Chemical Geology 412 (2015) 117–131

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

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

Alyssa J. Findlay [a,*], Amy Gartman [a,1], Timothy J. Shaw [b], George W. Luther III [a]

[a] School of Marine Science and Policy, College of Earth Ocean and Environment, University of Delaware 700 Pilottown Road, Lewes, DE 19958, United States
[b] Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street Columbia, SC 29208, United States

ARTICLE INFO

Article history:
Received 27 March 2015
Received in revised form 14 July 2015
Accepted 15 July 2015
Available online 20 July 2015

Keywords:
Trace metals
Metal sulfide
Nanoparticles
Hydrothermal vent
Mid-Atlantic Ridge

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 m of the rising plume at three vent fields (TAG, Snakepit, and Rainbow) along the Mid-Atlantic Ridge. A HCl/HNO_3 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 HNO_3-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.

1. Introduction

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

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

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

Abbreviations: MAR, Mid-Atlantic Ridge; TAG, Trans-Atlantic Geotraverse; ROV, Remotely Operated Vehicle; AVS, Acid Volatile Sulfide; CRS, Chromium Reducible Sulfide.

* Corresponding author.
E-mail address: afindlay@udel.edu (A.J. Findlay).
[1] Present address: United States Geological Survey, 400 Natural Bridges Drive, Santa Cruz, CA 95060, United States.

http://dx.doi.org/10.1016/j.chemgeo.2015.07.021
0009-2541/

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 m 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 et al., 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 μm 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 μm iron at the Rainbow, TAG, and Snakepit vent sites (up to 5% of <0.2 μm iron). In the study presented here, we present measurements of trace metal and sulfide concentration and speciation in unfiltered and <0.2 μm filtered samples taken from the vent fluid and within the first 1.5 m 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 μm HCl-extractable metals (consisting of dissolved metals, metal chloride complexes, and soluble metal sulfides); and unfiltered and <0.2 μm 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 (Fig. 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 m 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,

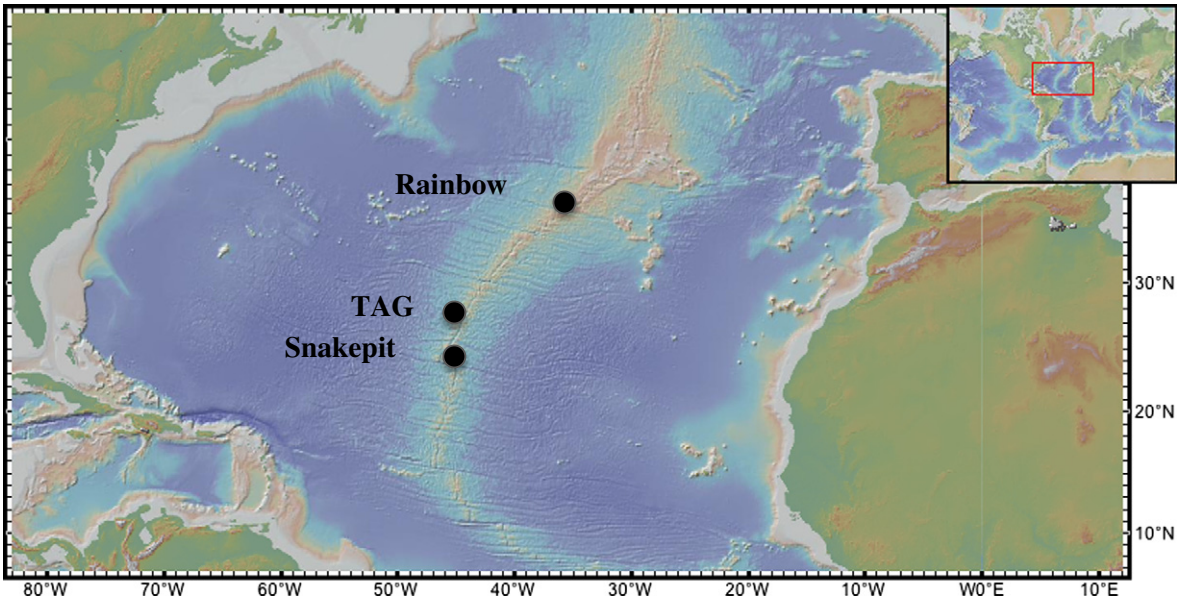

Fig. 1. Map showing the location of the vent sites visited along the MAR.
Map courtesy of http://www.geomapapp.org.