Earth and Planetary Science Letters 375 (2013) 280–290

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

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

The stabilisation and transportation of dissolved iron from high temperature hydrothermal vent systems

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ARTICLE INFO

Article history:
Received 28 November 2012
Received in revised form
8 May 2013
Accepted 28 May 2013
Editor: G. Henderson
Available online 4 July 2013

Keywords:
iron
ligand
colloid
hydrothermal plume
CLE–ACSV
speciation

ABSTRACT

Iron (Fe) binding phases in two hydrothermal plumes in the Southern Ocean were studied using a novel voltammetric technique. This approach, reverse titration–competitive ligand exchange–adsorptive cathodic stripping voltammetry, showed that on average 30 ± 21% of dissolved Fe in the hydrothermal plumes was stabilised by chemically labile binding to ligands. The conditional stability constant ($\log K'_{FeL}$) of the observed complexes was 20.61 ± 0.54 (mean ± 1 SD) for the two vent sites, intermediate between previous measurements of deep ocean ligands (21.4–23; Kondo et al., 2012) and dissolved weak estuarine ligands (< 20; Gerringa et al., 2007).

Our results indicate that approximately 7.5% of all hydrothermal Fe was stabilised by complexation with ligands. Furthermore, 47 ± 26% of the dissolved Fe in the plume existed in the colloidal size range (0.02–0.2 μm). Our data suggests that a portion (~7.5%) of hydrothermal Fe is sufficiently stabilised in the dissolved size fraction (< 0.2 μm) to make an important impact on deep ocean Fe distributions. Lateral deep ocean currents transport this hydrothermal Fe as lenses of enhanced Fe concentrations away from mid ocean ridge spreading centres and back arc basins.

1. Introduction

Iron (Fe) is an important and often limiting micronutrient in the world's oceans (Martin and Fitzwater, 1988). Dissolved Fe (DFe) concentrations in the surface ocean are typically < 0.3 nM, and range between ~0.2 and 1.2 nM in the deep ocean (> 1000 m) where Fe is buffered by strong organic ligands (De Baar and De Jong, 2001; Hunter and Boyd, 2007). The study of the sources, sinks and speciation of Fe is crucial to our understanding of the transport and bioavailability of this element. The supply of Fe to the world's oceans is poorly constrained, with atmospheric dust, rivers, sediments and remineralisation of sinking particles forming the main sources (De Baar and De Jong, 2001). Hydrothermal sources of stable DFe have recently been considered due to several observations of high DFe concentrations in the deep ocean close to tectonic spreading centres, often in regions containing elevated (hydrothermally sourced) ^{3}He (Klunder et al., 2011; Kondo et al., 2012; Nishioka et al., 2013; Wu et al., 2011).

Iron is highly enriched in high temperature hydrothermal fluids as it is leached from host rocks during hydrothermal circulation of seawater. End-member concentrations can range from < 2 μM (e.g. Menez Gwen, Mid Atlantic Ridge, Douville et al., 2002) to > 10 mM Fe (e.g. Edmond vent site, Central Indian Ridge, Gallant and Von Damm, 2006). The total (dissolved and particulate) contribution of Fe to the deep ocean by high temperature hydrothermal vents is estimated to be 7.2–450 Gmol Fe yr^{-1} (Baker et al., 1993; Bennett et al., 2008; Elderfield and Schultz, 1996; Tagliabue et al., 2010), while the total DFe inventory of the ocean is estimated to be 800–1600 Gmol (De Baar and De Jong, 2001). The impact of hydrothermal vents on global DFe distributions is still poorly understood due to the high spatial (German and Von Damm, 2004) and temporal (e.g. Butterfield and Massoth, 1994; Campbell et al., 1988) variability in hydrothermal fluid emissions, and the complexity of Fe speciation and removal in seawater.

A large portion of hydrothermal Fe is deposited close to vent sources as sulphide mineral phases (Mottl and McConachy, 1990) and the remaining Fe(II) is rapidly oxidised and forms oxyhydroxide particles (Feely et al., 1987; German et al., 1990; Field and Sherrell, 2000). However, Fe is often observed to oxidise or precipitate more slowly in hydrothermal plumes than predicted by laboratory kinetic studies, and this has been attributed to interaction of Fe(II) with organic matter and sulphides (Statham et al., 2005; Toner et al., 2009; Wang et al., 2012) and also stabilisation of Fe(III) in the dissolved phase by complexation with organic ligands

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0012-821X
http://dx.doi.org/10.1016/j.epsl.2013.05.047

(Bennett et al., 2008). Fine Fe containing particles (or "colloids") are also considered to contribute to the observed enhanced dissolved (usually <0.2 or <0.45 μm) Fe concentrations (Field and Sherrell, 2000), and both oxy-hydroxide (Fe(III)) colloids and pyrite nano-particles (Fe(II)) have been detected in hydrothermal vent systems (Sands et al., 2012; Yucel et al., 2011).

The only study that has considered DFe complexation in hydrothermal plumes was restricted to analysis of samples from the edges of the distal plume. It was suggested that a small percentage (~4%, 0.3 Gmol yr^{-1} globally) of hydrothermal Fe was transported to the deep ocean as DFe (Bennett et al., 2008). Here, we used a new voltammetric speciation technique to enable investigation of Fe speciation in the core of two hydrothermal plumes, where Fe is potentially saturating organic complexes. We also considered the differences between 'dissolved' Fe (<0.2 μm), "soluble" Fe (<0.02 μm) and "chemically labile" Fe (the Fe fraction that is complexed with an added electro-active ligand)—thus combining the study of physical and chemical speciation of Fe for the first time in hydrothermal plume systems.

The two vent sites (E2 and E9N; Rogers et al., 2012) are situated on the East Scotia Ridge (ESR) in the Southern Ocean and were sampled in 2010 for DFe ligand complexes. E9N was re-visited in 2011 to collect samples to determine the colloidal Fe (DFe minus soluble Fe) distributions. Sampling was conducted over a range of seawater to vent fluid mixing ratios (~200–160,000). However, due to the rapid dilution of vent fluid in hydrothermal buoyant plumes, the sample matrix (major ions, pH, temperature, etc.) was only ever slightly different from ambient seawater. Our aim was to investigate whether Fe in hydrothermal plumes is complexed by "ligand" phases that are co-diluted with Fe from the vent or by ambient ligands already present in the local deep seawater. We discuss the implications of our results for the transport of hydrothermal Fe to the deep ocean.

2. Materials and methods

2.1. Study areas

The East Scotia Ridge (ESR) is a back-arc basin spreading centre between the Scotia Plate and the South Sandwich Plate in the Atlantic sector of the Southern Ocean. Spreading at the ESR was initiated over 15 Ma ago and is currently proceeding at an intermediate rate of ~65–70 mm yr^{-1} (Bruguier and Livermore, 2001). It consists of 10 segments, E1–E10, of which two, E2 and E9, host hydrothermal activity (Rogers et al., 2012). The local deep ocean water was Weddell Sea Deep Water (WSDW), as defined by a potential temperature of −0.7 to 0.2 °C (Naveira-Garabato et al., 2002), see Supplementary information. At E2, the WSDW is partially mixed with Lower Circumpolar Deep Water (LCDW) which has a characteristic potential temperature of 0.2–0.7 °C.

The E2 site (located at 56.089°S, 30.317°W) is bathymetrically rough with large vertical displacements running north to south (Fig. 1). The E9 site (located at 60.043°S, 29.982°W) is comparatively flat and represents a local topographic elevation, a result of magmatic inflation in the centre of the ridge (Bruguier and Livermore, 2001). The principle geochemical features of the two sites are outlined in Table 1. Our samples were taken from hydrothermal plumes of the "Dog's Head" chimney at E2 and the "Black and White" chimney of the northern section of the E9 site (E9N) (Fig. 1).

The Fe concentrations in the end-member fluids were intermediate in a global context (see Supplementary information), and the concentration of hydrogen sulphide was high (6.7–9.5 mM, cf. Mid Atlantic Ridge range: 0.6–6.0 mM; Douville et al., 2002). This is likely due to the influence of the fluid rich subduction plate on the mantle at back arc basin sites (de Ronde et al., 2001; Baker et al., 2008), and probably leads to the early precipitation (as sulphides) of a higher portion of DFe (Baker and Massoth, 1987). Overall, the sites offer a typical environment in which to conduct a study into hydrothermal Fe seawater reactions.

2.2. Hydrothermal plume detection and sampling

Samples were collected and filtered at sea during two cruises on the RRS *James Cook* in the Southern Ocean, along the East Scotia Ridge (ESR) in 2010 (E2 and E9N; cruise JC042) and 2011 (E9N only; cruise JC055). The hydrothermal plume was detected and sampled using a Seabird +911 conductivity, temperature and the depth (CTD) profiler system that was mounted on a titanium frame with 24 trace metal clean 10 l OTE (Ocean Test Equipment) water sampling bottles. The frame was also equipped with a light scattering sensor (LSS) and a bespoke Eh detector (Ko-ichi Nakamura).

The buoyant part of the hydrothermal plume was identified by positive temperature and particle anomalies and a negative Eh anomaly, while the neutrally buoyant plume was identified by a positive particle anomaly and negative temperature and Eh

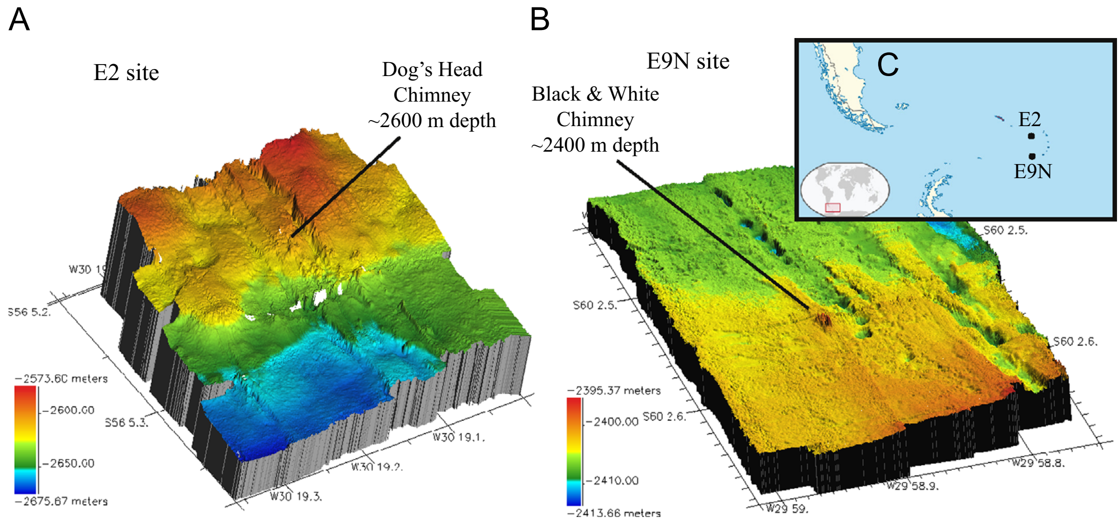

Fig. 1. A and B: Bathymetry of the E2 site surrounding the "Dog's Head" chimney and E9N site surrounding "Black and White" chimney, from which the sampled plumes emanate. C: Location of the E2 and E9N sites in Southern Atlantic Ocean. Scale bars = 30 m.