Rare earth elements (REEs) in the tropical South Atlantic and quantitative deconvolution of their non-conservative behaviour

Xin-Yuan Zheng\textsuperscript{a,1,\*}, Yves Plancherel \textsuperscript{a}, Mak A. Saito \textsuperscript{b}, Peter M. Scott \textsuperscript{a,2}, Gideon M. Henderson \textsuperscript{a}

\textsuperscript{a} Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN, UK

\textsuperscript{b} Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543, USA

\*Corresponding author.

E-mail address: xzheng75@wisc.edu (X.-Y. Zheng). Tel.: +1 (608) 262-4255.

\textsuperscript{1} Now at Department of Geoscience, University of Wisconsin–Madison, WI 53706, USA.

\textsuperscript{2} Now at Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK.
Abstract

This study presents new concentration measurements of dissolved REEs (dREEs) along a full-depth east-west section across the tropical South Atlantic (~12°S), and uses these data to investigate the oceanic cycling of the REEs. Enrichment of dREEs, associated with the redox cycling of Fe-Mn oxides, is observed in the oxygen minimum zone (OMZ) off the African shelf. For deeper-waters, a multi-parameter mixing model was developed to deconvolve the relative importance of physical transport (i.e. water mass mixing) from biogeochemical controls on the dREE distribution in the deep Atlantic. This approach enables chemical processes involved in REE cycling, not apparent from the measurements alone, to be distinguished and quantified. Results show that the measured dREE concentrations below ~1000 m are dominantly controlled (>75%) by preformed REE concentrations resulting from water mass mixing. This result indicates that the linear correlation between dREEs and dissolved Si observed in Atlantic deep waters results from the dominantly conservative behaviour of these tracers, rather than from similar chemical processes influencing both dREEs and Si. Minor addition of dREEs (~10% of dNd and ~5% of dYb) is observed in the deep (>~4000 m) Brazil Basin, resulting from either remineralization of particles in-situ or along the flow path. Greater addition of dREEs (up to 25% for dNd and 20% for dYb) is found at ~1500 m and below ~4000 m in the Angola Basin near the African continental margin. Cerium anomalies suggest that different sources are responsible for these dREE addition plumes. The 1500 m excess is most likely attributed to dREE release from Fe oxides, whereas the 4000 m excess may be due to remineralization of calcite. Higher particulate fluxes and a more sluggish ocean circulation in the Angola Basin may explain why the dREE excesses in
this basin are significantly higher than that observed in the Brazil Basin. Hydrothermal venting over the mid-Atlantic ridge acts as a regional net sink for light REEs, but has little influence on the net budget of heavy REEs. The combination of dense REE measurements with water mass deconvolution is shown to provide quantitative assessment of the relative roles of physical and biogeochemical processes in the oceanic cycling of REEs.
1. INTRODUCTION

The rare earth elements (REEs), a sequence of 14 naturally occurring elements with coherent chemical properties, are useful oceanic tracers. In seawater, REE complexation with aqueous ligands, predominantly carbonate ions (e.g., Byrne and Kim, 1990; Wood, 1990), or silicic acid (Akagi et al., 2011; Akagi, 2013), competes with adsorption by marine particles. Because the stability of their aqueous complexes increases with atomic number, the lighter REEs (LREEs) adsorb on particle surfaces relatively more easily (i.e. more particle-reactive) than the heavier REEs (HREEs) (e.g., Byrne and Kim, 1990; Sholkovitz et al., 1994). This dynamic equilibrium between aqueous complexation and particle scavenging fractionates dissolved REEs (dREEs) in characteristic ways.

Fractionations between trivalent dREEs in seawater are also influenced by other processes, including input from external REE sources and mixing of water masses (Elderfield et al., 1988; Byrne and Sholkovitz, 1996). The behavior of Ce is also mediated by redox transformation between more soluble Ce$^{3+}$ and insoluble Ce$^{4+}$. Fractionation between the dREEs are normally visualized by normalizing measured REE concentrations to a suitable reference, usually shale or another water mass in the ocean (e.g., Zhang and Nozaki, 1998; Nozaki et al., 1999; Alibo and Nozaki, 2004; Zhang et al., 2008; Haley et al., 2014). Such REE patterns can allow for tracing of a variety of oceanic processes (e.g., Sholkovitz et al., 1994; Alibo and Nozaki, 2004; Hatta and Zhang, 2006; Zhang et al., 2008).

Considerable field observations and laboratory experiments have been conducted to
study the marine cycling of REEs (e.g., Elderfield and Greaves, 1982; de Baar et al., 1985; Byrne and Kim, 1990; German et al., 1990; Bertram and Elderfield, 1993; Greaves et al., 1994; Zhang and Nozaki, 1996; Douville et al., 1999; Nozaki and Alibo, 2003; Johannesson et al., 2011; Haley et al., 2014). Other studies have primarily focused on Nd because of the utility of Nd isotopes as a tracer for ocean circulation (e.g., Amakawa et al., 2009; Carter et al., 2012; Grasse et al., 2012; Singh et al., 2012; Grenier et al., 2013; Jeandel et al., 2013; Pearce et al., 2013; Molina-Kescher et al., 2014). In spite of these efforts, substantial uncertainties remain about the processes that control the distribution of REEs in the ocean.

Our ability to unequivocally interpret marine REE patterns and Nd-isotope data is often limited by inability to quantify the influence of physical transport (i.e. water mass mixing) relative to biogeochemical processes (e.g., particle scavenging and remineralization), although both processes are recognized to be important for REEs (e.g., Bertram and Elderfield, 1993; Nozaki and Alibo, 2003; Siddall et al., 2008; Garcia-Solsona et al., 2014; Haley et al., 2014; Molina-Kescher et al., 2014; Hathorne et al., 2015; Stichel et al., 2015). Apparent incompatibility between the nutrient-like profiles of dNd concentrations in the water column and a strong circulation-controlled distribution of seawater Nd isotopic compositions, the so-called “Nd paradox” (Goldstein and Hemming, 2003 and references therein), is a notable example of this limitation.

Another limitation relates to incomplete understanding of exchange processes at the continent–ocean interface. Recent studies, mostly based on Nd, have demonstrated that seawater-sediment interactions on continental margins, a process termed as
“boundary exchange” (e.g., Lacan and Jeandel, 2005a; Jeandel et al., 2007), can significantly influence Nd concentration and isotope signature in seawater. Globally, it is thought that boundary exchange could represent the dominant source of the oceanic Nd budget (e.g., Tachikawa et al., 2003; Arsouze et al., 2009; Rempfer et al., 2011). The local expression of this boundary exchange, however, is neither well resolved geographically nor understood mechanically, and existing observations are heterogeneous. Observations suggest that REEs can either be added or removed from the water column near the continent–ocean interface (e.g., Zhang and Nozaki, 1998; Bayon et al., 2011; Carter et al., 2012; Grasse et al., 2012; Grenier et al., 2013; Garcia-Solsona et al., 2014).

Here we present a new set of concentration data for the 14 $d$REEs collected over full-water-column depths along an east–west zonal section near ~12°S in the tropical South Atlantic. These new measurements significantly augment limited $d$REE (often Nd alone) concentration data available in the South Atlantic (e.g., Jeandel, 1993; German et al., 1995; Rickli et al., 2009; Bayon et al., 2011; Stichel et al., 2012a; Garcia-Solsona et al., 2014), and permit a detailed investigation of processes controlling the $d$REE distribution on a basinal scale. Using a multi-parameter mixing model, we quantified the relative importance of transport and biogeochemical processes in governing the observed $d$REE distribution in the deep tropical South Atlantic for the first time.

2. REGIONAL HYDROGRAPHY

Seawater samples were collected during the CoFeMUG (KN195–2) cruise aboard the
**R/V Knorr** (16 November – 13 December 2007) along an E–W transect in the South Atlantic (~12°S) (Fig. 1).

Major water masses sampled in this location can be approximately separated by neutral density ($\gamma^\theta$) surfaces (Fig. 2a), as suggested by Vanicek and Siedler (2002). South Atlantic Central Water (SACW) is found below the mixed layer (~50 m) to ~500 m. Upper-ocean waters (~0–500 m) are transported broadly northwestward or westward via the southern branch of the South Equatorial Current (SSEC), but the eastern side of the section is also influenced by the cyclonic Angola Gyre in the Angola Basin (Fig. 1) (Stramma and England, 1999; Wienders et al., 2000; Mercier et al., 2003). A prominent oxygen minimum zone (OMZ), caused by regional high productivity and low ventilation (Lass and Mohrholz, 2008; Mohrholz et al., 2008), is observed between ~100 m and ~600 m (centred at ~400 m) off the Angolan coast (Fig. 2b).

Antarctic Intermediate Water (AAIW), characterized by a mid-depth salinity minimum immediately below surface waters, extends to ~800 m. Upper Circumpolar Deep Water (UCDW) is observed beneath AAIW. This water mass does not have a clear T–S signature, but can be recognized as a nutrient-rich layer centred at ~1000 m (Fig. 2a). Both AAIW and UCDW spread dominantly northward (Stramma and England, 1999).

North Atlantic Deep Water (NADW), observed below ~1500 m, predominantly spreads southward at the CoFeMUG section, via the major route of the Deep Western Boundary Current and a weaker route near the eastern boundary of the South Atlantic.
Previous studies have suggested that NADW can be further separated into several sub-layers (e.g., Rhein et al., 1995; Stramma and England, 1999; Smethie et al., 2000). The uppermost layer is referred to as upper Labrador Sea Water (ULSW) (e.g., Pickart et al., 1996; Smethie et al., 2000), and is responsible for relatively high temperature and salinity observed at ~1500 m on the western side of the CoFeMUG section (e.g., Rhein et al., 1995; Pickart et al., 1997; Smethie et al., 2000).

Northward-flowing Antarctic Bottom Water (AABW) is found below ~4000 m ($\gamma_n > 28.18$) in the Brazil Basin, as indicated by high dissolved Si content (Noble et al., 2012) (Fig. 2a). This water mass is less prominent in the Angola Basin because its northward transport is blocked by the Walvis Ridge to the south (Fig. 1). A small fraction of AABW enters the Angola Basin from the north through deflection at the Romanche Fracture Zone near the equator, but this tongue of AABW gradually loses its identity via mixing with NADW during its transport to the Angola Basin (Warren and Speer, 1991; Larqué et al., 1997; Stramma and England, 1999).

3. SAMPLES AND METHODS

3.1. Sample collection and ancillary data

119 seawater samples from 12 stations were analyzed for $\delta$REE concentrations. Samples were collected using trace-metal clean techniques; Teflon-coated X–Niskin sampling bottles were deployed on an epoxy-coated CTD rosette attached to a non-metallic line, and were programmed to trip at pre-determined depths. Immediately
Following collection, seawater was filtered through 142-mm 0.4-μm polycarbonate plastic sandwich filters in a class–100 laboratory. Filtered samples were acidified to pH of 1.7 with high-purity HCl (Seastar). All bottles, tubing and filters were acid-cleaned before use.

Salinity (S), potential temperature (T) and dissolved oxygen (dO2) were measured *in-situ* with CTD-mounted sensors. CTD data were not available at several water-depths (mostly ≥1000 m) at Station 1, 7, 9 and 18 due to sensor malfunction. For these depths, T and S data were interpolated from the World Ocean Atlas 2009 (WOA09) seasonal (October–December) climatology (Table A.1). The interpolated T and S values are in good agreement with shipboard measurements where both are available.

Nutrients (e.g., dissolved silica and phosphate), dFe, and dMn concentrations were also measured across the CoFeMUG section (Noble et al., 2012; Saito et al., 2013). Data are available from http://bcodmo.org, and also in the GEOTRACES Intermediate Data Product (Mawji et al., 2015).

### 3.2. Analytical procedure for dREE concentrations

Dissolved REE concentrations were measured at the Department of Earth Sciences, University of Oxford, following Zheng et al. (2015). Briefly, ~100 ml of filtered seawater was spiked with 142Ce–145Nd–171Yb. REEs were preconcentrated with Fe coprecipitation, followed by purification through a simple one-stage ion-exchange chromatographic separation using AG 1–X8 anion exchange resin (100–200 mesh, Bio-Rad) to remove Fe. Dissolved REEs were analyzed on a magnetic sector-field ICP–MS (Element 2, Thermo Scientific) coupled with a desolvating nebulizer system.
Oxide interferences (i.e. Ba oxides on Eu, and LREE oxides on HREEs) were negligible (~1%). The procedural blank, typically <1% for all REEs except for Ce (~8%), was monitored for each batch of sample pre-treatment, and corrected batch by batch. Repeated measurements of an in-house seawater standard throughout the course of this study yielded an external reproducibility of <3% (1σ, n=19) for all REEs. Measurements performed on GEOTRACES intercalibration samples (BATS) agree with results reported by other laboratories within 10% (van de Flierdt et al., 2012; Zheng et al., 2015).

3.3. Ce anomaly calculation

The extent of oxidative removal of Ce, due to formation of insoluble Ce⁴⁺, can be quantified by the “Ce anomaly”, which represents the ratio between the measured $d_{Ce}$ concentration and the predicted Ce concentration ($Ce^*$) that would occur without this oxidative removal process (i.e., the Ce concentration obtained by interpolating between its neighbouring REE elements). The Ce anomaly in this study is defined as $Ce/Ce^* = [(2 × Ce_{SN} / (La_{SN} + Pr_{SN}))$, where $REE_{SN}$ indicates REE concentrations normalized to the post-Archean Australian shale (PAAS; McLennan, 1989). Positive, or negative, Ce anomalies indicate that $Ce/Ce^*$ values are greater, or smaller, than 1.

3.4. Multi-parameter mixing model

3.4.1. Model description

The oceanic distribution of $d$REEs is controlled by mixing of different water masses,
and by non-conservative processes, such as particle scavenging, remineralization and boundary exchange (e.g., Bertram and Elderfield, 1993; Nozaki and Alibo, 2003; Siddall et al., 2008; Singh et al., 2012; Haley et al., 2014). An inverse model, based on optimum multiparameter (OMP) analysis, was developed to deconvolve the effect of conservative mixing and non-conservative processes from the observed concentrations (e.g., Tomczak and Large, 1989; Karstensen and Tomczak, 1998; Hupe and Karstensen, 2000; Singh et al., 2012).

Briefly, the observed concentration \( x_{obs}^j \) of a conservative tracer \( j \) in a given water parcel can be expressed as a mixture of \( n \) pre-defined end-member water types as:

\[
\sum_{i=1}^{n} f_i \times x_i^j = x_{obs}^j \quad \text{(Eq 1)}
\]

where \( f_i \) represents the fraction of end-member water type \( i \), and \( x_i^j \) represents the characteristic value of the tracer \( j \) in the pre-defined end-member water type \( i \).

For non-conservative tracers, a residual term \( \Delta x^j \) is added to capture the net effect of all non-conservative processes:

\[
\sum_{i=1}^{n} f_i \times x_i^j + \Delta x^j = x_{obs}^j \quad \text{(Eq 2)}
\]

Mass conservation requires that the mass fractions \( f_i \) sum to 1:

\[
\sum_{i=1}^{n} f_i = 1 \quad \text{(Eq 3)}
\]

The number and type of available tracers sets the total number of equations.
defining the end-member properties characteristic of each tracer ($x_i^j$), the system of conservation equations can be solved for the mixing fractions ($f_i$), and the non-conservative terms ($\Delta x^j$) simultaneously.

In this study, potential temperature and salinity were used as conservative tracers, and dissolved silicate (Si), phosphate (PO$_4$), $d$Nd and $d$Yb were used as non-conservative tracers. Nd and Yb were selected to represent the LREEs and HREEs respectively.

The analysis was limited to samples below water depths of ~1000 m at the CoFeMUG section to avoid complications associated with defining end-members in the shallow ocean, where local variability can be important, and where the concept of water mass mixing is less applicable. Four end-members were defined: UCDW, upper NADW (UNADW), lower NADW (LNADW) and AABW. UNADW corresponds to ULSW and classic Labrador Sea Water, and LNADW refers to the rest of NADW fed by overflows at the Greenland–Iceland–Scotland ridge (e.g., Marsh, 2000; Vanicek and Siedler, 2002).

The system described above consists of 7 equations (i.e. based on T, S, Si, PO$_4$, $d$Nd, $d$Yb and mass conservation). A fixed $\Delta$Si/$\Delta$PO$_4$ ratio of 40 was used in the model to reduce one unknown (i.e., $\Delta$Si), based on previously observed and modelled results (e.g., Takeda, 1998; Hupe and Karstensen, 2000). This system is just-determined (i.e., the number of unknowns equates to the number of equations) for 4 end-member mixing; the 7 unknowns are the mass fractions of each of the 4 end-member water masses ($f_1$ to $f_4$), and the non-conservative terms $\Delta$PO$_4$, $\Delta$Nd and $\Delta$Yb.
This system of equations was solved using the conjugate gradient method, which is a widely used iterative method for solving systems of linear equations (Tarantola, 2005). Computation using this method is inexpensive and fast for each iterative step, although sometimes it may require long iterations. The conjugate gradient method used in our model contrasts with the non-negative least-squares regression method used commonly in the extended OMP analysis, which forces solution to be non-negative for the non-conservative terms (e.g., Hupe and Karstensen, 2000). This change was necessary because the terms ΔNd and ΔYb can be either negative (i.e. removal) or positive (i.e. addition).

3.4.2. Definition of end-member characteristics

End-member properties (Table 1) for the 4 water masses (UCDW, UNADW, LNADW and AABW) were pre-defined based on observational data in the corresponding neutral-density layers (Vanicek and Siedler, 2002). End-member values for T, S, Si, PO₄ were selected using historical data from the World Ocean Circulation Experiment (WOCE, http://www.ewoce.org). For northerly-sourced waters, end-member values were based on data measured at 27.75 < γⁿ < 27.89 (~1000–2000 m) between 30°N and 60°N in the North Atlantic for UNADW, and at 27.89 < γⁿ < 28.12 (~2000–5000 m) in the same area for LNADW. For southerly-sourced waters, end-member values were taken from data collected in areas south of 15°S at 27.55 < γⁿ <27.75 (~500–2000 m) for UCDW, and at γⁿ >28.12 (>~4000 m) between 35°S and 45°S for AABW. Because of the limited availability of dNd and dYb concentration data relative to that of traditional hydrographic tracers, large geographic areas were chosen to cover reasonable amount of dNd and dYb data, so that end-member values for all tracers of
each water mass can be defined in the same geographic area. The hydrographic end-
member values defined in this study are consistent with those defined for these water
masses in previous studies (Larqué et al., 1997; Lee et al., 2003).

End-member values for $d_{\text{Nd}}$ and $d_{\text{Yb}}$ concentrations were based on the available data
in the same regions used to define other tracers, and are given in Table 1. The larger
areas used provide ~15–30 observations for $d_{\text{Nd}}$ and ~8–20 for $d_{\text{Yb}}$ for each end-
member. Characteristic $d_{\text{Nd}}$ and $d_{\text{Yb}}$ concentrations for UNADW and LNADW were
defined based on $d_{\text{REE}}$ data reported by Elderfield and Greaves (1982), de Baar et al.
and Stichel et al. (2015). The pre-defined $d_{\text{Nd}}$ end-member values for the two water
masses in this study agree well with the latest measurements from the GEOTRACES
GA02 section (Lambelet et al., 2016).

For UCDW and AABW, end-member values were based on $d_{\text{REE}}$ data reported in
Jeandel (1993), German et al. (1995), Rickli et al. (2010), Stichel et al. (2012a),
Garcia-Solsona et al. (2014), Hathorne et al. (2015) and our $d_{\text{REE}}$ data (>100 new
measurements) from GEOTRACES GA10 section along ~40°S
(http://www.egeotraces.org). Although $d_{\text{Nd}}$ and $d_{\text{Yb}}$ end-member values for UCDW
were based on a broadly defined geographic area (i.e., south of 15°S), they show little
difference if a geographic constraint consistent with AABW (i.e., 35–45°S) was
applied, because the majority of existing $d_{\text{Nd}}$ and $d_{\text{Yb}}$ data for UCDW were
measured around ~40°S. A major change in $d_{\text{Nd}}$ concentrations in AABW was
observed between the area around ~40°S (>30 pmol/kg Nd) and Polar regions south
of ~50°S (~25 pmol/kg dNd) (Stichel et al., 2012a; German et al., 1995; Garcia-Solsona et al., 2014; Hathorne et al., 2015), indicating significant addition of dNd within these areas. The detailed mechanism for this addition, however, is not clear. In this study, we defined dNd and dYb end-member values based on data close to ~40°S, so that our deconvolution results do not integrate any dREE addition occurring south of ~40°S.

3.4.3. Perturbation experiments and robustness evaluation

The sensitivity of the deconvolution results to the selection of end-member values was assessed by numerical Monte Carlo perturbation experiments. Uniformly distributed random noise was imposed on the pre-defined end-member values to account for the natural variability in regions where the end-members were defined (Table 1), and was also added on the measured data to reflect the uncertainty associated with the analytical precision of the measurements (Fig. S1). A uniform distribution of noise was used, rather than a normal distribution, so that the results of perturbation experiments were not biased towards the mean end-member values provided in Table 1. Any combination of end-member values within the range of ± 1 standard deviation provided in Table 1 had equal chance of being tested in our model. A total of 250,000 perturbation experiments were conducted for each sample in the section to fully characterize the probability distributions of the solutions.

The robustness of the spatial pattern of ΔNd and ΔYb values is assessed using a rank analysis technique. The ΔNd or ΔYb values for all the samples along the CoFeMUG section are first ranked, independently, for each Monte Carlo perturbation experiment.
The number of times that the $\Delta$Nd or $\Delta$Yb values of each sample rank in the bottom or top third, relative to other samples in the section, is then counted across all Monte Carlo experiments. This count provides a measure of the probability that a given sample produces $\Delta$Nd or $\Delta$Yb results low or high relative to other samples in the section across all perturbation experiments. To assess whether the resulting count is due to chance alone, it is compared with the number of counts expected from a random process. The probability that a particular $\Delta$Nd or $\Delta$Yb value ranks in the bottom or top third by chance alone is 1/3. For 250,000 Monte Carlo experiments, the binomial distribution predicts, with a 95% confidence level, that the number of times a random number will fall in the bottom or top third is $83,333 \pm 388$ (Borradaile, 2003). Samples with a count falling outside this range are therefore considered to have $\Delta$Nd (or $\Delta$Yb) values that are robustly low or high.

4. RESULTS

4.1. Dissolved REE concentrations

For simplicity, only the distributions of $d$Nd, $d$Yb, $d$Ce and Ce anomaly are shown in Fig. 3. Neodymium represents the $d$LREEs (La to Dy), and Yb represents $d$HREEs (Ho to Lu). Cerium is shown because of its unique redox properties. Dissolved concentrations for all 14 REEs are reported in Appendix (Table A.1). Representative vertical profiles are available in Supplemental Material (Fig. S2).

Characteristic $d$Nd profiles along the CoFeMUG section show a decrease from ~17 pmol/kg in the surface to ~13 pmol/kg at ~400–1000 m, followed by a continuous
increase towards the bottom. Notable exceptions are observed at stations affected by the OMZ off the Angola shelf (Stations 13–17), where secondary $d$Nd maxima develop at ~400 m, coincident with the core of the OMZ (Fig. 3). Typical $d$Yb profiles show a ~2-fold increase from ~2.5 pmol/kg in surface waters to ~5.5 pmol/kg at ~1000–1500 m, followed by a <~25% increase towards the bottom. The $d$Ce concentrations display surface maxima at all stations, followed by a rapid decrease with depth. They remain low below ~400 m. Secondary $d$Ce maxima are found at ~400 m at stations 15 and 17 within the OMZ.

The $d$REE distributions show clear lateral variability across the section (Fig. 3). Surface water $d$REE concentrations are high close to the Angola coast, and decrease offshore from Station 18 to Station 17 before reaching relatively constant values at the remaining open-ocean stations. Plumes of high $d$Nd, $d$Ce and Ce anomaly values are observed, coincident with the subsurface OMZ at ~400 m off the Angola shelf (Fig. 3). Similar elevated $d$Nd concentrations have previously been observed in the nearshore OMZ in the eastern North Atlantic (~20°N) (Stichel et al., 2015). A small east-to-west $d$Yb decrease gradient exists at ~400 m at the CoFeMUG section, although the $d$Yb plume is not well defined. Below ~4000 m, deep waters in the Brazil Basin show higher $d$Nd and $d$Yb concentrations than in the Angola Basin.

Three notable features characteristic of the $d$Ce distribution along the CoFeMUG section include the low concentrations above the mid-Atlantic ridge (MAR) (Fig. 3), a small plume of high $d$Ce in the OMZ at ~400 m off the Angola coast, and a prominent plume of $d$Ce near the African continental margin between ~1000 m and ~4000 m (Fig. 3).
Shale-normalized REE patterns from representative stations in the Brazil Basin (Station 4) and the Angola Basin (Station 15) are shown in Fig. 4. REE patterns are relatively flat in surface waters, showing only weak Ce negative anomalies. These features are commonly observed in other parts of the ocean (e.g., Bertram and Elderfield, 1993; Stichel et al., 2012b; Jeandel et al., 2013; Garcia-Solsona et al., 2014), and likely reflect the influence of terrigenous input. The degree of HREE enrichment and the negative Ce anomalies generally become stronger with increasing depth, as observed previously for the South Atlantic (German et al., 1995; Garcia-Solsona et al., 2014).

4.2. Deconvolution results of the end-member mixing model

4.2.1. Mixing fractions

The mixing fractions for UCDW, NADW (combined UNADW and LNADW) and AABW are shown in Fig. 5. The results are consistent with previous modelling results and the hydrographic observations for the South Atlantic (e.g., Larqué et al., 1997; Stramma and England, 1999).

The fraction of UCDW is maximum (~100%) at ~1000 m, and gradually decreases to <20% at ~2000 m. The diminished UCDW fraction with depth is balanced by the increased influence of NADW, which dominates the section between ~2000 m and ~3500 m with fractions reaching >80%. Below ~3500 m, the fraction of NADW progressively declines to <20% near the seafloor in the Brazil Basin, while AABW
fraction increases from <20% to >80%. Consistent with hydrographic observations, the fraction of NADW remains high (~80%) in the deep Angola Basin, where the fraction of AABW is low (i.e. ~20%).

4.2.2. Non-conservative components: ΔNd and ΔYb

The non-conservative components ΔNd and ΔYb represent the difference between measured dNd and dYb concentrations and the concentrations expected only by mixing of the pre-defined end-member water masses. The patterns of ΔNd and ΔYb for all samples deeper than 1000 m across the CoFeMUG section are shown in Fig. 6. Negative values indicate net removal; positive values imply net excess. The relative contributions of ΔNd and ΔYb to the total measured dNd and dYb concentrations are shown in Fig. 7. Results of the mixing model (Fig. 6 and 7) draw out features that are related to geochemical processes affecting the REEs, but are not visible from the distribution of total concentrations alone (Fig. 3).

The strongest dNd removal (ΔNd < -1 pmol/kg) is observed above the Mid-Atlantic Ridge (MAR) (Fig. 6), representing >5% of the measured dNd concentrations (Fig. 7). High Nd removal (ΔNd ≈ ~1 pmol/kg) was also found at depth between ~1000 m and 3000 m in the Brazil Basin (e.g., Station 1), representing ~5% of the total dNd concentrations for these samples. Addition of dNd, up to 5pmol/kg, was observed in the deep Brazil Basin (>~3500 m). Two plumes of significant dNd excess were found in the Angola Basin at depths of ~1500 m and below ~4000 m respectively, with ΔNd values generally increasing towards the Angola margin. The dNd excess at ~4000 m, with ΔNd values of up to ~8 pmol/kg, accounts for up to ~25% of the total dNd
concentrations, and is the strongest non-conservative signal along the section. In comparison, the excess $d$Nd plume at ~1500 m, with $\Delta$Nd values of ~4 pmol/kg, accounts for ~20% of the measured total $d$Nd concentrations.

In contrast to $d$Nd, no net removal of $d$Yb was found above the MAR, and, in most areas of the Brazil Basin, $d$Yb shows minor excess of <0.5 pmol/kg, representing only <5% of the measured $d$Yb. Excess $d$Yb values of up to ~1.25 pmol/kg, which accounts for as much as ~20% of the total $d$Yb concentrations, were observed in the Angola Basin. Unlike $d$Nd, $d$Yb shows almost ubiquitous excess throughout that basin. Although two plumes are suggested in the contour plots at ~1500 m and ~4000 m (Fig. 6 and 7), they are not as well-separated as those for $d$Nd.

4.2.4. Robustness of spatial patterns of the $\Delta$Nd and $\Delta$Yb results

The spatial patterns of $\Delta$Nd and $\Delta$Yb across the CoFeMUG section are robust, as revealed by the rank analysis on all results of Monte Carlo perturbation experiments (Fig. 8). The modelling results are not governed by chance, because $\Delta$Nd and $\Delta$Yb results that rank in the bottom or top third fall outside the counts predicted by the binomial distribution for a random process (i.e. 83,333 ± 388, 95% confidence level) for all samples.

The spatial distribution of probability shown in Figure 8 is based on the number of times that $\Delta$Nd (and $\Delta$Yb) results of a sample are higher or lower than the results of two thirds of samples in the section across all perturbation experiments. This treatment captures the inherent relationship of a $\Delta$Nd or $\Delta$Yb result, regardless of its
actual value, relative to all other samples in the CoFeMUG section across 250,000 perturbation experiments, and directly characterizes the likelihood of each $\Delta$Nd and $\Delta$Yb result being high (or low) across the section. The probability that $\Delta$Nd results rank in the bottom-third is highest (>0.9) in areas above the MAR and >0.7 between ~1000-3000 m at Station 1 (Fig. 8c). The probability that $\Delta$Nd results fall in the top-third is high in the deep Brazil Basin (~0.7), and is the highest (>~0.7-0.9) at ~1500 m and below ~4000 m near the continental margin in the Angola Basin (Fig. 8a).

Although the fraction of non-conservative behaviour for $d$Nd is high (up to ~15% of total $d$Nd) at ~1000 m in the west side of the section (Fig. 7), the probability that $\Delta$Nd results fall in the top-third in this area is ~0.4 (Fig. 8a), close to that predicted for a random process (~0.33), indicating that the results in this region are sensitive to the choice of end-member values. Except for this region, the probability distributions of $\Delta$Nd (Fig. 8a, c) are consistent with key features of the absolute and relative $\Delta$Nd patterns (Fig. 6 and 7), indicating that the $\Delta$Nd patterns are statistically stable. That is, patterns in Fig. 6 and 7 are relatively insensitive to the selected end-member values. Similarly, good agreement was observed between the probability distributions of $\Delta$Yb (Fig. 8b, d) and $\Delta$Yb patterns (Fig. 6 and 7), suggesting that $\Delta$Yb patterns are also robust.

5. DISCUSSION

5.1. Release of REEs from water-column reduction of oxides

High $d$REE concentrations in surface waters near the Angola coast (Station 17 and 18) are observed (Fig. 3), and agree with high $d$Nd concentrations observed previously in
this region (Rickli et al., 2010). Based on Nd-isotope evidence, the high $d_{\text{Nd}}$ concentration was attributed to local decomposition of Fe-Mn oxides in the water column, or in shelf sediments, under low oxygen conditions (Rickli et al., 2010). This interpretation is consistent with more recent $d_{\text{Fe}}$ and $d_{\text{Mn}}$ observations, which are also high in coastal surface waters (Noble et al., 2012).

Dissolved REE enrichment is also observed in the OMZ (Fig. 3). This enrichment is similar, albeit of smaller magnitude, to the enrichment observed at the oxic/anoxic interface in the water column in anoxic basins. It has been shown to be caused by the desorption of REEs upon reductive dissolution of Fe-Mn oxides (e.g., de Baar et al., 1988; German and Elderfield, 1989; German et al., 1991a; Sholkovitz et al., 1992; Schijf et al., 1995). The close association between $d_{\text{REEs}}$ and the redox cycling of Fe and Mn in the OMZ along the CoFeMUG section is demonstrated by the significant positive correlation between $d_{\text{REEs}}$ (including the Ce anomaly) and $d_{\text{Fe}}$, or $d_{\text{Mn}}$, observed for the data at stations in the OMZ ($dO_2 < \sim 60$ $\mu$M) at ~400 m (a quasi-isopycnic layer with density of $\sim 27.0-27.1$) (Fig. 9). No such correlation is visible in data from the same depth from stations located outside the OMZ.

The close association between REEs, Fe and Mn in the OMZ is also reflected in the REE patterns (Fig. 10). Seawater $d_{\text{REE}}$ concentrations at ~400 m were normalized to the mean $d_{\text{REE}}$ concentrations averaged across all CoFeMUG samples at ~1000 m to better reveal small variations in $d_{\text{REE}}$ patterns. Compared to seawater outside the OMZ (Station 1–9), seawater influenced by the OMZ shows REE patterns characterized by pronounced $d_{L_{\text{REE}}}$ enrichment and weak negative or positive Ce anomalies (Fig. 10a). These features are consistent with reduction of Fe-Mn oxides.
because these particles display typical LREE-enriched patterns with prominent Ce
extcess (e.g., de Baar et al., 1988; German and Elderfield, 1989; Sholkovitz et al.,
1994; Bayon et al., 2004; Freslon et al., 2014) (Fig. 10b).

The seawater REE patterns provide evidence for in-situ release of dREEs from
reduction of Fe-Mn oxides in the water-column of the OMZ. Lateral transport of
dREEs released from sediments on the African shelf may also occur, but if lateral
transport were the dominant REE source, one would have expected a progressive
depletion of dLREEs relative to dHREEs with increasing distance from shore due to
continuous scavenging, and progressive development of a negative Ce anomaly
towards that of seawater outside the OMZ. More pronounced dLREE enrichment and
positive Ce anomalies observed at Station 15 and 17 relative to the REE pattern found
at Station 18, however, clearly contradicts the expected trend, suggesting in-situ
regeneration of dREEs (Fig. 10a). This observation is consistent with that in the
eastern North Atlantic (~20°N), where Nd isotopes also indicate major release of
scavenged Nd from particles in the OMZ off the Mauritanian shelf (Stichel et al.,
2015). Our data indicate a local dO₂ threshold of ~25 μM (i.e., observed at Station 17
and 15) that enables reductive release of dREEs from Fe-Mn oxides. This value is
slightly higher than that reported for the OMZ in the northwest Indian Ocean (dO₂ <
~15 μM) where recycling of dREEs from particles occurs (German and Elderfield,
1990), but the observation in the OMZ in the eastern North Atlantic demonstrates that
desorption of dREEs from particles can happen at even higher dO₂ concentrations
(~40 μM) (Stichel et al., 2015).

In contrast, secondary concentration maxima are absent in dNd profiles at water
depths corresponding to the OMZs in the eastern equatorial Pacific, southeast Pacific
and Arabian Sea where local $\delta O_2$ concentrations can be <15 μM (Grasse et al., 2012;
Jeandel et al., 2013; Goswami et al., 2014). It remains unclear whether these previous
observations truly reflect a lack of $\delta$Nd enrichment in OMZs due to the relatively low
spatial and depth resolution of available data. Enrichment or depletion of an element
may only become apparent when individual profiles are considered in the context of
its distribution at the basinal scale, as demonstrated by $\delta$Yb from the CoFeMUG
section, whose enrichment in the OMZ is not visible from any individual profile
(Supplemental Material, Fig. S2), but is clearly suggested by an east–west
concentration gradient at ~400 m across the section (Fig. 3). Alternatively, the
contrasting observations indicate that, besides $\delta O_2$ contents, multiple parameters,
including regional REE input, particle dynamics and hydrographic conditions
collectively determine the REE cycling in OMZs.

5.2. The dominance of preformed $d$REEs in Atlantic deep waters

Concentrations of $d$REEs in deep-waters of the central Atlantic are dominantly
controlled by mixing of the major Atlantic water masses (>75%), rather than by
geochemical processes operating during transit of these waters from their source
regions (Fig. 7). Deviations from purely conservative mixing for the $d$REEs are up to
a maximum of 25%. The dominance of the preformed component in setting deep-
water $d$REE concentrations explains why these concentrations resemble the general
water mass structure of the South Atlantic (Fig. 2 and 3). For example, higher $d$REE
concentrations in the deep Brazil Basin than those observed in the deep Angola Basin
is largely related to the presence of AABW in the Brazil Basin.
Preformed $d$REEs are particularly important in setting observed $d$REE concentrations in the deep Brazil Basin (Fig. 7), where ~95% of the observed $dYb$, and ~90% of $dNd$, can be explained by conservative water-mass mixing. A slightly higher percentage of preformed $dYb$ than that of preformed $dNd$ is consistent with the general behaviour of REEs in the ocean that HREEs are less particle-reactive than LREEs (e.g., Wood, 1990; Sholkovitz et al., 1994).

The large preformed contribution to deep-waters in the Brazil Basin predicts that $d$REEs should correlate well with other conservative tracers, such as $dSi$, which behaves almost conservatively in the deep South Atlantic (e.g., Broecker et al., 1991; Sarmiento et al., 2007). This explains the particularly good linear correlation between $d$REE and $dSi$ ($R^2 > 0.9$) observed below ~2000 m in the Brazil Basin (Fig. 11). The larger non-conservative behaviour of $d$REE concentrations in the deep Angola Basin may explain the poorer $d$REE–$dSi$ relationship observed there (Fig. 11).

Our results indicate that the linear $d$REE–$dSi$ relationship in the deep tropical Atlantic results mostly from water mass mixing due to dominantly conservative behaviour of these elements, rather than from local biogeochemical processes coupling the two elements. This conclusion contrasts with studies that have suggested a direct link between the cycling of $dNd$ and $dSi$ in the high-latitude Southern Ocean based on the observed linear relationships between the two elements (e.g., Stichel et al., 2012a; Garcia-Solsona et al., 2014; Hathorne et al., 2015). A possible explanation that reconciles our results with these previous studies relies on the large contrast in opal fluxes between our study region and the Southern Ocean. High opal fluxes in the
Southern Ocean may facilitate strong local regeneration of \(d\)REEs from dissolution of biogenic silica in deep waters in this specific region. In addition, this \(d\)REE regeneration could be further promoted by strong vertical mixing in certain areas of the Southern Ocean. After deep-water \(d\)REEs and \(d\)Si are exported from the Southern Ocean into the sub-tropical and tropical South Atlantic where opal flux is low, their distributions are no longer controlled by a coupled REE and opal cycle, but essentially governed by water mass mixing. A coupled REE–Si cycle was proposed to explain general concentration profiles of \(d\)REEs in the ocean (Akagi, 2013), our results, however, demonstrate that such a coupling is not necessarily true on a global scale.

5.3. Suggested REE sources from sedimentary Fe oxides and remineralization of calcite

The deconvolution enables boundary addition of \(d\)REEs, previously observed for \(d\)Nd in other locations (e.g., Singh et al., 2012; Garcia-Solsona et al., 2014), to be quantified for waters of the tropical south Atlantic. Our deconvolution results show regions where up to 25% of the measured \(d\)REE concentrations cannot be explained by mixing of water-mass end-members, and, by contrasting the spatial pattern of the addition, provide clues about possible mechanisms of boundary addition.

Addition of \(d\)REEs (~10% for \(d\)Nd and ~5% for \(d\)Yb) is observed in AABW in the deep Brazil Basin (>~4000 m), and can be explained by release of \(d\)REEs from \textit{in-situ} remineralization of particles, or by accumulation of remineralized \(d\)REEs along the flow path of AABW from ~40°S. More significant REE addition (up to ~25%) is seen
on the eastern side of the section, in the Angola Basin, with Nd excess seen at two
depths (~1500 m and below ~4000 m), and Yb excess at all depths below ~1500 m
(Fig. 6 and 7). The different distribution of ΔNd and ΔYb in the Angola Basin may
result from different particle reactivity between LREEs and HREEs. Because HREEs
are less particle-reactive than LREEs in seawater (e.g., Wood, 1990; Sholkovitz et al.,
1994), signals of Yb addition are expected to survive longer in the water column, so
that they can be mixed or advected from their source. In contrast, Nd is more quickly
scavenged by particles, so that signs of its addition are likely to be more restricted
spatially.

In contrast to the increased dREE concentrations seen at ~400 m in the OMZ, it is
unlikely that remineralization of particulates in the water-column can explain the
excess REE concentrations seen at ~1500 m in the Angola Basin. The water is well-
oxygenated below ~1000 m (>100 μmol/kg), so that reduction of Fe-Mn oxides in the
water column can be ruled out. Because the strongest dREE excesses are seen close to
the margin (Fig. 6 and 7), release of dREEs from slope sediments seems the most
plausible source to explain the 1500 m REE excess. These dREE excesses are
accompanied by high dFe concentrations (Noble et al., 2012), suggesting that the
release of dREEs from sediments may involve reduction of Fe oxides in the sediment.
Iron oxides are characterized by positive Ce anomalies (e.g., de Baar et al., 1988;
German and Elderfield, 1989; Sholkovitz et al., 1994; Bayon et al., 2004; Freslon et
al., 2014), so their decomposition may also explain the less pronounced negative Ce
anomaly (i.e., higher Ce/ Ce* values) observed at this depth (Fig. 3).

There is no noticeable development of less pronounced negative Ce anomaly
associated with the REE excess below ~4000 m (Fig. 3), suggesting that a different processes must be responsible for this deep REE excess. This 4000 m \( d \)REE excess occurs just below the calcite saturation depth (CCD) (Feely et al., 2004), suggesting that dissolution of calcite might release REEs scavenged from shallower depths back to seawater. Carbonates commonly show seawater-like negative Ce anomalies (Palmer, 1985; Haley et al., 2005; Akagi et al., 2011), rather than positive Ce anomalies typically associated with Fe-Mn oxides and organic matters (Bayon et al., 2004; Freslon et al., 2014), so that dissolution of calcite might explain the absence of a Ce anomaly associated with the increased trivalent REEs below ~4000 m.

The excess \( d \)REEs in the Angola Basin is significantly higher than that found in the Brazil Basin, especially given the fact that AABW is almost absent from the deep Angola Basin (Fig. 5). One explanation for this asymmetry is that particulate fluxes near the African coast are higher, sustained by high surface productivity (Henson et al., 2012), and that seawater \( d \)REE concentrations in the upper ocean (<1000 m) in the Angola Basin are also elevated. Together, these two conditions produce a stronger “REE pump”, leading to higher downward REE fluxes in the deep Angola Basin relative to the Brazil Basin.

In addition, \( \Delta Nd \) and \( \Delta Yb \) results also contain a component of a path-integrated sum of all non-conservative processes along the flow path from the regions where end-member values were defined. Compared to more vigorous transport of NADW along the Deep Western Boundary Current and inflow of AABW, the higher percentage of non-preformed \( d \)REEs in the Angola Basin may be caused by older water mass ages and a more sluggish circulation in this basin, which allow for accumulation of more
regenerated dREEs as compared to the Brazil Basin.

5.4. Scavenging of dLREEs above the mid-Atlantic ridge (MAR)

Recent results have clearly indicated that mid-ocean ridges can represent significant sources of dissolved trace metals, such as Fe, to the water, and metals released from hydrothermal vents can transport over hundreds to thousands of kilometers away from the source (e.g., Klunder et al., 2012; Nishioka et al., 2013; Saito et al., 2013; Fitzsimmons et al., 2014; Hatta et al., 2015; Resing et al., 2015). Such addition has also been seen for dMn and dFe in the CoFeMUG section (Noble et al., 2012; Saito et al., 2013). These new field observations, together with increased recognition of organic metal-binding ligands in hydrothermal fluids (e.g., Sander et al., 2007; Bennett et al., 2008; Toner et al., 2009; Sander and Koschinsky, 2011), have overturned the previous assertion that mineral precipitation and scavenging quantitatively remove Fe from hydrothermal plumes (e.g., German et al., 1991b). Measurements of this study do not indicate any similar release of dREEs to the water-column (Fig. 3). The deconvolution results also confirm this conclusion, and instead quantify removal of dNd above the mid-ocean ridge rather than addition. The lack of dREE addition may be surprising, given that hydrothermal fluids are enriched in dREEs by several orders of magnitude compared to ambient seawater (e.g., Klinkhammer et al., 1994; Mitra et al., 1994; Bau and Dulski, 1999; Douville et al., 1999; Craddock et al., 2010; Schmidt et al., 2010), but is consistent with previous studies indicating quantitative scavenging of dREEs in hydrothermal plumes (e.g., German et al., 1990; Mitra et al., 1994; Bau and Dulski, 1999). The removal of
LREEs observed here is also consistent with previous studies that have demonstrated preferential scavenging of LREEs on Fe-Mn particles during dispersion of particles in neutrally buoyant hydrothermal plumes (German et al., 1990; Rudnicki and Elderfield, 1993; Mitra et al., 1994).

5.5. Apparent decoupling between Ce and Mn in the Angola Basin

Cerium often behaves similarly to Mn in the ocean due to their similar redox potential (e.g., Moffett, 1994b). This is the case, for example, in the OMZ where elevated $d\text{Ce}$ concentration coincides with high $d\text{Mn}$ concentrations at the CoFeMUG section. This is not the case at ~1500 m near the Angolan margin, however, where the plume of high Ce concentrations and Ce anomaly values is not accompanied by parallel enrichment in $d\text{Mn}$ (Noble et al., 2012). This mismatch indicates that some processes, besides inorganic oxidation–reduction, decouple the cycles of these two elements at this depth.

A similar decoupling between Ce and Mn, albeit of much smaller magnitude, was previously observed in the northwest Indian Ocean (German and Elderfield, 1990). This decoupling was attributed to a delicate environment where $d\text{O}_2$ concentrations are sufficiently high to allow for the oxidative precipitation of Mn at the sediment–seawater interface during diffusion of Mn from reduced sediments, but insufficient to cause oxidative removal of Ce from the same sedimentary source. This explanation, however, seems inconsistent with high $d\text{Fe}$ concentrations observed at ~1500 m at the CoFeMUG section (Noble et al., 2012). Because the standard redox potential follows the sequence Fe$<$Mn$<$Ce (Lu et al., 2010), if reduced sediments on the continental
margin serve as a local source of these metals to the water column, enrichment of $dFe$
and $dCe$ at ~1500 m, but not $dMn$, is inconsistent with the redox chemistry of these
elements during their diffusion out of sediments. A possible explanation for this
apparent inconsistency is that Mn content in sediments along the African continental
margin is much lower relative to Fe (Bremner and Willis, 1993), so that the supply of
Mn from the reduced sedimentary source would be intrinsically low. In addition, Ce
may be present as cerium oxides, or be mostly associated with Fe oxides in sediments,
rather than being associated with Mn oxides, as demonstrated previously by data from
pore waters off Peru and California margins (Haley et al., 2004).

6. CONCLUSIONS

This study presents $dREE$ concentrations along a full-depth, zonal section at ~12°S in
the tropical South Atlantic. High $dREE$ concentrations in surface waters and OMZ
(~400 m) near the Angolan coast are likely to result at least partially from
decomposition of Fe-Mn oxides in the water column.

The contribution of water mass mixing to $dREE$ concentrations in deep waters (>1000
m) was quantified using a multi-parameter end-member mixing model. Results show
that >75% of the $dREE$ concentrations are preformed. This explains the observed
strong correlation between $dREE$s and dissolved Si in the deep Brazil Basin; both
elements behave almost conservatively in deep-waters of the Atlantic. The
deconvolution also reveals $dREE$ addition of up to ~10% in AABW in the deep Brazil
Basin, which reflects remineralization of particulates in-situ or along the flow path
from ~40°S. More significant $dREE$ addition of up to 25% was found at ~1500 m and
below ~4000 m in the Angola Basin near the continent–ocean interface, the upper
associated with increased Ce anomalies values and the deeper not. The shallow plume
is attributed to release of $d$REEs from dissolution of sedimentary Fe oxides on the
continental margin, and the deep one to remineralization of calcite. The higher
percentage of $d$REE addition in the Angola Basin compared to that in the Brazil Basin
may reflect the higher particulate fluxes, together with older water masses and a more
sluggish circulation in the Angola Basin that permit accumulation of more non-
conservative $d$REEs during water mass advection from source regions. These
observations suggest that processes responsible for the boundary sources of REEs
differ significantly with region.

Hydrothermal venting at the MAR does not lead to a net $d$REE flux to the deep ocean,
despite injecting significant amount of $d$Fe and $d$Mn at this section. Instead, the
deconvolution indicates that the MAR acts as a net sink for $d$LREEs, and has
negligible effect on the $d$HREE budget.

ACKNOWLEDGEMENTS

We thank Abigail Noble for sub-sampling and shipping samples to Oxford, Chao Liu
for advice on developing the codes for REE deconvolution, and Jie Yang for helping
with sample preparation and stimulating discussions. X.-Y. Zheng was supported by
the Clarendon Scholarship, the Exeter College Mandarin Scholarship from University
of Oxford, the Chinese Student Awards from the Great Britain–China Educational
Trust (GBCET) and W Wing Yip and Brothers bursaries. Comments from Martin
Frank, Stuart Robinson, two anonymous reviewers and the editor Silke Severmann
have significantly improved the manuscript.

REFERENCES


Fig. 1. Map showing the sampling stations of the CoFeMUG cruise (red circles), and the schematic flow patterns of major water masses affecting the region, based on Stramma and England (1999). Blue lines indicate surface-ocean circulation; orange lines denote North Atlantic Deep Water (NADW); yellow dashed lines represent Antarctic Bottom Water (AABW). SSEC: southern branches of the South Equatorial Current; ABF: Angola–Benguela Front.

Fig. 2. (A) Dissolved silicate ($dSi$) along the CoFeMUG section (Noble et al., 2012), and depth ranges of major water masses according to characteristic neutral density surfaces (Vanicek and Siedler, 2002). TSW–Tropical Surface Water; SACW–South Atlantic Central Water; AAIW–Antarctic Intermediate Water; UCDW–Upper Circumpolar Deep Water; NADW–North Atlantic Deep Water; AABW–Antarctic Bottom Water. Numbers above section are CoFeMUG station numbers (Fig. 1). (B) Dissolved O$_2$ showing the OMZ on the Angolan margin (Noble et al., 2012).

Fig. 3. Measured $dNd$, $dYb$, $dCe$ concentrations and Ce anomaly ($Ce/Ce^*$) along the CoFeMUG section. Numbers above section are CoFeMUG station numbers (Fig. 1). Figures were created using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2015).

Fig. 4. Shale-normalized REE patterns from typical stations on either side of the section (Station 4 and 15).

Fig. 5. Results of modelled mixing fractions of UCDW, NADW (combined UNADW and LNADW) and AABW along the CoFeMUG section. Plotted results are the
arithmetic average of 250,000 Monte Carlo perturbation experiments. Figures were created using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2015).

**Fig. 6.** Modelled mean \( \Delta \text{Nd} \) (A) and \( \Delta \text{Yb} \) (B) results over 250,000 perturbation experiments in pmol/kg for depths below 1000 m. Positive values reflect addition of Nd or Yb, while negative values reflect removal, relative to conservative mixing of the water-mass end-members. Figures were created using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2015).

**Fig. 7.** Modelled \( \Delta \text{Nd} \) (A) and \( \Delta \text{Yb} \) (B) relative to respective total dissolved concentrations for depths below 1000 m. Positive values reflect addition of Nd or Yb, while negative values reflect removal. Figures were created using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2015).

**Fig. 8.** Probability distribution characterizing the stability of the spatial patterns of \( \Delta \text{Nd} \) and \( \Delta \text{Yb} \). The white dashed line shows the probability equal to \( 1/3 \) – the limit of statistical significance. Figures were created using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2015).

**Fig. 9.** \( d\text{REE} \) (Ce anomaly)–\( d\text{Fe} \) (\( d\text{Mn} \)) correlations at ~400 m. Significant linear relationships between \( d\text{REEs} \) and \( d\text{Fe} \) or \( d\text{Mn} \) were observed within the OMZ (orange), but not for stations outside the OMZ (black; \( d\text{O}_2 > \sim 60 \mu\text{M} \)).

**Fig. 10.** REE patterns normalized against the average of REE concentrations at ~1000 m at the CoFeMUG section. (A) Seawater measurements from this study from
~400 m, with samples outside the OMZ shaded in grey. Note the LREE and Ce enrichment for samples in the OMZ, consistent with release of REEs from Fe-Mn oxides. (B) Fe-Mn leachate from sediments in the Angola Basin (Bayon et al., 2004), demonstrating expected patterns of REEs from dissolution of Fe-Mn oxides.

**Fig. 11.** Deep-water (>2000 m) dREE–dSi relationship in the Brazil and Angola Basin.
Table 1. Characteristics of each tracer in the 4 pre-defined end-member water types

<table>
<thead>
<tr>
<th>Type</th>
<th>T (°C)</th>
<th>S</th>
<th>Silicate (μmol/L)</th>
<th>Phosphate (μmol/L)</th>
<th>dNd (pmol/kg)</th>
<th>dYb (pmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCDW</td>
<td>3.32 ± 0.52</td>
<td>34.51 ± 0.10</td>
<td>44.57 ± 8.84</td>
<td>2.22 ± 0.11</td>
<td>12.09 ± 0.96</td>
<td>5.37 ± 0.37</td>
</tr>
<tr>
<td>NADW</td>
<td>4.21 ± 1.38</td>
<td>35.02 ± 0.22</td>
<td>12.01 ± 1.82</td>
<td>1.14 ± 0.06</td>
<td>16.89 ± 5.07</td>
<td>4.50 ± 0.41</td>
</tr>
<tr>
<td>LNADW</td>
<td>2.61 ± 0.38</td>
<td>34.93 ± 0.03</td>
<td>24.94 ± 10.66</td>
<td>1.26 ± 0.16</td>
<td>19.17 ± 5.59</td>
<td>4.98 ± 0.53</td>
</tr>
<tr>
<td>AABW</td>
<td>0.49 ± 0.51</td>
<td>34.71 ± 0.04</td>
<td>113.47 ± 14.40</td>
<td>2.14 ± 0.14</td>
<td>32.20 ± 4.85</td>
<td>7.86 ± 0.98</td>
</tr>
</tbody>
</table>

\(^1\) see text for details on how end-member values were defined and on references cited.
Figure_04

Brazil Basin (station 4)

Angola Basin (station 17)
Figure 10 revised

(A) REE / Average (1000m)

(B) Fe-Mn leachate (Angola Basin sediments)

REE / AverageREE (1000m)

seawater at ~400 m

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

STN 1–9

STN 10

STN 11

STN 13

STN 15

STN 17

STN 18

(A)

(B) (X10^6)
Click here to download Appendix: Table A1_CoFeMUG REE.xlsx