Rare earth elements as indicators of hydrothermal processes within the East Scotia subduction zone system

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Abstract

The East Scotia subduction zone, located in the Atlantic sector of the Southern Ocean, hosts a number of hydrothermal sites in both back-arc and island-arc settings. High temperature (> 348 °C) ‘black smoker’ vents have been sampled at three locations along segments E2 and E9 of the East Scotia back-arc spreading ridge, as well as ‘white smoker’ (< 212 °C) and diffuse (< 28 °C) hydrothermal fluids from within the caldera of the Kemp submarine volcano. The composition of the endmember fluids (Mg = 0 mmol/kg) is markedly different, with pH ranging from <1 to 3.4, [Cl⁻] from ~90 to 536 mM, [H₂S] from 6.7 to ~200 mM and [F⁻] from 35 to ~1000 μM. All of the vent sites are basalt- to basaltic andesite-hosted, providing an ideal opportunity for investigating the geochemical controls on rare earth element (REE) behaviour. Endmember hydrothermal fluids from E2 and E9 have total REE concentrations ranging from 7.3 – 123 nmol/kg, and chondrite-normalised distribution patterns are either light REE-enriched (LaCN/YbCN = 12.8 – 30.0) with a positive europium anomaly (EuCN/Eu*CN = 3.45 – 59.5), or mid REE-enriched (LaCN/NdCN = 0.61) with a negative Eu anomaly (EuCN/Eu*CN = 0.59). By contrast, fluids from the Kemp Caldera have almost flat REE patterns (LaCN/YbCN = 2.1 – 2.2; EuCN/Eu*CN = 1.2 – 2.2).

We demonstrate that the REE geochemistry of fluids from the East Scotia back-arc spreading ridge is variably influenced by ion exchange with host minerals, phase separation, competitive complexation with ligands, and anhydrite deposition, whereas fluids from the Kemp submarine volcano are also affected by the injection of magmatic volatiles which enhances the solubility of all the REEs. We also show that the REE patterns of anhydrite deposits from Kemp differ from those of the present-day fluids, potentially providing critical information about the nature of hydrothermal activity in the past, where access to hydrothermal fluids is precluded.
1. INTRODUCTION

The chemical properties of the rare earth elements (REEs) are fundamentally similar, and differences in their behaviour in natural materials and fluids can usually be attributed to atomic radii controls on their speciation and mobility (Elderfield et al., 1988). In hydrothermal environments, the distribution of the REEs provides important information about fluid evolution during subsurface circulation (Elderfield et al., 1988; Haas et al., 1995), sources of fluid constituents and the extent of seawater mixing (Van Dover, 2000; Embley et al., 2007; Craddock et al., 2010), conditions of mineral deposition and venting history (Craddock and Bach, 2010) and the transport and fate of plume particulate material (German et al., 1990; Bau and Dulski, 1999; Sherrell et al., 1999).

Most hydrothermal fluids have remarkably uniform chondrite-normalised REE (REE$_{CN}$) distribution patterns, with enrichment in the light-REEs relative to the heavy-REEs and a positive europium anomaly (Michard and Albarède, 1986). This pattern has been observed in fluids from basalt-hosted hydrothermal systems on the Mid-Atlantic Ridge (MAR) (Mitra et al., 1994; James et al., 1995) and the East Pacific Rise (EPR) (Michard et al., 1983; Michard and Albarède, 1986), but also in fluids venting through basaltic andesite and andesite substrates in the Lau Basin (Douville et al., 1999), heavily-sedimented ridges such as the Guaymas Basin and Escanaba Trough (Klinkhammer et al., 1994), and ultramafic-hosted vent systems including Rainbow (Douville et al., 2002). This REE$_{CN}$ pattern has been attributed to exchange of REEs during plagioclase recrystallisation (Campbell et al., 1988; Klinkhammer et al., 1994), but more recent studies suggest that the REEs in hydrothermal fluids are largely derived from alteration minerals (Bach and Irber, 1998; Allen and Seyfried, 2005; Shibata et al., 2006), with their relative distributions determined by the type and concentration of REE ligands (Bau, 1991; Douville et al., 1999; Bach et al., 2003; Allen and Seyfried, 2005; Craddock et al., 2010).
It is now clear however that, under some circumstances, REE distribution patterns in hydrothermal fluids can differ from that described above. At 5 °S on the MAR, fluids venting close to the critical point of seawater have extremely high REE concentrations, are enriched in the mid-REEs, and have a negative Eu anomaly (Schmidt et al., 2010). A recent study of hydrothermal fluids from the Manus back-arc basin has also revealed a wide range of REE\(_{\text{CN}}\) distribution patterns, from fluids that are enriched in the heavy REE elements, to fluids with relatively flat REE\(_{\text{CN}}\) patterns (Craddock et al., 2010). These different distribution patterns are attributed to differences in REE solubility due to variations in the relative abundance and stability of REE-chloride, fluoride and sulphate complexes as a function of fluid temperature, pH and ligand concentration. To this end, these authors suggest that the REEs can be used as tracers for input of fluoride- and sulphur-rich magmatic volatiles in seafloor hydrothermal fluids.

To test whether variable REE\(_{\text{CN}}\) patterns are characteristic of arc and back-arc environments, we have determined REE concentrations in hydrothermal fluids and chimney sulphates recovered from newly-discovered vent sites in the East Scotia subduction zone system (Rogers et al., 2012). Two sites (E2 and E9) are located on the East Scotia Ridge (ESR) back-arc spreading ridge; the other is a recently erupted submarine volcano (Kemp Caldera) that forms part of the South Sandwich Island volcanic arc. The chemical composition and temperature of the hydrothermal fluids differs significantly between the sites (German et al., 2000; Rogers et al., 2012; James et al., in review), allowing us to examine the controls on REE abundances and REE\(_{\text{CN}}\) distribution patterns. We show that the REEs can provide key information as to subsurface hydrothermal processes in back-arc and island-arc systems such as fluid-rock interaction, phase separation, secondary-mineral dissolution, and magmatic gas injection. Further, we show that deposits of anhydrite can preserve past fluid compositions and consequently record changes in hydrothermal and magmatic regimes.
2. GEOLOGIC SETTING AND VENT CHEMISTRY

2.1 East Scotia Ridge

The East Scotia Ridge (ESR) is an isolated inter-oceanic back-arc spreading centre associated with subduction of the South American plate beneath the overriding Sandwich plate in the East Scotia Sea, Southern Ocean (Figure 1) (Barker, 1970; German et al., 2000). Spreading was initiated between the Scotia and Sandwich plates > 15 Ma ago (Larter et al., 2003), and current spreading rates vary between 60-70 mm y\(^{-1}\) along the ridge (Thomas et al., 2003). Despite its intermediate spreading rate, the ESR has an axial morphology more typical of a slow spreading ridge (Leat et al., 2000). Deep median valleys, associated with most of the ridge segments, are attributed to reduced mantle temperature and melt production by subduction-related conduction and convection (Livermore et al., 1994; 1997).

The ESR consists of nine ridge segments (E1-E9), separated by non-transform faults (Livermore et al., 1994). Segments E2 and E9 are distinct in that they possess magmatically inflated axial high, more characteristic of fast-spreading ridges (Leat et al., 2000; Bruguier and Livermore, 2001). Locally enhanced melting and magma production is evident from the seismically imaged melt lens beneath E2 and that postulated to exist beneath E9 (Leat et al., 2000). Eastward tearing of the South American plate, as suggested from intense seismic activity at 50-130 km depth beneath the northern ESR (Brett, 1977), may facilitate mantle flow from the South Atlantic around the edges of the subducting slab, feeding these axial magma chambers. Mantle flow by displacement may also be important as a result of the rapid eastward rollback of the South Sandwich Trench (Pelayo and Wiens, 1989; Bruguier and Livermore, 2001). The enriched volatile flux derived from dehydration of the sinking plate may also be responsible for the observed melt anomalies (Livermore et al., 1997).
The dominant crustal lithology of the ESR is basalt to basaltic andesite, with limited subduction influence (Leat et al., 2000, 2004; Fretzdorff et al., 2002). Radiogenic isotope analysis of basalts from the summit of E2 compared with the segment ends indicates the presence of an enriched mantle source beneath the axial volcanic ridge (AVR), characteristic of a mantle plume (Leat et al., 2000). Whilst seismic profiles have revealed a highly focused, shallow melt body beneath the AVR of E2, no melt reservoir has been imaged beneath E9 (Bruguier and Livermore, 2001). However, a large axial summit caldera, the ‘Devil’s Punchbowl’, is thought to represent collapse associated with magma withdrawal, suggesting that a magma chamber has existed beneath this ridge segment in the past (Bruguier and Livermore, 2001).

Hydrothermal plumes were first detected above segments E2 and E9 of the ESR in 1998 from geochemical surveys of the water column (German et al., 2000). In 2009, active, high-temperature ‘black smoker’ vents were observed for the first time using a deep-towed camera system, and these were subsequently sampled by the remotely operated vehicle (ROV) ISIS during RRS James Cook cruise 42 in early 2010 (Rogers et al., 2012).

The E2 hydrothermal site is located just south of the AVR, between 56˚5.2′ and 56˚5.4′ S and between 30˚19.0′ and 30˚19.35′ W at ~2600 m water depth. ‘Dog’s Head’ consists of a series of four chimneys, up to ~10 m high, that actively vent black smoker fluids at temperatures of up to 351 °C. The ‘Sepia’ vent site lies 75 m to the south east of Dog’s Head, and chimneys up to ~10 m high vent fluids at temperatures of up to 353 °C. The chloride concentration ([Cl⁻]) of the endmember fluids (532 – 536 mM) is close to local bottom seawater (540 mM) and the lowest recorded fluid pH is 3.02 (James et al., in review). Sulphate behaves conservatively during seawater mixing and extrapolates to a near-zero concentration in endmember fluids (0.97 - 1.31 mM). Concentrations of H₂S and fluoride in the endmember fluids (respectively, 6.7 – 7.1 mM and ~39 μM) are typical of basalt-hosted
mid-ocean ridge systems (Von Damm, 1990; Kelley et al., 2002), suggesting that input of magmatic volatiles is negligible (James et al., in review).

There are two sites of high temperature hydrothermal activity at E9, located between 60° 02.5’ and 60° 03.0’ S and between 29° 59.0’ and 29° 58.6’ W at ~2400 m water depth. At the northern site, fluids issue from the ~10 m high ‘Black & White’ chimney at temperatures of up to 383 °C. At the southern site, high temperature fluids (348 – 351 °C) are expelled from three chimney structures. ‘Ivory Towers’ is located to the north of the site, and emits high temperature fluids through a number of exits, including clusters of ‘beehive’ diffusers. Approximately 50 m to the south of Ivory Towers two further structures, ‘Pagoda’ and ‘Launch Pad’, occur in close proximity. In contrast to E2, the chloride concentration of the E9 fluids is distinctly lower than local bottom seawater, ranging from 98.2 mM at Black & White, to 179 mM at Launch Pad and 220 mM at Ivory Towers and Pagoda. This is attributed to phase separation of the fluids (James et al., in review); note that the temperature of the Black & White fluids lies on the two-phase boundary for seawater at this depth (Bischoff and Rosenbauer, 1984). As a consequence, concentrations of H₂S in the endmember fluids are higher (9.5 – 14 mM) than they are in the higher-Cl fluids from E2. The pH (3.08 – 3.42) and fluoride (34.6 – 54.4 μM) concentrations of the endmember fluids are similar to E2, again indicating that input of magmatic volatiles is negligible (James et al., in review). Sulphate concentrations of endmember fluids from the southern sites (Launch Pad, Ivory Tower and Pagoda) are close to zero (0.25 ± 0.71 mM), but considerably higher at Black & White (3.57 mM). This suggests that Black & White fluids are affected by input of anhydrite, either because of entrainment of chimney material during sampling, or dissolution of material precipitated at lower temperatures in the subsurface and subsequent incorporation into the venting fluids (James et al., in review).
2.2 South Sandwich Island Arc

The South Sandwich Island Arc is an intra-oceanic, volcanic arc associated with the subduction of the southernmost South American plate beneath the Sandwich plate (Larter et al., 2003). Basement crust here is young (8 – 10 Ma), generated by back-arc spreading at the ESR and has a thickness of 16 - 20 km (Leat et al., 2004). The arc consists of seven main islands (up to 3 km from seafloor to summit) and several smaller islands and seamounts varying in composition from basaltic to rhyolitic (Leat et al., 2004). Kemp Seamount is a volcanically active, submerged component of the southern part of the arc, located ~50 km west-south-west of Thule Island and ~70 km north of the southern subducting edge. The dominant crustal lithology of Kemp is tholeiitic basalt and basaltic andesite, but high concentrations of Nd, and high $^{87}\text{Sr}/^{86}\text{Sr}$, Nd/Hf and Ba/Th ratios indicate a strong subduction component, although there is minimal sediment-melt influence (Leat et al., 2004).

Hydrothermal activity was discovered within a submarine volcanic crater to the west of Kemp Seamount (59° 42’S and 28° 18.59’W), at a water depth of ~ 1420m, in 2009. White smoker-type fluids issue from friable chimney structures at temperatures of up to 212 °C to the west of the centre of the caldera, at a site named ‘Winter Palace’. Low temperature (< 28 °C) diffuse fluids issue through a seafloor fissure at another site, called Great Wall, ~ 100 m to the northwest of Winter Palace. Sulphur-rich minerals precipitate from the fluids, forming a ~50 cm high ‘wall’ along the fissure. The floor of the caldera is currently covered with sulphur and ash deposits, suggesting that there has been a recent volcanic blow-out event (de Ronde et al., 2011; Leybourne et al., 2012).

Although no vent fluids with very low [Mg] were collected from Kemp (Section 4.1), the chloride concentration of endmember fluids is likely to be low (90 ± 37 mM). The endmember fluids also appear to have very high levels of H$_2$S (200 ± 15 mM) and fluoride (1000 ± 110 μM), and low pH (1 ± 1). This strongly suggests that the fluids are phase
separated, and they are affected by input of magmatic volatiles (Powell et al., 2011). The fluids also appear to have been affected by deposition of anhydrite in the subsurface, as sulphate concentrations extrapolate to negative values (-8 ± 3 mM) at zero [Mg].

3. METHODS

3.1 Sample Collection and Preparation

3.1.1 Focused and diffuse fluids

Focused and diffuse vent fluids were collected by ROV ISIS from E2, E9 and Kemp Caldera in 2010 during RRS James Cook cruise JC42. Titanium syringe samplers, equipped with an inductively coupled link (ICL) temperature sensor at the nozzle tip, were inserted into the chimney orifice to collect focused vent fluids. Diffuse fluids were collected using a specially-constructed diffuse sampler, consisting of a pseudo venture tube, constructed in titanium, fitted with a heat-resistant weighted ‘skirt’ at its base to form a seal with the seafloor. The diffuse sampler was placed over the target area, and fluids were sampled by insertion of a Ti syringe into the top of the tube. Entrainment of ambient seawater was minimised by delaying syringe activation until a constant temperature reading was observed. Back onboard, the fluids were transferred to acid-cleaned 1L HDPE bottles, and any solid material (‘dregs’) that had presumably precipitated as the sample cooled was rinsed from the Ti samplers into a 30ml acid-cleaned HDPE bottle. All samples were acidified to pH 2 using thermally distilled (TD) HNO₃.

Onshore, fluid samples were filtered through a polycarbonate membrane filter (0.2 μm; Whatman) to separate any particles that had precipitated during storage. The filtrate was diluted with 2% HNO₃ for analysis of major elements. Particulate material retained on the filters was dissolved in 50% TD HNO₃ at 60 °C for several days, and then transferred to a
microwave digestion vessel and microwaved at 400W for 3 minutes. This step was repeated as necessary until the filter had completely dissolved. The digested sample was then transferred to a 15 mL Savillex vial with Milli-Q water, and evaporated to dryness. Finally, the sample was dissolved in 10 mL of 1.6M HNO₃ and its mass was determined. The ‘dregs’ were filtered, dissolved, dried-down and re-dissolved in the same way. The concentration of the REEs was determined in each fraction (Section 3.2), and the overall composition of the vent fluids was reconstructed (Table 1).

3.1.2 Chimney samples

Samples of the uppermost section of the vent chimneys from Dog’s Head (E2), Black & White, Ivory Towers and Launch Pad (E9) and Winter Palace (Kemp Caldera) were taken using the ROV manipulator arm and transferred to the ROV basket. Back on board the ship, the samples were photographed and their dimensions noted. Onshore, individual grains of anhydrite were handpicked from cut cross sections through the chimney wall using a binocular microscope. Mineral identification was confirmed by X-ray diffraction (Philips X’Pert pro XRD) at the National Oceanography Centre, Southampton.

3.2 Analytical Methods

3.2.1. REE concentration of fluids

Rare earth element concentrations in filtered fluid samples were determined by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500) at GEOMAR, Kiel, using a SeaFast system for online matrix-removal and pre-concentration of the REEs following the method of Hathorne et al., (2012). Based on replicate analyses (n = 8) of a well-characterised seawater sample from 2000 m depth in the Southern Ocean (Circumpolar Deep Water (CDW) sample ts PS71 131-1; (Hathorne et al., 2012; Stichel et al., 2012)), the external reproducibility of this method at the 95% confidence level (2σ) is < 10% for La – Pr,
Eu, Dy – Lu; 11 – 17% for Nd, Sm, Yb, Tb and < 22% for Gd. The accuracy of this technique has been demonstrated in an inter-laboratory comparison exercise (van de Flierdt et al., 2012).

The REE content of the particulate and dregs fractions was determined by ICP-MS (Thermo Fisher Scientific ELEMENT) at the National Oceanography Centre in Southampton. Single-element standards of Ba, Ce, Pr and Sm (Inorganic Ventures) were analysed alongside the samples to enable interference corrections to be made on Eu and the heavy REEs. Samples were calibrated against a set of five rock standards; BIR-1 and BHVO-2 (US Geological Survey), and JB-3, JA-2, JGb-1 (Geological Survey of Japan). Instrument drift was assessed by addition of internal standards (In and Re). Based on duplicate analyses of the rock standards, the external reproducibility (2σ) of this technique is < 5% for La – Sm and Dy - Lu; < 8% for Eu and Tb and < 16% for Gd.

3.2.2 REE concentration of anhydrite

A minimum of 10 mg of anhydrite was dissolved in ~5 ml of Milli-Q water and a drop of 50% TD HNO₃ by heating on a hotplate at 60 °C for several days. Once dissolved, the anhydrite sample was transferred into a 20 ml acid-cleaned LDPE bottle. A volume of fluid equivalent to 6 mg of anhydrite was sub-sampled, dried down and re-dissolved in 4 ml of 3% TD HNO₃ spiked with 10 ppb In, Re, and 20 ppb Be as internal standards. Concentrations of the REEs, Y, and major cations (Ba, Ca, Sr) were determined by ICP-MS (Thermo Scientific X-Series) at the National Oceanography Centre, Southampton, calibrated against five rock standards; BIR-1 and BHVO-2 (US Geological Survey), and JB-3, JA-2, JGb-1 (Geological Survey of Japan), as well as matrix-matched synthetic standards. The external reproducibility (2σ) of these analyses was < 4% for all of the REEs, based on duplicate analyses of the rock standards. The concentration of REEs in anhydrite was
calculated by normalising to the mass of anhydrite, determined by the measured calcium concentration. Anhydrite is assumed to be the only source of REEs in each sample.

3.2.3 Sr isotope composition of fluids and anhydrite

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of both the vent fluids and anhydrite were determined by thermal ionisation mass spectrometry (TIMS; VG Sector 54) at the National Oceanography Centre, Southampton. Sr was separated from a sub-sample of fluid or dissolved anhydrite containing $\sim1$ µg of Sr by cation-exchange chromatography using Sr-spec resin (Eichrom). Matrix elements were eluted with 3M TD HNO$_3$, and the Sr fraction was collected in Milli-Q water, then dried down, re-dissolved in 1.5 µl of 1M TD HCl, and loaded with a Ta activator solution onto single Ta filaments. Analyses of the NIST987 Sr isotope standard, measured over the course of this work, give $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of $0.710245 \pm 0.000020$ (2σ, n = 3), within error of the certified value ($0.710250$; National Institute of Standards and Technology).

4. RESULTS

4.1 REE Composition of Hydrothermal Fluids

Results of REE analyses of the fluids with lowest Mg recovered from each vent site are reported in Table 1. Of the samples collected from E2 and E9, all but 2 contain <5 mmol/kg Mg and thus consist of <10% bottom seawater. The zero-Mg endmember concentrations for these vents are calculated, as is the usual practise, by extrapolating from the composition of bottom seawater through the Mg concentration measured in samples from a given vent, to zero-Mg. Endmember concentrations are given in Table 1.

Fluids recovered from Kemp Caldera have much higher levels of Mg (> 43 mM). This is almost certainly due to mixing with seawater during the sampling procedure. To this end, the temperature of the vent fluids measured using the ICL probe (~212 °C) was significantly higher than that recorded when the fluid was sampled (< 28 °C), as a result of
break-up of the friable chimney. Thus, although endmember fluids with Mg > 0 have been
reported for some back-arc basin vents (e.g. Douville et al., 1999; Craddock et al., 2010), this
scenario is unlikely to apply here. Because the REEs do not behave conservatively during
mixing with seawater, due to coprecipitation with iron and manganese (oxy)hydroxides and
anhydrite (German et al., 1990; Bau and Dulski, 1999; Sherrell et al., 1999), it is not possible
to accurately estimate the REE composition of the vent fluid endmember. For this reason, all
subsequent discussion of the Kemp Caldera fluids will focus on $\text{REE}_\text{CN}$ distribution patterns
rather than absolute concentrations.

The total REE concentration ($\sum$REE) of ESR endmember fluids varies from 30 - 40
nmol/kg at E2, to 123 nmol/kg at E9 North, and 7.3 - 8.2 nmol/kg at E9 South. This
compares to a $\sum$REE value of 0.1 nmol/kg for Circumpolar Deep Water (Hathorne et al.,
2012).

REE distribution patterns, normalised to chondrite using values given in Taylor and
McClenan (Taylor and McClenan, 1985), are presented in Figure 2 together with
representative patterns for fluids from basalt-hosted mid-ocean ridge systems (MAR: TAG,
Lucky Strike, Two Boats; EPR: 13°N, 17-19°S), the Lau back-arc basin (Vai Lili), and the
Manus back-arc basin (DESMOS, North Su, Suzette, Satanic Mills, Snowcap), as well as
Southern Ocean seawater from 2000 m depth. Three distinct $\text{REE}_\text{CN}$ patterns can be
identified in fluids from the East Scotia Sea. Endmember fluids from E2 and E9 South are
enriched in the light REEs ($\text{La}_{\text{CN}}/\text{Yb}_{\text{CN}} = 25.2$ and 30.0 for Dog’s Head and Sepia, and 17.2,
14.9 and 21.8 for Ivory Towers, Pagoda and Launch Pad, respectively; Table 2) and have a
positive europium anomaly ($\text{Eu}_{\text{CN}}/\text{Eu}_{*\text{CN}} = 3.45$ and 3.84 for Dog’s Head and Sepia, and
14.3, 50.9 and 59.5 for Ivory Towers, Pagoda and Launch Pad, respectively). By contrast,
endmember fluids from E9 North are enriched in the middle REEs ($\text{La}_{\text{CN}}/\text{Nd}_{\text{CN}} = 0.61$;
$\text{Nd}_{\text{CN}}/\text{Yb}_{\text{CN}} = 21.0$), and have a negative Eu anomaly ($\text{Eu}_{\text{CN}}/\text{Eu}_{*\text{CN}} = 0.59$). They also have
extremely high REE concentrations ($\Sigma$REE = 123 nmol/kg). Finally, white smoker and diffuse fluids sampled from the Kemp Caldera have almost flat REE patterns, with $\text{La}_{CN}/\text{Yb}_{CN} = 2.1 - 2.2$ and $\text{Eu}_{CN}/\text{Eu}^*_{CN} = 1.2 - 2.2$.

4.2 $^{87}\text{Sr}/^{86}\text{Sr}$ Composition of Vent Fluids

The Sr isotopic composition of the endmember hydrothermal fluids is calculated by extrapolating measured values to ($\text{Mg}/\text{Sr}) = 0$. Lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values were obtained for fluids from Sepia (E2; 0.704035), with more radiogenic ratios observed in fluids from Black & White at E9 North (0.705762), Ivory Tower (0.704610), Launch Pad (0.705014), and Pagoda (0.704890) at E9 South (Table 1). These values are similar to those measured in fluids from other back-arc spreading systems, such as Lau Basin (0.7044 – 0.7056) and Manus Basin (0.70425 – 0.70435) (Fouquet et al., 1991; Mottl et al., 2011; Reeves et al., 2011), and are higher than typical mid-ocean ridge fluids, such as TAG and 21°N EPR (0.7029 – 0.7034) (Palmer, 1992; Gamo et al., 1996).

4.3 REE Composition of Chimney Anhydrites

The REE-Y compositions of chimney anhydrites sampled from some of the sites on the ESR and within the Kemp Caldera are presented in Table 3. Total REE abundance in anhydrite is much higher in chimney samples recovered from E9 North (24.3 ppm) than at any of the other vent sites (4.75 – 9.13 ppm at E2, 0.33 – 5.44 ppm at E9 South, and 0.61 – 5.19 ppm at Winter Palace, Kemp Caldera) (Table 4). At all sites, $\Sigma$REE is far higher for anhydrite than for the endmember hydrothermal fluids, by a factor of up to 1600 at E2, 1400 at E9 North and 4600 at E9 South. Differences in $\Sigma$REE between sites are mainly related to differences in the extent of seawater mixing in fluids from which the anhydrite precipitates (Table 4). The extent of seawater mixing can be calculated from $^{87}\text{Sr}/^{86}\text{Sr}$ ratios by mass balance (Bach et al., 2005):
% seawater = \frac{\left( (R_{HF} \times [Sr]_{HF}) - (R_{anh} \times [Sr]_{HF}) \right) \times 100}{\left( (R_{HF} \times [Sr]_{HF}) - (R_{sw} \times [Sr]_{sw}) - R_{anh} \right) \times ([Sr]_{HF} - [Sr]_{sw})},

where $R$ is the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of endmember hydrothermal fluid (HF), anhydrite (anh.) and seawater (sw), and [Sr] is the concentration of Sr. Most anhydrite precipitates from a fluid consisting of >50% seawater (Table 4), but anhydrite from E9 North, appears to precipitate from a fluid that has undergone very little mixing with seawater, consisting of ~98% vent fluid. This is likely to be an artefact of dissolution of anhydrite affecting the strontium concentration of the hydrothermal fluid, as discussed in Section 5.4.

Chondrite-normalised REE distribution patterns for anhydrite samples from E9 (Figure 3) are similar to those measured in the hydrothermal fluids. Thus, samples from E9 South are enriched in the light REEs ($\text{La}_{CN}/\text{Yb}_{CN} = 16.6 - 26.1$; Table 4) and have a positive Eu anomaly ($\text{Eu}_{CN}/\text{Eu}^*_{CN} = 13.9 - 18.8$), and samples from E9 North are enriched in the middle REEs ($\text{La}_{CN}/\text{Nd}_{CN} = 0.7$; $\text{Nd}_{CN}/\text{Yb}_{CN} = 24.7$) and have a small negative Eu anomaly ($\text{Eu}_{CN}/\text{Eu}^*_{CN} = 0.61$). Normalisation of REE abundance to the vent fluids generates almost flat REE patterns (with the exception of Launch Pad, where anhydrite is depleted in Eu relative to the fluid), confirming that there is negligible fractionation of the REEs between anhydrite and the vent fluids (Figure 4).

By contrast, the REE$_{CN}$ patterns of anhydrite recovered from E2 (Dog’s Head) and Kemp Caldera (Winter Palace) are different from the vent fluid pattern. Like the vent fluids, anhydrite from E2 is enriched in the light REEs ($\text{La}_{CN}/\text{Yb}_{CN} = 14.3 - 21.6$), but anhydrite has a negative, rather than a positive, Eu anomaly ($\text{Eu}_{CN}/\text{Eu}^*_{CN} = 0.35 - 0.85$). At Kemp Caldera, anhydrite is strongly enriched in the heavy REEs relative to the light REEs ($\text{La}_{CN}/\text{Yb}_{CN} = 0.03 - 0.09$), whereas the vent fluids have relatively flat REE$_{CN}$ patterns.
As a consequence, the vent fluid-normalised REE pattern for anhydrite from Kemp Caldera shows strong enrichment in the heavy REEs (Figure 4).
5. DISCUSSION

Despite their close proximity, and similar host rock compositions, the REE patterns of hydrothermal fluids and chimney anhydrite from the different vent sites are variable. The fluids are also different in terms of their pH, temperature, Cl, H₂S, F and SO₄ concentrations. Accordingly, these vent fluids can be used to identify the key controls on REE solubility in submarine hydrothermal fluids in subduction zone settings.

5.1 Host-Rock Influence

Hydrothermal fluids primarily derive their REE load through high-temperature reaction with the oceanic crust during subsurface circulation and are consequently highly enriched in all REEs compared with seawater (Michard et al., 1983; Klinkhammer et al., 1994). Comprehensive REE data for ESR and Kemp Caldera basalts, from dredge and wax core samples, are reported by Leat et al., (2000; 2004) and Fretzdorff et al., (2002). Basalts from the AVR of segments E2 and E9 have similar total REE concentrations (respectively, 65 - 78 and 60 - 75 ppm), and they are slightly enriched in the light REEs compared with the heavy REEs (LaCN/YbCN = 1.98 and 1.71). Basalts from Kemp Caldera have lower ∑REE (21 – 25 ppm) and relatively flat REE patterns (LaCN/YbCN = 1.00). The relative concentration of the REEs in hydrothermal fluids typically varies systematically with ionic radius, with larger ions preferentially partitioning into solution. Whilst it has been suggested that this reflects crystal-chemical exchange between plagioclase phenocrysts and seawater circulating in the reaction zone (Klinkhammer et al., 1994), similar REE distribution patterns are also observed in fluids derived from hydrothermal alteration of ultramafic peridotite, which does not contain plagioclase (Allen and Seyfried, 2005). Further, leaching experiments have shown that REEs in fluids mainly originate from secondary alteration minerals and interstitial material (Bach and Irber, 1998; Shibata et al., 2006), with fluid speciation exerting the dominant control on their relative distributions.
Partition coefficients for the REEs between hydrothermal fluids and basalt are presented for each site on the ESR and for Kemp Caldera in Figure 5. Fractionation of the REEs into fluids at E2 and E9 South increases with ionic radius, in line with the effects of crystal-chemical exchange demonstrated for plagioclase during magma segregation (Campbell et al., 1988; Klinkhammer et al., 1994). By contrast, the middle REE enriched patterns of E9 North vent fluids, and the relatively flat REE patterns of Kemp Caldera vent fluids, cannot be explained by plagioclase leaching, or fractionation due to differences in ionic radius. If exchange reactions are involved, their original REE signatures must be overprinted by other processes.

5.2 Influence of Chlorinity and Phase Separation

The solubility of the REEs is strongly influenced by the availability of anionic ligands, which stabilise these elements in fluids through complexation (Wood, 1990; Gammons et al., 1996; Douville et al., 1999). Chloride is typically a major constituent of hydrothermal fluids and speciation calculations indicate that, at temperatures above 300 °C, 97 - 100 % of all REEs are stabilised as chloride complexes (Gammons et al., 1996; Douville et al., 1999). Chloride forms stronger complexes with the LREEs compared to the HREEs and is likely to be an important driver behind the light REE-enrichment observed in vent fluids from E2 and E9 South on the ESR, and for most mid-ocean ridge hydrothermal systems (Haas et al., 1995; Migdisov et al., 2009).

Endmember vent fluids at E9 South have typical mid-ocean ridge-type REE_{CN} patterns, i.e. they are enriched in the light REEs and have a positive Eu anomaly, but they have very low total REE concentrations, ~5 times lower than those measured at E2, and the Eu anomaly is more than an order of magnitude higher. Because of phase separation, the E9 South vent fluids have extremely low [Cl\textsuperscript{-}] (179 - 220 mM); thus low ∑REE values likely
reflect the reduced availability of chloride ligands for complexation. Note that low [Cl] vent fluids from 17-19 °S on the East Pacific Rise also have low ∑REE (Table 2; Figure 2).

Although the effects of phase separation on the major-element chemistry of vent fluids have been well studied (Bischoff and Rosenbauer, 1984; Von Damm and Bischoff, 1987; Butterfield et al., 1990; Auzende et al., 1996; Charlou et al., 1996; Coumou et al., 2009), the effects on REE behaviour are less well known and, to our knowledge, there are no REE data in the literature for very low Cl fluids from subduction zone settings. REE concentrations tend to be higher in chloride-rich brines and lower in low-chloride fluids (Douville et al., 1999; 2002), and low-Cl fluids tend to have larger Eu\(_{\text{CN}}$/Eu\(^*_{\text{CN}}\) anomalies (Douville et al., 1999). Experimentally-determined partition coefficients for Eu between vapour and liquid in a NaCl-H\(_2\)O system at the critical point are similar to those for its neighbouring REEs (Shmulovich et al., 2002). However, thermodynamic calculations suggest that Eu is more strongly complexed by ligands including chloride, fluoride and sulphate at 350 °C compared to Gd and Sm (Wood, 1990), and experimental studies have shown that Eu\(^{2+}\) builds stronger complexes with chloride relative to the trivalent REEs (Allen and Seyfried, 2005). The fact that the low-Cl fluids at E9 South have a high Eu\(_{\text{CN}}$/Eu\(^*_{\text{CN}}\) anomaly suggests that Eu\(^{2+}\) has the strongest affinity for chloride, even when chloride concentrations are low.

### 5.3 Influence of Magmatic Volatiles

The chemical composition of hydrothermal fluids sampled at Kemp Caldera is markedly different from E2 and E9 fluids. Based on the assumption of a zero-Mg endmember, Kemp Caldera fluids have very high fluoride (~ 1000 μM) and hydrogen sulphide (~ 200 mM) concentrations, and very low pH (1 ± 1). In comparison to the ESR, Kemp Caldera is located in close proximity to the subducting arc, where the entrainment of volatile gases (H\(_2\)O, CO\(_2\), SO\(_2\), HCl, HF) into circulating hydrothermal fluids (Reeves et al.,
2011) is likely to influence pH and the type and availability of anionic ligands (Bai and Koster van Groos, 1999). The distinctive composition of Kemp Caldera hydrothermal fluids, together with the widespread deposition of native sulphur (derived from disproportionation of SO₂; Iwasaki and Ozawa (1960); Gamo et al. (1997); Reeves et al. (2011)), is indicative of input of magmatically sourced acid volatiles (Powell et al., 2011). These acid volatiles provide an additional source of anionic ligands capable of complexing with the REEs.

Hydrothermal fluids from mid-ocean ridge settings typically have low [F⁻] relative to seawater (Edmond et al., 1979; Von Damm et al., 1985), because mineral phases such as magnesite and magnesium hydroxide sulphate hydrate have a strong affinity for fluoride ions (Seyfried and Ding, 1995). In arc settings, however, the release of HF by magmatic degassing (Aiuppa et al., 2009) can generate fluids with high [F⁻] and low pH, resulting in enhanced REE mobility in fluids as observed in the Eastern Manus Basin (Bach et al., 2003; Craddock et al., 2010; Reeves et al., 2011). Our data support this. Extrapolation of the Kemp Caldera fluid sample with lowest [Mg] to zero [Mg], which provides a minimum value for the REE content of the vent fluid endmember (because of precipitation; see Section 4.1), indicates that the endmember ∑REE value of Great Wall fluids is ~ 70 nmol/kg. This value is an order of magnitude higher than it is for fluids from E9 South (~ 8 nmol/kg), which have similarly low [Cl⁻], suggesting that input of acid volatiles has significantly enhanced the solubility of the REEs.

Input of acid volatiles may also affect REE-CN distribution patterns. Fractionation between the LREEs and HREEs (LaCN/YbCN) generally decreases as the abundance of fluoride relative to chloride ([F⁻]/[Cl⁻]) increases (Figure 6). This is because stability constants for complexation of the REEs with chloride are higher for the LREE than the HREEs (Wood, 1990; Migdisov et al., 2009), but this effect is reduced if fluoride concentrations are high. In the Manus Basin, fluids sampled from Suzette and Satanic Mills,
which have very high $[F]/[Cl]$ (0.6 – 0.8 µM/mM), are also highly enriched in the HREEs (Figure 2; Craddock et al., 2010). Similarly, fluids venting from the Kemp Caldera may have displayed this pattern of HREE-enrichment in the past, as recorded in anhydrite in Winter Palace chimney material (See Section 5.5). Fluoride complexes of the heavy REEs are predicted to be more stable than those of the light REEs and Eu$^{2+}$ (Wood, 1990), and thermodynamic calculations of species distribution in Manus Basin fluids indicate that the HREEs are predominantly complexed with fluoride in F-rich solutions (Craddock et al., 2010). However experimental data suggest that formation constants for HREE-F complexes in seawater have been significantly overestimated at high (> 150 °C) temperatures (Migdisov et al., 2009). Further, Williams-Jones et al. (2012) suggest that fractionation of the LREEs from the HREEs in hydrothermal fluids is primarily controlled by temperature rather than fluid speciation. We note, however, that while these studies support the importance of chloride complexation in REE fractionation in typical MOR-style hydrothermal fluids, they cannot explain the diversity in REE$_{CN}$ patterns measured in vent fluids from Kemp Caldera, or the Manus Basin.

Vent fluids from Kemp Caldera, and ‘acid-sulphate’ fluids from the Manus Basin (Craddock et al., 2010), have low La$_{CN}$/Yb$_{CN}$ and Eu$_{CN}$/Eu*$_{CN}$ values for a wide range of $[F]/[Cl]$ (Figure 6). Speciation calculations by Craddock et al. (2010) indicate that complexation exerts a relatively minor influence on REE solubility in acid-sulphate fluids. At low pH, REEs are readily leached from the host rock with minimal fractionation, and are stable in solution as free ions. REE solubility may be further enhanced by complexation with sulphate (e.g. DESMOS), and at higher temperatures (>200 °C) by the formation of REE-Cl complexes (e.g. North Su) (Craddock et al., 2010). The relatively flat REE$_{CN}$ distribution patterns for fluids recovered from Kemp Caldera may therefore be characteristic of very low pH fluids.
5.4 Influence of Anhydrite

Anhydrite will precipitate in hydrothermal environments at temperatures > 150 °C, due to conductive heating of seawater or as high-temperature fluids mix with seawater. Anhydrite precipitation represents a major sink for rare earth elements in hydrothermal environments (Mills and Elderfield, 1995), and deposits of this mineral within vent chimneys on the ESR and Kemp Caldera are enriched in the REEs by a factor of several thousand relative to hydrothermal fluids.

The rare earth element chemistry of hydrothermal fluids can therefore be potentially influenced by anhydrite precipitation and dissolution (Craddock et al., 2010; Schmidt et al., 2010). At Black & White (E9 North), vent fluids have very high ∑REE, despite their low chlorinity (Douville et al., 2002), a negative Eu anomaly and, unlike the other vent sites, they exhibit a positive correlation between ∑REE and [Ca] (Figure 7; R² = 0.72 compared with < 0.14 for all other sites). In addition, the sulphate concentration of the endmember fluids is ~4 mM, rather than zero as it is in most vent fluids (Von Damm, 1990). All of this suggests that the vent fluids are affected by dissolution of anhydrite, which makes up the inner wall of the Black & White chimneys (James et al., in review). Addition of ~4 mM of SO₄ is equivalent to dissolution of 544 mg anhydrite per kg of vent fluid. We calculate that < 1 g of anhydrite from the Black & White chimneys, added to 1 kg of a vent fluid unaffected by anhydrite dissolution (i.e. the low Cl fluids from E9 South), is sufficient to produce a vent fluid with high ∑REE and a negative Eu anomaly, that is enriched in the middle REEs.

REECN distribution patterns similar to those in Black & White fluids have previously been observed at the ‘Two Boats’ hydrothermal site at 5 °S on the Mid-Atlantic Ridge (Figure 2; Schmidt et al., 2010). Crucially, the temperature and pressure of the fluids venting
at these sites is close to the critical point of seawater. Very high REE concentrations may
reflect the dramatic increase in stability of chloride complexes as fluids approach a
supercritical state (Ding and Seyfried, 1992; Shmulovich et al., 2002), and the enhanced
capacity of the vapour-phase fluid for metal dissolution by ion hydration (Pokrovski et al.,
2005). Sulphate also forms strong complexes with the REEs at high temperatures, and
stability constants with SO$_4^{2-}$ are highest for the MREE (Schijf and Byrne, 2004). However,
as complexes with chloride are strongest for the LREEs, and the availability of free sulphate
ions is substantially reduced at such high temperatures, complexation effects are unlikely to
generate the observed REE fractionation in fluids at Black & White and Two Boats (Schmidt
et al., 2010). Model simulations indicate that vapour-phase fluids mix continuously with
conductively heated seawater in the shallow subsurface, which facilitates precipitation of
anhydrite (Coumou et al., 2009). Consequently, we suggest that entrainment of anhydrite
into fluids may be characteristic of fluids close to the critical point of seawater, resulting in
high REE concentrations. Assimilation of the REEs into anhydrite is controlled by a
combination of crystal lattice constraints and fluid speciation, as discussed in Section 5.5.
Hydrothermal anhydrite recovered from the chimney of Black & White is enriched in the
MREE (Figure 3), which likely overprints a more ‘typical’ REE distribution pattern in fluids,
consistent with observations at Two Boats.

The large ionic radius of divalent europium inhibits its partitioning into anhydrite, and
the magnitude of the Eu anomaly in the remaining fluid is thought to be a proxy for the
degree of fluid evolution in mid-ocean ridge systems (Humphris, 1998; Schmidt et al., 2010).
Figure 8 indicates that there is an inverse relationship between the size of the Eu anomaly and
the total REE concentration in endmember fluids from the ESR. Fluids from Black & White
(E9 North) have high $\Sigma$REE and a negative Eu anomaly, which may be indicative of an early
evolutionary stage, prior to significant anhydrite deposition (Schmidt et al., 2010). This is
also suggested as an alternative explanation for the $\text{REE}_{\text{CN}}$ distribution pattern reported for Two Boats by Schmidt et al. (2010). In this connection, the water-rock ratio in the reaction zone at Black & White is ~2 times higher than those estimated for the other E9 vent sites (and ~4 times higher than estimated for E2 sites) (James et al., in review). This indicates that the extent of water-rock interaction is more limited, so REE concentrations are less extensively modified by alteration reactions, complexation and/or sorption effects (Shibata et al., 2006; Schmidt et al., 2010). Moreover, it has been suggested that the composition of hydrothermal fluids is significantly modified during transport from the reaction zone to the seafloor (Bach and Irber, 1998). These authors suggest that fluids in the reaction zone have high $\Sigma$REE, relatively flat $\text{REE}_{\text{CN}}$ distribution patterns, and a negative Eu anomaly. During ascent to the seafloor, REE concentrations are modified by complexation with chloride and other aqueous ligands, exchange reactions and mineral precipitation, resulting in a LREE-enriched fluid with a positive Eu anomaly. Thus, the Black & White (and Two Boats) fluids may represent rarely sampled, primary reaction-zone fluids. By contrast, fluids from E9 South have low $\Sigma$REE but large positive Eu anomalies which point to extensive subsurface anhydrite deposition, potentially augmented by more extensive water-rock reactions, and strong Eu-Cl complexation.

5.5 Anhydrite as a Recorder of Past Vent Fluid Compositions

The distribution pattern of the REEs in anhydrites recovered from white smoker chimneys at Winter Palace in the Kemp Caldera is very different from that of the vent fluids being expelled today. The anhydrites are remarkably enriched in the HREEs ($\text{La}_{\text{CN}}/\text{Yb}_{\text{CN}} = 0.03 - 0.09$; Table 4), whereas the vent fluids have relatively flat $\text{REE}_{\text{CN}}$ patterns, with $\text{La}_{\text{CN}}/\text{Yb}_{\text{CN}} = 2.1 - 2.2$. Thus, either the REEs are strongly fractionated during anhydrite
deposition, or the anhydrite precipitated from a fluid that had a different composition from
the fluids venting at this site today.

Rare earth elements are incorporated into the CaSO₄ lattice by substitution of Ca²⁺, so
crystallographic constraints dictate that ion exchange will favour those REEs with an ionic
radius similar to calcium (Morgan and Wandless, 1980). Experimentally determined
partition coefficients (K_D) for the REEs in solution and anhydrite are highest for Ce³⁺, Nd³⁺,
and Sm³⁺, so the MREEs should be preferentially incorporated into anhydrite (Kagi et al.,
1993; Schmidt et al., 2010). However, REE distribution patterns in anhydrite recovered from
the TAG hydrothermal site on the Mid-Atlantic Ridge, normalised to the vent fluids, are
variable (Humphris, 1998), and K_D values for La, Ce and Nd are anomalously low (Mills and
Elderfield, 1995). It has therefore been suggested that uptake of the REEs into anhydrite is
principally controlled by fluid composition, because of the effects of complexation on the
availability of free ions in fluids (Humphris and Bach, 2005). In support of this, variable
REE distribution patterns in anhydrites from PACMANUS (including enrichments in the
middle- and heavy-REEs) are considered to reflect variations in the concentration of
magmatic volatiles in the vent fluids from which they precipitated (Craddock and Bach,
2010).

As the anhydrites sampled from Kemp Caldera are strongly enriched in the HREEs
(Figures 3 and 4), REE uptake cannot be primarily controlled by crystallographic constraints.
By contrast, if the REE composition of the anhydrite reflects that of the fluid, then the
composition of the vent fluids must have been different at the time the anhydrite was
deposited. According to Craddock et al. (2010), heavy-REE enrichments are favoured in
hydrothermal fluids with high fluoride concentrations, and high F/Cl⁻ ratios, whereas
enrichment of all REEs (and relatively flat REE_CN patterns, as observed in Kemp Caldera
fluids today) is due to very low fluid pH.
As discussed in Section 2.2, the floor of the Kemp Caldera is covered in ash and sulphur deposits, which suggests that there has been a magmatic blow out event at this site in the recent past. Such a surge in magmatic activity would enhance the supply of REE-binding ligands, including F, and high temperatures would promote phase separation which would increase the F/Cl ratio of the vent fluids, enhancing the mobilisation of the HREEs in particular (Wood, 1990). As the extent of water-rock interaction is likely to have been reduced during a burst of magmatic activity, SO₂ disproportionation in the subsurface may have been limited, and fluid pH would be higher than it is today (1 ± 1; Section 2.2). Consequently, a strong efflux of magmatic HF would provide free F⁻ for complexation, enhancing the concentration of HREE in fluids for incorporation into anhydrite. By contrast, the low pH of the fluids venting today results in non-selective REE mobilisation and limits the availability of fluoride as a complexing ligand, producing flat REE distribution patterns.

6. SUMMARY AND CONCLUSIONS

Rare earth element data are reported for a suite of high-temperature and diffuse hydrothermal fluids, and conjugate chimney anhydrite, for newly-discovered vent sites in the East Scotia Sea subduction zone system. High temperature fluids from E2 and E9 South are enriched in the light REEs and have positive Eu anomalies, like most vent fluids from basalt-hosted mid-ocean ridge spreading centres. This REE pattern is best described in terms of differential leaching of the REEs from alteration minerals in the host rock, and stabilisation of the REEs as chloride complexes. The fluids appear to be unaffected by inputs of material from the nearby subduction zone. By contrast, fluids from E9 North are enriched in the middle REEs and have negative Eu anomalies, whereas fluids from Kemp Caldera have flat chondrite-normalised REE patterns. Fluids from E9 North appear to be affected by dissolution of anhydrite, which has high ∑REE and a negative Eu anomaly. Alternatively,
the extent of water-rock interaction at E9 North may be limited, resulting in a relatively un-evolved REE pattern. At Kemp Caldera, REE solubility in the fluids venting at the present-day appears to be critically dependent on very low pH.

The REE \textsubscript{CN} patterns of chimney anhydrites from E2 and E9 are similar to their conjugate high temperature fluids, but anhydrite recovered from the Winter Palace site at Kemp Caldera is strongly enriched in the heavy REEs relative to the present-day vent fluids. We suggest that these anhydrites precipitated from fluids that were strongly enriched in HF, probably introduced during a relatively recent magmatic blow-out event.

This study indicates that the REE composition of hydrothermal fluids can provide critical information about sub-seafloor geochemical processes associated with hydrothermal activity in subduction zone settings. These include reactions between host rock and circulating fluids, phase separation and fluid evolution, magmatic acid volatile degassing, and mineral precipitation. We have also shown that analysis of the REE composition of associated anhydrite deposits can provide insight as to the nature of hydrothermal activity in the past, where access to hydrothermal fluids is precluded.

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Hydrology, Marine Ecosystems and Climate Change Studies, Oceanographic Museum of Monaco, 27 March – 1 April 2011.


Theoretical predictions of speciation in hydrothermal solutions to 350°C at saturation
### Table 1. Total REE concentrations and $^{\text{87}}$Sr/$^{\text{86}}$Sr ratios of sampled (s.) and end-member (EM) hydrothermal fluids from the East Scotia Ridge and Kemp Caldera.

<table>
<thead>
<tr>
<th>Fluid Source</th>
<th>$T_{\text{max}}$ °C</th>
<th>Mg (nmol/kg)</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>$\Sigma$REE (nmol/kg)</th>
<th>$^{\text{87}}$Sr/$^{\text{86}}$Sr</th>
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<tr>
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<tr>
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<td>2200</td>
<td>9140</td>
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<td>1880</td>
<td>1900</td>
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<td>1100</td>
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<td>190</td>
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<td></td>
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<td>16,000</td>
<td>2000</td>
<td>8120</td>
<td>1800</td>
<td>2290</td>
<td>1800</td>
<td>201</td>
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| Seawater    | 0                   | 53          | 42   | 6.2 | 6.3 | 27  | 5.0 | 1.2 | 6.8 | 1.0 | 7.7 | 2.1 | 7.2 | 1.1 | 7.7 | 1.4 | 0.1 | 0.709182

s. = sampled fluids; EM = endmember fluids; $T_{\text{max}}$ = highest measured fluid temperature; n/a = not available; concentrations in pmol/kg unless otherwise stated; seawater is Southern Ocean Circumpolar Deep Water (ts PS71 131-1) analysed in this study.
Table 2. Temperature, [Cl], [Mg], [SO$_4$] and chondrite-normalised REE ratios of endmember fluids from the East Scotia Ridge and sampled fluids from Kemp Caldera, as well as other representative hydrothermal vent sites. The ratios La$_{CN}$/Yb$_{CN}$, La$_{CN}$/Nd$_{CN}$, and Nd$_{CN}$/Yb$_{CN}$ allow comparison of, respectively, light to heavy (LREE/HREE), light to mid (LREE/MREE) and mid to heavy (MREE/HREE) REE abundance. The europium anomaly, (Eu$_{CN}$/Eu$^*_{CN}$), where Eu$^*$ represents the averaged concentration of neighbouring REEs, Sm and Gd, is also given.

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<th></th>
<th>$T_{\text{max}}$</th>
<th>[Cl] mM</th>
<th>[Mg] mM</th>
<th>$\sum$REE nM</th>
<th>La$<em>{CN}$/Yb$</em>{CN}$</th>
<th>La$<em>{CN}$/Nd$</em>{CN}$</th>
<th>Nd$<em>{CN}$/Yb$</em>{CN}$</th>
<th>Eu$<em>{CN}$/Eu$^*</em>{CN}$</th>
<th>[SO$_4$]$^2-$ mM</th>
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<td>104</td>
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<td>2.27</td>
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$^g$Douville et al., 1999; $^c$Craddock et al., 2010; $^t$Schmidt et al., 2010. $T_{\text{max}}$ indicates the maximum temperature measured during fluid sampling, with the exception of Winter Palace where parentheses indicate $T_{\text{max}}$ prior to fluid sampling. Only the sample with lowest [Mg] is shown for the Kemp Caldera vent sites. Sulphate values of < 0 indicate removal by subsurface anhydrite deposition.
Table 3. REE-Y concentrations (ppm) in hydrothermal chimney anhydrite from the East Scotia Ridge and Kemp Caldera

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<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>Y</th>
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<td>2.73</td>
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<td>0.24</td>
<td>0.03</td>
<td>0.07</td>
<td>0.01</td>
<td>0.04</td>
<td>0.005</td>
<td>0.87</td>
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<td>0.04</td>
<td>0.10</td>
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<td>0.05</td>
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<td>0.33</td>
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<td>0.09</td>
<td>0.48</td>
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<td>Winter Palace</td>
<td>0.01</td>
<td>0.02</td>
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<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.04</td>
<td>0.02</td>
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<td>0.02</td>
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<td>957C-6W-1\textsuperscript{a}</td>
<td>TAG-1</td>
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<td>1.05</td>
<td>0.14</td>
<td>0.61</td>
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<td>0.09</td>
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<td>957H-5N-2\textsuperscript{a}</td>
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<td>0.33</td>
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<tr>
<td>123 ROV-4\textsuperscript{b}</td>
<td>Two Boats, 5°S</td>
<td>1.39</td>
<td>2.78</td>
<td>0.40</td>
<td>2.05</td>
<td>0.59</td>
<td>0.13</td>
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<td>0.10</td>
<td>0.53</td>
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<td>139-415\textsuperscript{c}</td>
<td>Two Boats, 5°S</td>
<td>0.53</td>
<td>1.26</td>
<td>0.21</td>
<td>1.17</td>
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<td>0.11</td>
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<td>0.05</td>
<td>0.26</td>
<td>0.04</td>
<td>0.07</td>
<td>0.007</td>
<td>0.03</td>
<td>0.003</td>
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<tr>
<td>1188A-7R-1\textsuperscript{e}</td>
<td>Snowcap</td>
<td>1.37</td>
<td>3.77</td>
<td>0.60</td>
<td>2.98</td>
<td>0.91</td>
<td>0.31</td>
<td>1.36</td>
<td>0.23</td>
<td>1.59</td>
<td>0.37</td>
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<td>0.24</td>
<td>9.89</td>
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<td>Snowcap</td>
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<td>1.98</td>
<td>-</td>
<td>1.68</td>
<td>0.52</td>
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<td>0.76</td>
<td>-</td>
<td>0.65</td>
<td>0.16</td>
<td>0.48</td>
<td>-</td>
<td>0.62</td>
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<td>1188A_7R_1; #19\textsuperscript{d}</td>
<td>Snowcap</td>
<td>0.29</td>
<td>1</td>
<td>-</td>
<td>0.8</td>
<td>0.31</td>
<td>0.07</td>
<td>0.46</td>
<td>-</td>
<td>0.35</td>
<td>0.08</td>
<td>0.26</td>
<td>-</td>
<td>0.34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>227_7R2; #9\textsuperscript{d}</td>
<td>North Su</td>
<td>1.39</td>
<td>4.73</td>
<td>-</td>
<td>5.01</td>
<td>1.90</td>
<td>1.20</td>
<td>1.98</td>
<td>-</td>
<td>2.02</td>
<td>0.39</td>
<td>1.04</td>
<td>-</td>
<td>1.16</td>
<td>-</td>
<td>-</td>
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<td>227_7R2; #17\textsuperscript{d}</td>
<td>North Su</td>
<td>0.58</td>
<td>1.71</td>
<td>-</td>
<td>1.45</td>
<td>0.61</td>
<td>0.64</td>
<td>0.79</td>
<td>-</td>
<td>0.91</td>
<td>0.18</td>
<td>0.49</td>
<td>-</td>
<td>0.49</td>
<td>-</td>
<td>-</td>
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<td>227_7R2; #18\textsuperscript{d}</td>
<td>North Su</td>
<td>0.62</td>
<td>1.72</td>
<td>-</td>
<td>2.98</td>
<td>1.31</td>
<td>0.83</td>
<td>2.55</td>
<td>-</td>
<td>3.64</td>
<td>0.83</td>
<td>2.44</td>
<td>-</td>
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\textsuperscript{a}Humphris, 1998; \textsuperscript{b}Schmidt et al., 2010; \textsuperscript{c}Bach et al., 2003; \textsuperscript{d}Craddock and Bach, 2010
Table 4. Total REE concentration, REE ratios, and Sr isotope data for anhydrite samples from the East Scotia Ridge and Kemp Caldera. Data for anhydrites sampled from Mid-Atlantic Ridge and Manus Basin hydrothermal sites are also provided for comparison.

<table>
<thead>
<tr>
<th>Region</th>
<th>Sample Location</th>
<th>∑REE ppm</th>
<th>La&lt;sub&gt;CN&lt;/sub&gt; /Yb&lt;sub&gt;CN&lt;/sub&gt;</th>
<th>La&lt;sub&gt;CN&lt;/sub&gt; /Nd&lt;sub&gt;CN&lt;/sub&gt;</th>
<th>Nd&lt;sub&gt;CN&lt;/sub&gt; /Yb&lt;sub&gt;CN&lt;/sub&gt;</th>
<th>Eu&lt;sub&gt;CN&lt;/sub&gt; /Eu*&lt;sub&gt;CN&lt;/sub&gt;</th>
<th>⁸⁷Sr/⁸⁶Sr</th>
<th>[Sr] ppm</th>
<th>% SW</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>East Scotia Ridge</strong></td>
<td>E2 (Dog’s Head 130-1)</td>
<td>7.34</td>
<td>21.6</td>
<td>1.50</td>
<td>14.4</td>
<td>0.85</td>
<td>0.70678</td>
<td>1520</td>
<td>55</td>
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<td>E2 (Dog’s Head 130-2)</td>
<td>9.13</td>
<td>20.9</td>
<td>1.55</td>
<td>13.5</td>
<td>0.63</td>
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<td>E2 (Dog’s Head 132)</td>
<td>4.75</td>
<td>14.3</td>
<td>1.37</td>
<td>10.4</td>
<td>0.35</td>
<td>0.70816</td>
<td>1050</td>
<td>82</td>
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<tr>
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<td>E9 North (B&amp;W)</td>
<td>24.3</td>
<td>17.1</td>
<td>0.69</td>
<td>24.7</td>
<td>0.61</td>
<td>0.70607</td>
<td>1310</td>
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<td>E9 South (Ivory Tower)</td>
<td>0.33</td>
<td>16.6</td>
<td>1.78</td>
<td>9.31</td>
<td>13.9</td>
<td>0.70876</td>
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<td>E9 South (Launch Pad)</td>
<td>5.44</td>
<td>26.1</td>
<td>1.79</td>
<td>14.6</td>
<td>18.8</td>
<td>0.70669</td>
<td>2170</td>
<td>14</td>
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<td><strong>Kemp Caldera</strong></td>
<td>Winter Palace (149)</td>
<td>5.19</td>
<td>0.03</td>
<td>1.05</td>
<td>0.03</td>
<td>3.84</td>
<td>0.70658</td>
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<td>Winter Palace (152)</td>
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<td>0.09</td>
<td>1.43</td>
<td>0.07</td>
<td>1.87</td>
<td>0.70886</td>
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<td><strong>Mid-Atlantic Ridge</strong></td>
<td>TAG-1 (957C-6W-1)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.18</td>
<td>11.4</td>
<td>1.66</td>
<td>6.86</td>
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<td>12.2</td>
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<td>8.55</td>
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<td>10.3</td>
<td>8.93</td>
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<td>Two Boats (123 ROV-4)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.04</td>
<td>10.1</td>
<td>1.30</td>
<td>7.78</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
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<td>Two Boats (139-415c)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>4.52</td>
<td>12.4</td>
<td>0.88</td>
<td>14.1</td>
<td>0.85</td>
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<td><strong>Manus Basin</strong></td>
<td>Snowcap (1188A-7R-1)&lt;sup&gt;c,d&lt;/sup&gt;</td>
<td>16.3</td>
<td>0.67</td>
<td>0.88</td>
<td>0.76</td>
<td>0.87</td>
<td>0.70835</td>
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<td>Snowcap (1188A-7R-1; #2)&lt;sup&gt;e&lt;/sup&gt;</td>
<td>7.80</td>
<td>0.70</td>
<td>0.74</td>
<td>0.95</td>
<td>1.48</td>
<td>0.70856</td>
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<td>Snowcap (1188A_7R_1; #19)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>3.96</td>
<td>0.57</td>
<td>0.70</td>
<td>0.82</td>
<td>0.57</td>
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<td>1.51</td>
<td>1.90</td>
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<td>0.79</td>
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<td>1.03</td>
<td>2.85</td>
<td>0.70627</td>
<td>3650</td>
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<td>North Su (227_7_R2; #18)&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>0.44</td>
<td>1.38</td>
<td>0.70675</td>
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<sup>a</sup>Humphris et al., 1998; <sup>b</sup>Schmidt et al., 2010; <sup>c</sup>Bach et al., 2003; <sup>d</sup>2005; <sup>e</sup>Craddock and Bach, 2010.
**Figure 1.** Location of the East Scotia Ridge (ESR) and Kemp Caldera in the Scotia Sea, in relation to the South American plate (SAM), the Antarctic plate (ANT), the Scotia plate (SCO) and the Sandwich plate (SAN). ESR segments E1 – E9 are labelled. Confirmed sites of hydrothermal activity are indicated by grey circles (E2 and E9) and by the grey star at the base of the South Sandwich Island Arc (Kemp Caldera). SFZ: Shackleton Fracture Zone, NSR: North Scotia Ridge, SSR: South Scotia Ridge, SCT: Southern Chile Trench, SST: South Sandwich Trench and SAAR: South American-Antarctic Ridge. Adapted from Rogers *et al.* (2012); Thomas *et al.* (2003); Fretzdorff *et al.* (2002).
Figure 2. Chondrite-normalised REE patterns in endmember vent fluids from E2 (Dog’s Head and Sepia), E9 North (Black & White) and E9 South (Ivory Tower, Launch Pad, Pagoda) on the East Scotia Ridge, and in sampled fluids from Kemp Caldera (Winter Palace and Great Wall). Patterns for a typical mid-ocean ridge hydrothermal fluid (TAG), as well as for other vent sites that exhibit similar $\text{REE}_{\text{CN}}$ patterns to sites from the ESR, are also shown. These data are from: Douville et al. (1999) (Lau Basin: Vai Lili; MAR: TAG, Lucky Strike; EPR: 13 °N, 17-19 °S); Schmidt et al. (2010) (MAR: Two Boats); Craddock et al. (2010) (Manus Basin: DESMOS, North Su, Suzette, Satanic Mills, Snowcap). Seawater data (Circumpolar Deep Water) were determined in this study; see also Hathorne et al. (2012).
Figure 3. Chondrite-normalised REE distribution patterns for chimney anhydrite from E2 (Dog’s Head), E9 North (Black & White), E9 South (Launch Pad and Ivory Towers), and Kemp Caldera (Winter Palace). Data for other vent sites are from: Humphris (1998) (TAG), Schmidt et al. (2010) (Two Boats), Bach et al. (2003) (Snowcap) and Craddock and Bach (2010) (Snowcap and North Su).
Figure 4. Vent fluid-normalised REE fractionation patterns for chimney anhydrite from E2 (Dog’s Head), E9 North (Black & White), E9 South (Ivory Tower and Launch Pad), and Kemp Caldera (Winter Palace). Samples from the ESR are normalised to the endmember vent fluid composition; samples from Kemp Caldera are normalised to the composition of the vent fluid with lowest [Mg].
Figure 5. Distribution of the REEs between basalt and hydrothermal fluids, presented in terms of the partition coefficient, $K_D$, versus effective ionic radius (Å) in octahedral coordination (Shannon, 1976). Endmember and sampled (lowest Mg) fluids are used for ESR and Kemp, respectively. Data for E2 and E9 basalts are from Leat et al. (2000; 2004); Fretzdorff et al. (2002). Also shown are $K_D$ values for the REEs in plagioclase during magma segregation (Phinney and Morrison, 1990).
Figure 6. Relationship between (a) $\text{La}_{\text{CN}}/\text{Yb}_{\text{CN}}$ and (b) $\text{Eu}_{\text{CN}}/\text{Eu}^*_{\text{CN}}$ and fluoride/chloride ratio in sampled hydrothermal fluids from the East Scotia subduction zone system. Only low Mg (< 8 mM) values are included for ESR fluids, alongside sampled (Mg > 43 mM) fluids for Kemp Caldera. Data for vent fluids from the Manus Basin (black smoker- and acid sulphate-type) are also shown for comparison (Craddock et al., 2010).
Figure 7. Total REE concentration ($\sum$REE) versus Ca concentration in sampled fluids from E2, E9 North, E9 South and Kemp Caldera. Fluids recovered from E9 North (including two fluids for which no ‘dregs’ were available for analysis, in addition to the fluids reported in Table 1) exhibit a positive correlation between $\sum$REE and [Ca], indicated by the trend line ($R^2 = 0.72$).
Figure 8. Chondrite-normalised Eu anomaly (Eu$_{CN}$/Eu*$_{CN}$) versus total REE concentration in endmember fluids from the ESR.