of mixing between vent fluid and ambient seawater in the rising plume. End-member vent fluid has Mg concentrations of 0 mM (Edmond et al., 1982), and end-member seawater has a Mg concentration of 53 mM. Once the magnesium concentration for each sample is known, it is then possible to calculate the percentage of seawater that has been entrained in the vent fluid as the plume rises, and to correct concentrations for this dilution (von Damm et al., 1985). Concentrations of metals, sulfide, and silicon in end-member solutions (extrapolated to Mg = 0) are calculated only when a negative correlation with Mg was observed (Table 2).

The end-member metal concentrations that we report are within an order of magnitude of those previously reported for these vent sites (Desbruyeres et al., 2001; Douville et al., 2002; Charlou et al., 2002). Cu at TAG is a notable exception, with concentrations an order of magnitude lower than previously measured values. Metal to sulfide ratios (M:S) were calculated for each vent site as an average for all samples using the sum of the chalcophile elements (unfiltered, HNO_3 -extractable Fe, Co, Cu, Zn, Cd, Pb) to total AVS (labile sulfide). Rainbow has a M:S of 31.2 ± 16 , TAG has M:S 1.88 ± 1.1 , and Snakepit has M:S 1.94 ± 2.7 . Metal concentrations are higher and sulfide concentrations are lower at Rainbow than at TAG or Snakepit due to the ultramafic, rather than basaltic, rocks from which the vent emanates (Charlou et al., 2002).

3.2 The effect of seawater mixing on unfiltered trace metals

3.2.1 TAG

Figure 2a shows the relationship between < 0.2 μm (filtered) and unfiltered trace metals and < 0.2 μm (filtered) magnesium at TAG for all HNO_3 -treated samples.

All metals except for Ni decrease in concentration with increasing seawater dilution (r^2 values > 0.57). Fe and Mn are both present predominantly in the $< 0.2 \mu\text{m}$ fraction, whereas Cu and Co are mainly present in the unfiltered fraction. Zn, Cd, and Pb are also mainly particulate; however with increased seawater mixing and increased distance from the orifice the percentage of the metal in the $< 0.2 \mu\text{m}$ fraction increases. This decrease of metal in the particulate fraction may occur as larger particles settle from the plume more rapidly than smaller ones, or also may indicate that there is little metal sulfide particle growth in this stage of the buoyant plume.

3.2.2 Snakepit

At Snakepit, concentrations of Fe, Mn, Cd, Zn, and Pb all decrease as Mg concentrations increase and seawater is entrained in the vent fluid. Fe and Mn are predominantly present in the $< 0.2 \mu\text{m}$ fraction whereas Cu, Co, Zn, Cd, and Pb are in the particulate fraction (Figure 2b).

The partitioning of Mn, Cu, and Zn into HCl/HNO₃-extractable, and particulate ($> 0.2 \mu\text{m}$)/filtered ($< 0.2 \mu\text{m}$) fractions in the buoyant plume at Moose (Figure 3) provides an example of different behavior with respect to particle formation. Mn is present predominantly in the $< 0.2 \mu\text{m}$ fraction, and only 13 % is particulate in the most well mixed sample (93 % seawater). There is no significant difference between Mn extracted by the HCl and HNO₃ leaches. In contrast, Cu is mainly in the unfiltered fraction. Although the majority of Cu remains in the unfiltered fraction, the $< 0.2 \mu\text{m}$ fraction increases from 2.5-16 % with seawater mixing. Cu is extracted by HNO₃, and not HCl, consistent with its incorporation into pyrite or chalcopyrite. Finally, the fraction of zinc that is particulate decreases from 95-61 % as the plume rises and mixes with seawater. Zn

is extracted in the HCl leach, consistent with the solubility of ZnS in HCl. ZnS₂ has not been observed in the environment.

3.2.3 Rainbow

Figure 2c shows < 0.2 µm and unfiltered metal versus < 0.2 µm Mg concentrations for all HNO₃-extracted samples from Rainbow. Fe, Co and Mn decrease with increasing Mg. In the rising plume, Fe and Mn remain predominantly in the < 0.2 µm fraction and Co, Cu, Zn, Cd, and Pb are mainly in the unfiltered fraction and do not correlate with Mg.

3.3 Sulfur speciation in the plume

Figure 4 shows the distribution of the AVS and CRS sulfide fractions and elemental sulfur in the rising plume at each of the three sites. AVS is composed of H₂S, HS⁻, FeS, and other labile metal sulfides (ZnS, CdS, PbS) (Morse and Luther, 1999). CRS is composed of FeS₂ and FeCuS₂ (Fossing and Jørgensen, 1989; Morse and Luther, 1999). TAG has the highest measured total sulfide concentration (4130 µM) composed of unfiltered AVS (3110 µM) and CRS (1030 µM) in the hydrothermal fluid. Unfiltered CRS is the dominant sulfide fraction at Snakepit with concentrations up to 771 µM. Rainbow has the lowest total sulfide concentrations of any of the vent sites studied. In an end-member vent sample at Rainbow, (pH of 2.8) unfiltered CRS is the largest fraction at 683 µM, followed by unfiltered AVS (463 µM). With further mixing there is no significant difference between the unfiltered fractions (Figure 4c). CRS in the < 0.2 µm fraction is present at all three sites. Particulate and nanoparticulate elemental sulfur reported as S⁰ were found at all three vent sites at concentrations up to 33 µM (Findlay et

al., 2014). TAG had the highest concentrations of total elemental sulfur, while Rainbow had the highest concentration of elemental sulfur (12 μM) in the $< 0.2 \mu\text{m}$ fraction.

3.4 Association of trace metals in the buoyant plume

At TAG (Figure 5a,d) and Snakepit (Figure 5b,e), Cu is correlated with Co, and Cd and Pb are correlated with Zn, indicating that these metals are co-precipitating. This is significant as unfiltered Cu is mainly extracted in the HNO_3 leach (which consists of metals in pyrite or chalcopyrite), but unfiltered Zn is extracted in HCl (which consists of soluble metal sulfides), consistent with different metal sulfide phases within the unfiltered fraction of these metals. At Rainbow (Figure 5 c,f) Cd and Pb correlate with Zn, but unlike the other two sites Cu and Co are not correlated.

3.4.1 Iron

In the first 1.5 meters of the plume, Fe is mainly present in the $< 0.2 \mu\text{m}$ fraction. Previous study of the Fe speciation in these samples demonstrated that the $< 0.2 \mu\text{m}$ fraction at all three sites contains pyrite nanoparticles, which may incorporate other metals into their structure or cap other minerals, as demonstrated with SEM-EDS data by Gartman et al. (2014). Thus, the $< 0.2 \mu\text{m}$ fraction contains not only dissolved Fe(II), but also iron sulfide (FeS , FeS_2) nanoparticles. At TAG, unfiltered Cu, Zn, and Pb are correlated with unfiltered Fe (Figure 6a,b). The correlation between Zn and Fe at TAG could be due to precipitation of iron sulfides around zinc sulfide particles (Koski et al., 1994) or incorporation of Fe into sphalerite (Scott, 1983). At Snakepit (Figure 6c) only Mn and Cu are correlated with Fe, and at Rainbow (Figure 6d) only Mn and Co are correlated with Fe. Mn is correlated with Fe at all three sites because both are present mainly in the same fraction ($< 0.2 \mu\text{m}$). The correlation is not likely due to the

precipitation of Fe-Mn phases or adsorption of Mn onto iron oxides as oxidized Fe was not detected in any samples taken from the three vent sites.

3.4.2 Manganese

Mn is correlated with Fe (Figure 6), as both of these elements are present in the < 0.2 μm fraction in the first meter of the plume at all three vent sites (Figure 2). Despite this initial similarity in their behavior, Fe is much more reactive than Mn with respect to both oxidation and particle formation: the residence time of Fe in the neutrally buoyant plume is minutes to hours (Field and Sherrell, 2000), but the residence time of Mn is weeks to years (Mandernack and Tebo, 1993). In modeling element behavior and particle formation in the plume, Klevenz et al. (2011) predict low concentrations of Mn in particles, and no precipitation of manganese oxides should occur close to the vents due to slow oxidation kinetics of Mn^{2+} at $\text{pH} < 9$ (Morgan, 2005; Luther, 2010). At all three vent sites, Mn is mainly present in the < 0.2 μm fraction, a result consistent with prior studies (Klinkhammer et al., 1985; Sands et al., 2012).

3.4.3 Copper and cobalt

Unfiltered Cu trends with unfiltered Fe at TAG and Snakepit (Figure 6a,b,c) as it readily precipitates with Fe in sulfide minerals such as chalcopyrite (FeCuS_2) and is incorporated as a trace constituent into pyrite (FeS_2). Co is correlated with Cu at TAG and Snakepit, but not at Rainbow (Figure 5), and Cu and Fe are not correlated at Rainbow. Co typically precipitates with Cu in chalcopyrite at temperatures greater than 350 $^{\circ}\text{C}$ (Metz and Trefry, 2000). The lower sulfide concentrations and higher metal:sulfide ratio at Rainbow means that fewer metals will precipitate as metal sulfides (Klevenz et al., 2011). Unfiltered Cu concentrations in our samples are an order of

magnitude lower than expected based on the end-member values presented in Douville et al. (2002) and do not correlate to Mg at Snakepit or Rainbow (Figure 2b-c).

3.4.4 Zinc, lead, and cadmium

Unfiltered Zn is correlated with both unfiltered Cd and Pb at all three vent sites (Figure 5d, e, f). The unfiltered fraction of Cd and Pb also shows a correlation to $< 0.2 \mu\text{m}$ Mg concentrations at TAG and Snakepit (Figure 2). Due to the lower temperature at which ZnS forms, these metals have not been considerably precipitated from the plume, in contrast to Cu, and demonstrate more conservative behavior within the dilution range of our samples. Zn, Cd, and Pb are not correlated with Mg at Rainbow.

3.4.5 Nickel

Unfiltered Ni concentrations show no trend with unfiltered Fe, Mn or $< 0.2 \mu\text{m}$ Mg at any of the vent sites. Trocine and Trefry (1988) reported similar findings in the TAG plume, where Ni did not correlate with Fe, Mn, or total suspended matter. Ni is not leached in hydrothermal circulation, and is slow to react in mineral formation processes (Morse and Luther, 1999).

3.5 Metal dynamics in the $< 0.2 \mu\text{m}$ fraction

At these sites, most metals, with the exception of Fe and Mn, are predominantly particulate; however, it is important also to investigate the $< 0.2 \mu\text{m}$ fraction, as (nano)particles present in this portion will be much slower to settle and could be transported to the wider ocean (Yücel et al., 2011, Gartman et al., 2014; Tagliabue, 2014). The $< 0.2 \mu\text{m}$ fraction can be characterized by comparing the metals extractable in HCl (consisting of dissolved metals and metal monosulfides) and HNO₃ (consisting of dissolved metals, metal monosulfides, and pyrite/chalcopyrite nanoparticles). The

concentration of a metal that is only soluble in HNO₃ (Δ -N), and therefore present in pyrite, chalcopyrite, or other species recalcitrant to HCl dissolution is obtained by subtracting the HCl-extractable concentration from the HNO₃-extractable concentration (equation 1).

$$(1) \Delta\text{-N} = [\text{M}]_{\text{HNO}_3} - [\text{M}]_{\text{HCl}}$$

A two-tailed t-test was conducted to determine significant differences between the two fractions, with p-values less than 0.1 used to establish significance.

The concentration of HNO₃-extractable metal and the percentage of the total < 0.2 μm fraction are presented in Table 3. These results demonstrate the diversity of metal speciation within the < 0.2 μm fraction. At least some portion of < 0.2 μm Co, Cu, Zn, Cd, and Pb is present in the HNO₃ soluble fraction at each vent site, with the exception of Cd and Pb at TAG. Metals with significant HNO₃-extractable concentrations follow the order [Cu]> [Co] $\approx$ [Zn]>[Pb]>[Cd], consistent with the preferential partitioning of these metals as trace constituents in pyrite (Morse and Luther, 1999).

A greater portion of Cu is removed from solution at Rainbow, with less than 2 % of Cu present in the < 0.2 μm fraction in the first meter except for vent fluid sample (RB-5) that had < 0.2 μm Cu as 74 % of the total Cu concentration. The composition of Rainbow vent fluid should be similar because it comes from a single source (Charlou et al., 2002); thus this difference may be due to variability in either precipitation in the chimney or sample heterogeneity. Rainbow also has the lowest percentage of Mn in the < 0.2 μm fraction (70 to 80 %) of the three vent sites. Although the neutrally buoyant plume at Rainbow is enriched in iron oxide particles (Edmonds and German, 2004), we find that within the first meter Fe is present as Fe(II) and remains > 94 % in the < 0.2 μm

fraction. HNO₃ extraction and analysis of these samples showed that a significant portion (up to 5.24 %) of < 0.2 µm Fe at Rainbow is present as pyrite nanoparticles and TEM data suggest formation of iron silicate nanoparticles (Gartman et al., 2014). Iron oxides are not present in the first 1.5 m of the rising plume, as we detected neither Fe(III) nor oxygen (Findlay et al., 2014) in the plume over the range sampled.

4 Discussion

4.1 Differences in particle formation between vent sites

Our dataset is unique in that it allows the investigation of possible particle formation processes and metal partitioning during the early stages of the rising plume, less than 1.5 meters from the vent orifice. Moreover, because similar samples were obtained for three different vent fields we are also able to make inter-site comparisons between the hydrothermal fluids, and processes occurring in the early stages of the plume < 1.5 meter from the vent orifice.

As demonstrated by Figures 5 and 6, the associations between metals are similar at both TAG and Snakepit, but differ at Rainbow, which suggests that different precipitates are forming in the plumes of each vent site. There are several possible reasons for this observed difference. First, the Rainbow vent fluid contains higher concentrations of chloride (750 mM) than TAG (650 mM) and Snakepit (550 mM) (Douville et al., 2002). Chloride increases the solubility of many metals, and so may keep greater quantities of these metals in solution. More importantly, the total metal:sulfide ratio at Rainbow is the highest of the three vent sites. This ratio affects the type and quantity of metal sulfide minerals that will reach saturation and precipitate. German et al. (2010) calculated that only 4 % of total Fe at Rainbow could precipitate as sulfide

minerals, and present evidence for very little Fe precipitation between end member fluid and the neutrally buoyant plume, despite iron oxide formation in the neutrally buoyant plume.

Rainbow also has a higher percentage of particulate Mn than TAG or Snakepit (Table 3). Because manganese oxides are not expected to form in this portion of the buoyant plume, the higher percentage of particulate Mn is likely due to the adsorption of Mn^{2+} onto other particles, or incorporation into silicates. The formation of manganese sulfides as observed in Breier et al. (2012) is unlikely due to the high metal: sulfide ratio at Rainbow.

Finally, although Rainbow has lower Si than the other sites, Si concentrations are higher than sulfide concentrations (Table 2), and thus are likely to be important for particle formation and trace metal distribution at Rainbow. Iron concentrations are over an order of magnitude higher than sulfide (Table 2). If sulfide precipitated quantitatively with iron in an 1:1 ratio (FeS), millimolar concentrations of Fe would remain in the buoyant plume, and could precipitate in, or adsorb to silicates. The formation of significant quantities of iron silicate or oxide (nano)particles with respect to iron sulfides would result in changes in trace metal distribution, as trace metal partitioning in oxides and silicates is very different from that in sulfides (Walther, 2005). Sulfide readily precipitates with the transition metals studied here (Fe, Cu, Co, Zn, Cd, Pb), whereas silicates form with metals such as Al, Mn, and Fe. The oxidative dissolution of metal sulfides releases elements such as Cu, Cd, and Pb, which are scavenged onto iron oxides in the neutrally buoyant plume (Metz and Trefry, 1993). Thus, the type of minerals (e.g.

monosulfides, pyrite, silicates) formed in the buoyant plume affects processes and metal distribution further in plume development.

The results in Table 3, and in Figures 5 and 6, highlight the importance of studying the early portions of the buoyant plume in understanding the dynamics of a particular vent field. In a study of particles from the neutrally buoyant plume approximately 200-300 meters above the vents at Rainbow, Edmonds and German (2004) found partitioning behavior for chalcophile elements (Fe, Cu, Zn) to be similar to that observed in other neutrally buoyant plumes emanating from basalt-hosted vent sites. Our data demonstrate, however, that nearer to the vent orifice and before the hydrothermal fluid is extensively diluted with seawater, there exist clear differences in the behavior of these metals between vent sites with respect to particle formation and trace metal association, which could have implications for the quantity and type of metal transported from the site.

Differences between vent sites are evident in (1) the changing association of trace metals with Fe among the three vent sites, (2) the correlations between Cu, Co, Zn, Pb, and Cd at TAG and Snakepit, but not at Rainbow, (3) the higher percentage of $< 0.2 \mu\text{m}$ Cu and Co at TAG and Zn, Cd, and Pb at Snakepit, and (4) the higher percentage of Mn that is particulate at Rainbow compared to the other two sites. These differences indicate an important role for early plume processes in controlling the distribution of these metals and suggest that other processes occur as the plume ages, resulting in the more homogeneous distribution pattern farther from the vent orifice as observed by Edmonds and German (2004).

4.2 Precipitation of metal sulfides in the buoyant plume

A shift occurs in plume composition from metal sulfides to metal oxides as the plume entrains additional seawater and becomes more oxidizing (Trocine and Trefry, 1988), further from the vent orifice. At this stage metal sulfides can begin to oxidize and dissolve, and particle reactive elements such as Cu, Mg, and Pb can be scavenged by iron oxides. No oxidized Fe was detected for either unfiltered or $< 0.2 \mu\text{m}$ fractions in any of our samples, indicating that within the initial meter of these buoyant plumes, metal speciation is mainly controlled by metal sulfides. Furthermore, oxygen was not detected $\geq 1.5 \text{ m}$ from the vent orifice in the buoyant plume (Findlay et al., 2014). An Fe catalytic cycle with sulfide and oxygen likely occurs, consuming O_2 and maintaining reduced Fe concentrations at this point in the plume (Findlay et al., 2014). In this cycle, O_2 oxidizes Fe(II) to form Fe(III). The Fe(III) then oxidizes sulfide to form elemental sulfur, reforming Fe(II) in the process.

A significant amount of chalcophile metals precipitate ($10^6 - 10^7 \text{ kg/year}$) with sulfide in the rising plume (James and Elderfield, 1996) and are preferentially removed in the following order: $\text{Cu} > \text{Co} > \text{Zn} > \text{Cd}$ (Douville et al., 2002), a finding similar to data reported here. Copper sulfides precipitate first, followed by zinc sulfides, then iron sulfides, and later iron oxides. Our data set, consistent with the thermodynamic modeling of Klevenz et al. (2011), demonstrates that at all three sites, initially both Fe and Mn are present in the $< 0.2 \mu\text{m}$ fraction, and Cu and Zn precipitate rapidly compared to Fe at low seawater mixing (Figure 2). Although it is possible that some of these particles form during sample recovery, the decreasing percentage of metals in particulates ($> 0.2 \mu\text{m}$) in

502 samples taken from the rising plume suggests that significant quantities of metal sulfide
503 particles are not forming in the Major Samplers.

504 Similar to previous studies (Hsu – Kim et al., 2008) we find that Zn typically
505 forms a discrete sulfide precipitate apart from pyrite, incorporating both Cd and Pb
506 (Figure 5d, e, f). Zn, Cd, and Pb correlate because the water exchange rates of these
507 metals (measured at 25 °C) are faster than those of Fe and thus will form independent of
508 iron sulfides (Morse and Luther, 1999; Yücel et al., 2011). In contrast, Co^{2+} has a slower
509 water exchange rate than Fe^{2+} , and is thus incorporated into pyrite or chalcopyrite, as
510 indicated in our data by the correlation between Co and Cu at both TAG and Snakepit
511 (Figure 5a-b). Cu concentrations in these samples are approximately an order of
512 magnitude lower than previous reports (Douville et al., 2002) and are consistently low in
513 all subsamples taken from the Major Samplers. It is likely that much of the Cu has
514 already been precipitated as chalcopyrite at high temperatures within the vent chimney
515 (Seyfried and Ding, 1995; Tivey, 1995). As a result of the initial cooling of hydrothermal
516 fluid from 400-300 °C, the solubility of chalcopyrite decreases several orders of
517 magnitude (Seyfried and Ding, 1995), resulting in rapid formation in the end-member
518 fluid within the chimney and removal of the majority of the Cu from solution prior to
519 formation of other metal sulfides (Rickard and Cowper, 1994). Chalcopyrite and other
520 copper sulfide minerals were detected via XRD in samples from the TAG fluids that were
521 taken within the chimney orifice (Gartman et al., 2014).

522 The precipitation of metal (mono)sulfides may provide a site for further
523 nucleation of pyrite (Yücel et al., 2011, Gartman et al., 2014) because the nucleation of
524 pyrite in acidic ($\text{pH} < 7$) waters below 300 °C is slow (Shoonen and Barnes, 1991; Wilkin

and Barnes, 1997). We calculated the maximum rate of pyrite formation in the high temperature fluid at TAG to be $7.7 \text{ nmol L}^{-1}\text{s}^{-1}$, decreasing to $6.80 \times 10^{-5} \text{ nmol L}^{-1}\text{s}^{-1}$ at 37.6°C (calculations based on kinetics from Rickard, (1997)). Thus, the nucleation of other metal sulfides may provide energetically favorable surfaces for continued precipitation of pyrite in the plume. Furthermore, silicates may also form around metal sulfide centers, as was observed in nanoparticles from Lau Basin vent fluid (Gartman et al., 2014).

Metals in the $< 0.2 \text{ }\mu\text{m}$ fraction are present as constituents of pyrite nanoparticles (HNO_3 -extractable fraction), as discrete metal sulfides and dissolved entities (HCl -extractable fraction), or as silicate nanoparticles. The portion of metals present in this fraction may be underestimated if any particle formation occurs in the Major Samplers. These species will each have different reactivity with respect to oxidation and particle growth. In particular, pyrite nanoparticles oxidize slowly (Gartman and Luther, 2014), so the presence of trace metals means that pyrite nanoparticles may serve not only as a source of Fe to the larger oceans (Yücel et al., 2011), but also as a source of other trace metals as demonstrated by the 2011 North Atlantic GEOTRACES cruises for total Fe (Hatta et al., 2015), particulate Fe (Ohnemus and Lam, 2015), soluble Fe(II) (Sedwick et al., 2015), and soluble Hg (Bowman et al., 2015) near the TAG vent field.

4.3 Effect of metal: sulfide ratio on particle formation

Other studies have observed similar patterns of metal distribution to those detailed here for end-member and buoyant plume samples. In particular, both Schmidt et al. (2007) and Klevenz et al. (2011) find correlations between Zn and Pb at Logatchev and 5°S at the MAR, and Trefry et al. (1994) also report strong associations between Zn and

Cd in vent fluid samples at the Juan de Fuca Ridge. Trocine and Trefry (1988) report similar findings in samples from the plume at TAG, and additionally found Cu to be present in a different phase than Zn. Moreover, high Co concentrations were observed in particles containing high Cu concentrations at Logatchev (Schmidt et al., 2007) and 5°S (Klevenz et al., 2011) along the MAR. Mottl and McConachy (1990) find Mn to be dissolved (> 99 %) in samples taken 4 – 20 m from the vent orifice at the East Pacific Rise, similar to our findings that Mn remains dissolved. The consistency between these results and our findings at Snakepit and TAG suggests that at vents with low metal:sulfide ratios, the reactivity of metals with respect to sulfide as described above (section 4.2) will dictate the major mineral formation processes in the initial stages of the buoyant plume. At vents with high metal:sulfide ratios, such as Rainbow, other particle formation processes, which are of secondary importance in high metal sulfide systems will be important, such as the formation of silicates or oxides.

5 Conclusions

An investigation of trace metal partitioning and size fractionation was conducted in the vent fluid and within the first 1.5 meters of three hydrothermal plumes along the MAR. At each vent site, Fe and Mn remain in the < 0.2 µm fraction (up to 100 %), whereas Cu, Co, Zn, Pb, and Cd are predominantly particulate (up to 99 %). Mn behavior contrasts with the chalcophile elements with increased seawater mixing; however up to 30 % of Mn is particulate at high seawater: vent fluid ratios at Rainbow, potentially due to incorporation of Mn into silicate particles, but for other metals the percentage of particulates decreases.

At TAG and Snakepit, Cu was correlated with Co as Co enters chalcopyrite, and Zn was correlated with Cd and Pb as they form discrete metal sulfide phases. At Rainbow, Zn correlates with Cd and Pb; but Cu and Co are not correlated. The differences in metal associations between the vent sites indicate that different precipitates are forming in the Rainbow plume than at TAG or Snakepit due to the unique chemical composition of the Rainbow vent fluid. These speciation differences have implications for the ultimate fate of metals emitted from the vents. The results at TAG and Snakepit are consistent with the generally accepted conceptual model for metal sulfide mineral precipitation in the plume (Trocine and Trefry, 1988; Seyfried and Ding, 1995; Metz and Trefry, 2000; Klevenz et al., 2011). As vent fluid rises and mixes with seawater, first Cu and Co precipitate in chalcopyrite, then Zn, Pb, and Cd precipitate in a discrete sulfide phase, followed by the formation of larger quantities of iron sulfides. Significant HNO_3 -extractable concentrations of all trace metals ($[\text{Cu}] > [\text{Co}] \approx [\text{Zn}] > [\text{Pb}] > [\text{Cd}]$) were measured in the $< 0.2 \mu\text{m}$ fraction at all three vent sites, indicating that they are likely incorporated into nanoparticulate pyrite and/or chalcopyrite, which is resistant to oxidation and may be transported from the vent site (Yücel et al., 2011; Gartman et al., 2014). At Rainbow, other processes, such as the formation of iron silicates, may play an important role in affecting the distribution of metals. Taken together with prior observations of vent fluid geochemistry, these results indicate that at low metal: sulfide ratios, sulfide controls particle formation and trace metal distribution, whereas at high metal: sulfide ratios, other processes dominate.

Our dataset is unique in that it focuses on the very early stages of the buoyant plume (within 1.5 m from the orifice). That these particle formation processes are

593 observed within the first meter of the plume highlights how rapidly particle nucleation
594 and growth occur in this dynamic environment, and thus the importance of this initial
595 mixing zone for controlling metal fluxes from the vents to the larger oceans.

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Figures

Figure 1: Map showing the location of the vent sites visited along the MAR. Map courtesy of <http://www.geomapapp.org>.

Figure 2: Correlation of unfiltered total and filtered (< 0.2 μm) metals with filtered Mg at (a) TAG, (b) Snakepit, and (c) Rainbow from samples extracted with HNO_3 . For reference, an estimate of temperature is given on the upper x-axis based on an approximation between seawater mixing and temperature. Note that for Cu, Zn, Pb, and Cd the scale for the filtered concentration is presented on the right y axis.

(a) TAG

(b) Snakepit

(c) Rainbow

Figure 3: Partitioning of Mn, Cu, and Zn in samples from the buoyant plume at Snakepit between HCl (soluble metal sulfides) and HNO₃ (metals in pyrite or chalcopyrite) extractable fractions. The pie charts indicate the percentage of the metal in the > 0.2 μm (particulate) and < 0.2 μm (nanoparticulate/dissolved) fractions as the vent fluid mixes with seawater. Mn is mainly in the < 0.2 μm fraction and is soluble in HCl. Cu is mostly particulate and has a significant component that is soluble only in HNO₃. The percentage of zinc that is particulate decreases with seawater mixing, and is soluble in HCl.

Figure 4: Concentrations of filtered (<0.2 μm) and unfiltered AVS/CRS and total elemental sulfur in the rising plume at (a) Snakepit and (b) TAG. Sulfur concentrations are from Findlay et al. (2014) and methods described therein.

Figure 5: Correlation between concentrations of Co and Cu, Zn and Cd, and Zn and Pb at (a, d) Snakepit (b, e) TAG and (c, f) Rainbow (r^2 Co=0.41). Copper and cobalt are not correlated at Rainbow. Metal concentrations are from unfiltered, HNO₃-treated samples.

Figure 6: Trace metals (unfiltered, HNO₃ leach) correlated to iron (unfiltered, HNO₃ leach) at (a, b) TAG (r^2 Mn=0.98, Cu=0.88, Zn=0.65, Pb=0.74) (c) Snakepit (r^2 Mn=0.88, Cu=0.87) and (d) Rainbow (r^2 Mn=0.78, Co=0.88).

Tables

Table 1: Sample information for all hot vent-fluid samples.

Vent Field	Sample	Shipboard pH	<i>in situ</i> T (°C)	Location
<i>Rainbow</i>	RB-1	5.34	353	Regner
	RB-2	2.87	367	Ennuyer
	RB-3	3.16	370	Jean Luc
	RB-4	3.28	367	Guillarme
	RB-5	4.65	368	Trident
<i>TAG</i>	TAG-1	3.01	365	Top of mound
	TAG-2	3.2	301	Top of mound
	TAG-3	3.03	313	Top of mound
	TAG-4	4.36	270	Diffuse flow
	TAG-5	4.8	356	Top of mound
	TAG-6	2.98	310	Top of mound
	TAG-7	4.15	190	Top of mound
	TAG-8	5.11	347	Top of mound
	TAG-9	4.56	303	Top of mound
	TAG-10	4.92	360	Top of mound
	TAG-11	3.38	347	Top of mound
<i>Snakepit</i>	SP-1	5.17	340	Beehive
	SP-2	4.42	358	Beehive
	SP-3	3.22	346	Beehive
	SP-4	3.45	351	Beehive
	SP-5	3.29	342	Beehive
	SP-6	3.19	336	Moose

Table 2: Calculated trace metal, silicon, and sulfide concentrations for end-member vent fluid (Mg=0). Concentrations obtained from the unfiltered nitric acid portion of samples obtained from the vent orifice were used for the calculation. Sulfide is from the sum of unfiltered AVS and unfiltered CRS. Values are only given for metals that correlated with Mg ($r^2 > 0.5$).

Element		Endmember concentration		
		Snakepit ^a	TAG ^b	Rainbow ^c
Fe	mM	3.5	5.4	24
Mn	μM	350	430	1350
Co	μM	n/a	1.9	15
Ni	μM	n/a	n/a	n/a
Cu	μM	n/a	12	n/a
Zn	μM	23	25	n/a
Cd	nM	160	120	n/a
Pb	nM	640	350	n/a
ΣH ₂ S	μM	4500	4300	660
Si	mM	8.5	7.2	3.1

^a End-member concentrations for Snakepit were determined for Beehive

^b End-member concentrations for TAG were determined using samples from the top of the mound.

^c End-member concentrations for Rainbow were determined using samples from all vents.

Table 3: Composition of the < 0.2 μm fraction for all samples. The percentage of < 0.2 μm metal concentration/unfiltered metal concentrations is presented for HNO₃-extractable Fe, Mn, Co, Cu, Zn, Cd, and Pb in vent fluid and in the first 1.5 meters of the rising plume at each vent site. The concentration of < 0.2 μm, nitric acid soluble metal (Δ-N) is presented for Co, Cu, Zn, Cd, and Pb in samples where there is a significant difference between HNO₃ (metals present in a pyritic structure) and HCl (soluble metal sulfides) leaches. Samples in bold are samples that also contained nanoparticulate pyrite (Gartman et al., 2014). Samples in italics are from the rising plume and are presented with mixing information. The plume samples at Snakepit are from the Moose vent. %Δ-N/total is the percentage of nitric acid-extractable metal/total < 0.2 μm metal concentration.

VENT	Sample	Fe	Mn	Co	Cu	Zn	Cd	Pb	% Δ -N /total
		% NP ^a	% NP ^a	% NP ^a	% NP ^a	% NP ^a	% NP ^a	% NP ^a	% Δ -N /total
		Δ -N (μ M)	Δ -N (μ M)	Δ -N (μ M)	Δ -N (μ M)	Δ -N (μ M)	Δ -N (nM)	Δ -N (nM)	% Δ -N /total
RAINBOW	RB-2	100	100	73	0.40	0.0393	0.71	0.90	1.6
	RB-4	95	100	30	0.66		1.5	2.0	3.6
	RB-5	96	84	10	74		45	69	82
	RB-1	91	71	93	5.1	1.01	9.0	11	16
<i>plume samples</i>									
<i>(% mixing with seawater)</i>									
	8.1	94	81	21	0.614	17.9	1.1	12.0	94.2
	17	100	80	24	1.9		6.8	0.133	16.1
	72	100	70	50	0.31		0.87	1.4	3.3
<i>plume samples</i>									
<i>(% mixing with seawater)</i>									
TAG	TAG-7	100	94	81	0.56		3.1	4.2	6.1
	TAG-1	100	100	72	0.56	0.0104	16	2.6	5.3
	TAG-6	97	89	23	0.75		3.7	5.6	7.6
	TAG-3	100	90	7	0.70	8.64x10 ⁻³	3.5	4.2	8.1
	TAG-2	87	100	94	1.1		5.2	5.1	10
	TAG-11	90	96	6	0.45		4.6	5.0	10
	TAG-15	71	62	3	0.56		3.5	3.9	9.5
	TAG-9	80	100	5	9.89x10 ⁻³	29.3	6.8	6.5	17
	TAG-5	72	100	6	8.46x10 ⁻³	18.0	7.9	9.5	16
	TAG-10	92	100	14	2.9		21	0.146	20.2
	TAG-4	95	100	25	2.8		7.8	7.7	23
	TAG-8	86	100	43	0.0438	42.7	27	0.427	45.2
<i>plume samples</i>									
<i>(% mixing with seawater)</i>									
	61	96	85	7	1.1	0.0182	43	26	23
	78	87	100	22	4.6	0.0413	55	16	35
	86	81	73	28	0.0122	33.1	31	41	45
<i>plume samples</i>									
<i>(% mixing with seawater)</i>									
SNAKEPIT	SP-5	100	96	13	3.1	0.013	26	3.6	0.180
	SP-4	100	100	100	4.2	9.57x10 ⁻³	19	2.8	0.146
	SP-3	100	90	7.5	6.4	0.008	15	7.1	7.5
	SP-1	76	95	1.0	0.186	93.5	23	40	8.86
	SP-2	66	100	17	5.4	0.017	25	6.2	57.0
<i>plume samples</i>									
<i>(% mixing with seawater)</i>									
	15	100	100	17	0.0206	38.5	4.7	4.1	4.3
	66	40	100	2.4	1.8		7.5	7.0	7.6
	77	81	87	43	16		39	23	24

^a Percentage of < 0.2 μ m metal concentration/total unfiltered metal for nitric acid extractable concentrations.[2]