

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

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20 **Abstract**

21

22 This study presents new concentration measurements of dissolved REEs (*d*REEs)
23 along a full-depth east-west section across the tropical South Atlantic (~12°S), and
24 uses these data to investigate the oceanic cycling of the REEs. Enrichment of *d*REEs,
25 associated with the redox cycling of Fe-Mn oxides, is observed in the oxygen
26 minimum zone (OMZ) off the African shelf. For deeper-waters, a multi-parameter
27 mixing model was developed to deconvolve the relative importance of physical
28 transport (i.e. water mass mixing) from biogeochemical controls on the *d*REE
29 distribution in the deep Atlantic. This approach enables chemical processes involved
30 in REE cycling, not apparent from the measurements alone, to be distinguished and
31 quantified. Results show that the measured *d*REE concentrations below ~1000 m are
32 dominantly controlled (>75%) by preformed REE concentrations resulting from water
33 mass mixing. This result indicates that the linear correlation between *d*REEs and
34 dissolved Si observed in Atlantic deep waters results from the dominantly
35 conservative behaviour of these tracers, rather than from similar chemical processes
36 influencing both *d*REEs and Si. Minor addition of *d*REEs (~10% of *d*Nd and ~5% of
37 *d*Yb) is observed in the deep (>~4000 m) Brazil Basin, resulting from either
38 remineralization of particles *in-situ* or along the flow path. Greater addition of *d*REEs
39 (up to 25% for *d*Nd and 20% for *d*Yb) is found at ~1500 m and below ~4000 m in the
40 Angola Basin near the African continental margin. Cerium anomalies suggest that
41 different sources are responsible for these *d*REE addition plumes. The 1500 m excess
42 is most likely attributed to *d*REE release from Fe oxides, whereas the 4000 m excess
43 may be due to remineralization of calcite. Higher particulate fluxes and a more
44 sluggish ocean circulation in the Angola Basin may explain why the *d*REE excesses in

45 this basin are significantly higher than that observed in the Brazil Basin.
46 Hydrothermal venting over the mid-Atlantic ridge acts as a regional net sink for light
47 REEs, but has little influence on the net budget of heavy REEs. The combination of
48 dense REE measurements with water mass deconvolution is shown to provide
49 quantitative assessment of the relative roles of physical and biogeochemical processes
50 in the oceanic cycling of REEs.

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70 **1. INTRODUCTION**

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

82

83 Fractionations between trivalent *d*REEs in seawater are also influenced by other
84 processes, including input from external REE sources and mixing of water masses
85 (Elderfield et al., 1988; Byrne and Sholkovitz, 1996). The behavior of Ce is also
86 mediated by redox transformation between more soluble Ce³⁺ and insoluble Ce⁴⁺.
87 Fractionation between the *d*REEs are normally visualized by normalizing measured
88 REE concentrations to a suitable reference, usually shale or another water mass in the
89 ocean (e.g., Zhang and Nozaki, 1998; Nozaki et al., 1999; Alibo and Nozaki, 2004;
90 Zhang et al., 2008; Haley et al., 2014). Such REE patterns can allow for tracing of a
91 variety of oceanic processes (e.g., Sholkovitz et al., 1994; Alibo and Nozaki, 2004;
92 Hatta and Zhang, 2006; Zhang et al., 2008).

93

94 Considerable field observations and laboratory experiments have been conducted to

95 study the marine cycling of REEs (e.g., Elderfield and Greaves, 1982; de Baar et al.,
96 1985; Byrne and Kim, 1990; German et al., 1990; Bertram and Elderfield, 1993;
97 Greaves et al., 1994; Zhang and Nozaki, 1996; Douville et al., 1999; Nozaki and
98 Alibo, 2003; Johannesson et al., 2011; Haley et al., 2014). Other studies have
99 primarily focused on Nd because of the utility of Nd isotopes as a tracer for ocean
100 circulation (e.g., Amakawa et al., 2009; Carter et al., 2012; Grasse et al., 2012; Singh
101 et al., 2012; Grenier et al., 2013; Jeandel et al., 2013; Pearce et al., 2013; Molina-
102 Kescher et al., 2014). In spite of these efforts, substantial uncertainties remain about
103 the processes that control the distribution of REEs in the ocean.

104

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

116

117 Another limitation relates to incomplete understanding of exchange processes at the
118 continent–ocean interface. Recent studies, mostly based on Nd, have demonstrated
119 that seawater-sediment interactions on continental margins, a process termed as

120 “boundary exchange” (e.g., Lacan and Jeandel, 2005a; Jeandel et al., 2007), can
121 significantly influence Nd concentration and isotope signature in seawater. Globally,
122 it is thought that boundary exchange could represent the dominant source of the
123 oceanic Nd budget (e.g., Tachikawa et al., 2003; Arsouze et al., 2009; Rempfer et al.,
124 2011). The local expression of this boundary exchange, however, is neither well
125 resolved geographically nor understood mechanically, and existing observations are
126 heterogeneous. Observations suggest that REEs can either be added or removed from
127 the water column near the continent–ocean interface (e.g., Zhang and Nozaki, 1998;
128 Bayon et al., 2011; Carter et al., 2012; Grasse et al., 2012; Grenier et al., 2013;
129 Garcia-Solsona et al., 2014).

130

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

141

142 **2. REGIONAL HYDROGRAPHY**

143

144 Seawater samples were collected during the CoFeMUG (KN195–2) cruise aboard the

145 *R/V Knorr* (16 November – 13 December 2007) along an E–W transect in the South
146 Atlantic (~12°S) (Fig. 1).

147

148 Major water masses sampled in this location can be approximately separated by
149 neutral density (γ^n) surfaces (Fig. 2a), as suggested by Vanicek and Siedler (2002).

150 South Atlantic Central Water (SACW) is found below the mixed layer (~50 m) to

151 ~500 m. Upper-ocean waters (~0–500 m) are transported broadly northwestward or

152 westward via the southern branch of the South Equatorial Current (SSEC), but the

153 eastern side of the section is also influenced by the cyclonic Angola Gyre in the

154 Angola Basin (Fig. 1) (Stramma and England, 1999; Wienders et al., 2000; Mercier et

155 al., 2003). A prominent oxygen minimum zone (OMZ), caused by regional high

156 productivity and low ventilation (Lass and Mohrholz, 2008; Mohrholz et al., 2008), is

157 observed between ~100 m and ~600 m (centred at ~400 m) off the Angolan coast (Fig.

158 2b).

159

160 Antarctic Intermediate Water (AAIW), characterized by a mid-depth salinity

161 minimum immediately below surface waters, extends to ~800 m. Upper Circumpolar

162 Deep Water (UCDW) is observed beneath AAIW. This water mass does not have a

163 clear T–S signature, but can be recognized as a nutrient-rich layer centred at ~1000 m

164 (Fig. 2a). Both AAIW and UCDW spread dominantly northward (Stramma and

165 England, 1999).

166

167 North Atlantic Deep Water (NADW), observed below ~1500 m, predominantly

168 spreads southward at the CoFeMUG section, via the major route of the Deep Western

169 Boundary Current and a weaker route near the eastern boundary of the South Atlantic

170 (Larqué et al., 1997; Stramma and England, 1999; Arhan et al., 2003). Previous
171 studies have suggested that NADW can be further separated into several sub-layers
172 (e.g., Rhein et al., 1995; Stramma and England, 1999; Smethie et al., 2000). The
173 uppermost layer is referred to as upper Labrador Sea Water (ULSW) (e.g., Pickart et
174 al., 1996; Smethie et al., 2000), and is responsible for relatively high temperature and
175 salinity observed at ~1500 m on the western side of the CoFeMUG section (e.g.,
176 Rhein et al., 1995; Pickart et al., 1997; Smethie et al., 2000).

177

178 Northward-flowing Antarctic Bottom Water (AABW) is found below ~4000 m ($\gamma^n >$
179 28.18) in the Brazil Basin, as indicated by high dissolved Si content (Noble et al.,
180 2012) (Fig. 2a). This water mass is less prominent in the Angola Basin because its
181 northward transport is blocked by the Walvis Ridge to the south (Fig. 1). A small
182 fraction of AABW enters the Angola Basin from the north through deflection at the
183 Romanche Fracture Zone near the equator, but this tongue of AABW gradually loses
184 its identity via mixing with NADW during its transport to the Angola Basin (Warren
185 and Speer, 1991; Larqué et al., 1997; Stramma and England, 1999).

186

187 **3. SAMPLES AND METHODS**

188

189 **3.1. Sample collection and ancillary data**

190

191 119 seawater samples from 12 stations were analyzed for d REE concentrations.
192 Samples were collected using trace-metal clean techniques; Teflon-coated X-Niskin
193 sampling bottles were deployed on an epoxy-coated CTD rosette attached to a non-
194 metallic line, and were programmed to trip at pre-determined depths. Immediately

195 following collection, seawater was filtered through 142-mm 0.4- μm polycarbonate
196 plastic sandwich filters in a class-100 laboratory. Filtered samples were acidified to
197 pH of 1.7 with high-purity HCl (Seastar). All bottles, tubing and filters were acid-
198 cleaned before use.

199

200 Salinity (S), potential temperature (T) and dissolved oxygen ($d\text{O}_2$) were measured *in-*
201 *situ* with CTD-mounted sensors. CTD data were not available at several water-depths
202 (mostly ≥ 1000 m) at Station 1, 7, 9 and 18 due to sensor malfunction. For these
203 depths, T and S data were interpolated from the World Ocean Atlas 2009 (WOA09)
204 seasonal (October–December) climatology (Table A.1). The interpolated T and S
205 values are in good agreement with shipboard measurements where both are available.
206 Nutrients (e.g., dissolved silica and phosphate), $d\text{Fe}$, and $d\text{Mn}$ concentrations were
207 also measured across the CoFeMUG section (Noble et al., 2012; Saito et al., 2013).
208 Data are available from <http://bcodmo.org>, and also in the GEOTRACES Intermediate
209 Data Product (Mawji et al., 2015).

210

211 **3.2. Analytical procedure for $d\text{REE}$ concentrations**

212

213 Dissolved REE concentrations were measured at the Department of Earth Sciences,
214 University of Oxford, following Zheng et al. (2015). Briefly, ~ 100 ml of filtered
215 seawater was spiked with ^{142}Ce – ^{145}Nd – ^{171}Yb . REEs were preconcentrated with Fe co-
216 precipitation, followed by purification through a simple one-stage ion-exchange
217 chromatographic separation using AG 1–X8 anion exchange resin (100–200 mesh,
218 Bio-Rad) to remove Fe. Dissolved REEs were analyzed on a magnetic sector-field
219 ICP–MS (Element 2, Thermo Scientific) coupled with a desolvating nebulizer system

220 (Aridus 1, CETAC). Oxide interferences (i.e. Ba oxides on Eu, and LREE oxides on
221 HREEs) were negligible (<~1%). The procedural blank, typically <1% for all REEs
222 except for Ce (~8%), was monitored for each batch of sample pre-treatment, and
223 corrected batch by batch. Repeated measurements of an in-house seawater standard
224 throughout the course of this study yielded an external reproducibility of <3% (1σ ,
225 $n=19$) for all REEs. Measurements performed on GEOTRACES intercalibration
226 samples (BATS) agree with results reported by other laboratories within 10% (van de
227 Flierdt et al., 2012; Zheng et al., 2015).

228

229 **3.3. Ce anomaly calculation**

230

231 The extent of oxidative removal of Ce, due to formation of insoluble Ce^{4+} , can be
232 quantified by the “Ce anomaly”, which represents the ratio between the measured dCe
233 concentration and the predicted Ce concentration (Ce^*) that would occur without this
234 oxidative removal process (i.e., the Ce concentration obtained by interpolating
235 between its neighbouring REE elements). The Ce anomaly in this study is defined as
236 $Ce/Ce^* = [(2 \times Ce_{SN} / (La_{SN} + Pr_{SN}))]$, where REE_{SN} indicates REE concentrations
237 normalized to the post-Archean Australian shale (PAAS; McLennan, 1989). Positive,
238 or negative, Ce anomalies indicate that Ce/Ce^* values are greater, or smaller, than 1.

239

240 **3.4. Multi-parameter mixing model**

241

242 *3.4.1. Model description*

243

244 The oceanic distribution of $dREEs$ is controlled by mixing of different water masses,

245 and by non-conservative processes, such as particle scavenging, remineralization and
 246 boundary exchange (e.g., Bertram and Elderfield, 1993; Nozaki and Alibo, 2003;
 247 Siddall et al., 2008; Singh et al., 2012; Haley et al., 2014). An inverse model, based
 248 on optimum multiparameter (OMP) analysis, was developed to deconvolve the effect
 249 of conservative mixing and non-conservative processes from the observed
 250 concentrations (e.g., Tomczak and Large, 1989; Karstensen and Tomczak, 1998; Hupe
 251 and Karstensen, 2000; Singh et al., 2012).

252

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

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

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

257

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

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

260

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

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

262

263 The number and type of available tracers sets the total number of equations. After

264 defining the end-member properties characteristic of each tracer (x_i^j), the system of
265 conservation equations can be solved for the mixing fractions (f_i), and the non-
266 conservative terms (Δx^j) simultaneously.

267

268 In this study, potential temperature and salinity were used as conservative tracers, and
269 dissolved silicate (Si), phosphate (PO_4), $d\text{Nd}$ and $d\text{Yb}$ were used as non-conservative
270 tracers. Nd and Yb were selected to represent the LREEs and HREEs respectively.

271

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

280

281 The system described above consists of 7 equations (i.e. based on T, S, Si, PO_4 , $d\text{Nd}$,
282 $d\text{Yb}$ and mass conservation). A fixed $\Delta\text{Si}/\Delta\text{PO}_4$ ratio of 40 was used in the model to
283 reduce one unknown (i.e., ΔSi), based on previously observed and modelled results
284 (e.g., Takeda, 1998; Hupe and Karstensen, 2000). This system is just-determined (i.e.,
285 the number of unknowns equates to the number of equations) for 4 end-member
286 mixing; the 7 unknowns are the mass fractions of each of the 4 end-member water
287 masses (f_1 to f_4), and the non-conservative terms ΔPO_4 , ΔNd and ΔYb .

288

289 This system of equations was solved using the conjugate gradient method, which is a
290 widely used iterative method for solving systems of linear equations (Tarantola, 2005).
291 Computation using this method is inexpensive and fast for each iterative step,
292 although sometimes it may require long iterations. The conjugate gradient method
293 used in our model contrasts with the non-negative least-squares regression method
294 used commonly in the extended OMP analysis, which forces solution to be non-
295 negative for the non-conservative terms (e.g., Hupe and Karstensen, 2000). This
296 change was necessary because the terms ΔNd and ΔYb can be either negative (i.e.
297 removal) or positive (i.e. addition).

298

299 *3.4.2. Definition of end-member characteristics*

300

301 End-member properties (Table 1) for the 4 water masses (UCDW, UNADW, LNADW
302 and AABW) were pre-defined based on observational data in the corresponding
303 neutral-density layers (Vanicek and Siedler, 2002). End-member values for T, S, Si,
304 PO_4 were selected using historical data from the World Ocean Circulation Experiment
305 (WOCE, <http://www.ewoce.org>). For northerly-sourced waters, end-member values
306 were based on data measured at $27.75 < \gamma^n < 27.89$ (~1000–2000 m) between 30°N
307 and 60°N in the North Atlantic for UNADW, and at $27.89 < \gamma^n < 28.12$ (~2000–5000
308 m) in the same area for LNADW. For southerly-sourced waters, end-member values
309 were taken from data collected in areas south of 15°S at $27.55 < \gamma^n < 27.75$ (~500–
310 2000 m) for UCDW, and at $\gamma^n > 28.12$ (>~4000 m) between 35°S and 45°S for AABW.
311 Because of the limited availability of dNd and dYb concentration data relative to that
312 of traditional hydrographic tracers, large geographic areas were chosen to cover
313 reasonable amount of dNd and dYb data, so that end-member values for all tracers of

314 each water mass can be defined in the same geographic area. The hydrographic end-
315 member values defined in this study are consistent with those defined for these water
316 masses in previous studies (Larqué et al., 1997; Lee et al., 2003).

317

318 End-member values for dNd and dYb concentrations were based on the available data
319 in the same regions used to define other tracers, and are given in Table 1. The larger
320 areas used provide ~15–30 observations for dNd and ~8–20 for dYb for each end-
321 member. Characteristic dNd and dYb concentrations for UNADW and LNADW were
322 defined based on $dREE$ data reported by Elderfield and Greaves (1982), de Baar et al.
323 (1983, 1985), Piegras and Wasserburg (1983, 1987), Sholkovitz and Schneider
324 (1991), Sholkovitz et al. (1994), Lacan and Jeandel (2004, 2005b), Rickli et al. (2009)
325 and Stichel et al. (2015). The pre-defined dNd end-member values for the two water
326 masses in this study agree well with the latest measurements from the GEOTRACES
327 GA02 section (Lambelet et al., 2016).

328

329 For UCDW and AABW, end-member values were based on $dREE$ data reported in
330 Jeandel (1993), German et al. (1995), Rickli et al. (2010), Stichel et al. (2012a),
331 Garcia-Solsona et al. (2014), Hathorne et al. (2015) and our $dREE$ data (>100 new
332 measurements) from GEOTRACES GA10 section along ~40°S
333 (<http://www.egeotraces.org>). Although dNd and dYb end-member values for UCDW
334 were based on a broadly defined geographic area (i.e., south of 15°S), they show little
335 difference if a geographic constraint consistent with AABW (i.e., 35–45°S) was
336 applied, because the majority of existing dNd and dYb data for UCDW were
337 measured around ~40°S. A major change in dNd concentrations in AABW was
338 observed between the area around ~40°S (>30 pmol/kg Nd) and Polar regions south

339 of $\sim 50^\circ\text{S}$ (~ 25 pmol/kg $d\text{Nd}$) (Stichel et al., 2012a; German et al., 1995; Garcia-
340 Solsona et al., 2014; Hathorne et al., 2015), indicating significant addition of $d\text{Nd}$
341 within these areas. The detailed mechanism for this addition, however, is not clear. In
342 this study, we defined $d\text{Nd}$ and $d\text{Yb}$ end-member values based on data close to $\sim 40^\circ\text{S}$,
343 so that our deconvolution results do not integrate any $d\text{REE}$ addition occurring south
344 of $\sim 40^\circ\text{S}$.

345

346 *3.4.3. Perturbation experiments and robustness evaluation*

347

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

360

361 The robustness of the spatial pattern of ΔNd and ΔYb values is assessed using a rank
362 analysis technique. The ΔNd or ΔYb values for all the samples along the CoFeMUG
363 section are first ranked, independently, for each Monte Carlo perturbation experiment.

364 The number of times that the ΔNd or ΔYb values of each sample rank in the bottom or
365 top third, relative to other samples in the section, is then counted across all Monte
366 Carlo experiments. This count provides a measure of the probability that a given
367 sample produces ΔNd or ΔYb results low or high relative to other samples in the
368 section across all perturbation experiments. To assess whether the resulting count is
369 due to chance alone, it is compared with the number of counts expected from a
370 random process. The probability that a particular ΔNd or ΔYb value ranks in the
371 bottom or top third by chance alone is 1/3. For 250,000 Monte Carlo experiments, the
372 binomial distribution predicts, with a 95% confidence level, that the number of times
373 a random number will fall in the bottom or top third is $83,333 \pm 388$ (Borradaile,
374 2003). Samples with a count falling outside this range are therefore considered to
375 have ΔNd (or ΔYb) values that are robustly low or high.

376

377 **4. RESULTS**

378

379 **4.1. Dissolved REE concentrations**

380

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

386

387 Characteristic $d\text{Nd}$ profiles along the CoFeMUG section show a decrease from ~ 17
388 pmol/kg in the surface to ~ 13 pmol/kg at $\sim 400\text{--}1000$ m, followed by a continuous

389 increase towards the bottom. Notable exceptions are observed at stations affected by
390 the OMZ off the Angola shelf (Stations 13–17), where secondary dNd maxima
391 develop at ~400 m, coincident with the core of the OMZ (Fig. 3). Typical dYb
392 profiles show a ~2-fold increase from ~2.5 pmol/kg in surface waters to ~5.5 pmol/kg
393 at ~1000–1500 m, followed by a <~25% increase towards the bottom. The dCe
394 concentrations display surface maxima at all stations, followed by a rapid decrease
395 with depth. They remain low below ~400 m. Secondary dCe maxima are found at
396 ~400 m at stations 15 and 17 within the OMZ.

397

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

408

409 Three notable features characteristic of the dCe distribution along the CoFeMUG
410 section include the low concentrations above the mid-Atlantic ridge (MAR) (Fig. 3), a
411 small plume of high dCe in the OMZ at ~400 m off the Angola coast, and a prominent
412 plume of dCe near the African continental margin between ~1000 m and ~4000 m
413 (Fig. 3).

414

415 Shale-normalized REE patterns from representative stations in the Brazil Basin
416 (Station 4) and the Angola Basin (Station 15) are shown in Fig. 4. REE patterns are
417 relatively flat in surface waters, showing only weak Ce negative anomalies. These
418 features are commonly observed in other parts of the ocean (e.g., Bertram and
419 Elderfield, 1993; Stichel et al., 2012b; Jeandel et al., 2013; Garcia-Solsona et al.,
420 2014), and likely reflect the influence of terrigenous input. The degree of HREE
421 enrichment and the negative Ce anomalies generally become stronger with increasing
422 depth, as observed previously for the South Atlantic (German et al., 1995; Garcia-
423 Solsona et al., 2014).

424

425 **4.2. Deconvolution results of the end-member mixing model**

426

427 *4.2.1. Mixing fractions*

428

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

433

434 The fraction of UCDW is maximum (~100%) at ~1000 m, and gradually decreases to
435 <20% at ~2000 m. The diminished UCDW fraction with depth is balanced by the
436 increased influence of NADW, which dominates the section between ~2000 m and
437 ~3500 m with fractions reaching >80%. Below ~3500 m, the fraction of NADW
438 progressively declines to <20% near the seafloor in the Brazil Basin, while AABW

439 fraction increases from <20% to >80%. Consistent with hydrographic observations,
440 the fraction of NADW remains high (~80%) in the deep Angola Basin, where the
441 fraction of AABW is low (i.e. ~20%).

442

443 4.2.2. Non-conservative components: ΔNd and ΔYb

444

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

454

455 The strongest dNd removal ($\Delta Nd < -1$ pmol/kg) is observed above the Mid-Atlantic
456 Ridge (MAR) (Fig. 6), representing >5% of the measured dNd concentrations (Fig. 7).
457 High Nd removal ($\Delta Nd \approx -1$ pmol/kg) was also found at depth between ~1000 m and
458 3000 m in the Brazil Basin (e.g., Station 1), representing ~5% of the total dNd
459 concentrations for these samples. Addition of dNd , up to 5pmol/kg, was observed in
460 the deep Brazil Basin (>~3500 m). Two plumes of significant dNd excess were found
461 in the Angola Basin at depths of ~1500 m and below ~4000 m respectively, with ΔNd
462 values generally increasing towards the Angola margin. The dNd excess at ~4000 m,
463 with ΔNd values of up to ~8 pmol/kg, accounts for up to ~25% of the total dNd

464 concentrations, and is the strongest non-conservative signal along the section. In
465 comparison, the excess dNd plume at ~1500 m, with ΔNd values of ~4 pmol/kg,
466 accounts for ~20% of the measured total dNd concentrations.

467

468 In contrast to dNd , no net removal of dYb was found above the MAR, and, in most
469 areas of the Brazil Basin, dYb shows minor excess of <0.5 pmol/kg, representing only
470 <5% of the measured dYb . Excess dYb values of up to ~1.25 pmol/kg, which
471 accounts for as much as ~20% of the total dYb concentrations, were observed in the
472 Angola Basin. Unlike dNd , dYb shows almost ubiquitous excess throughout that
473 basin. Although two plumes are suggested in the contour plots at ~1500 m and ~4000
474 m (Fig. 6 and 7), they are not as well-separated as those for dNd .

475

476 *4.2.4. Robustness of spatial patterns of the ΔNd and ΔYb results*

477

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

484

485 The spatial distribution of probability shown in Figure 8 is based on the number of
486 times that ΔNd (and ΔYb) results of a sample are higher or lower than the results of
487 two thirds of samples in the section across all perturbation experiments. This
488 treatment captures the inherent relationship of a ΔNd or ΔYb result, regardless of its

489 actual value, relative to all other samples in the CoFeMUG section across 250,000
490 perturbation experiments, and directly characterizes the likelihood of each ΔNd and
491 ΔYb result being high (or low) across the section. The probability that ΔNd results
492 rank in the bottom-third is highest (>0.9) in areas above the MAR and >0.7 between
493 ~ 1000 - 3000 m at Station 1 (Fig. 8c). The probability that ΔNd results fall in the top-
494 third is high in the deep Brazil Basin (~ 0.7), and is the highest ($>\sim 0.7$ - 0.9) at ~ 1500 m
495 and below ~ 4000 m near the continental margin in the Angola Basin (Fig. 8a).
496 Although the fraction of non-conservative behaviour for $d\text{Nd}$ is high (up to $\sim 15\%$ of
497 total $d\text{Nd}$) at ~ 1000 m in the west side of the section (Fig. 7), the probability that ΔNd
498 results fall in the top-third in this area is ~ 0.4 (Fig. 8a), close to that predicted for a
499 random process (~ 0.33), indicating that the results in this region are sensitive to the
500 choice of end-member values. Except for this region, the probability distributions of
501 ΔNd (Fig. 8a, c) are consistent with key features of the absolute and relative ΔNd
502 patterns (Fig. 6 and 7), indicating that the ΔNd patterns are statistically stable. That is,
503 patterns in Fig. 6 and 7 are relatively insensitive to the selected end-member values.
504 Similarly, good agreement was observed between the probability distributions of ΔYb
505 (Fig. 8b, d) and ΔYb patterns (Fig. 6 and 7), suggesting that ΔYb patterns are also
506 robust.

507

508 **5. DISCUSSION**

509

510 **5.1. Release of REEs from water-column reduction of oxides**

511

512 High $d\text{REE}$ concentrations in surface waters near the Angola coast (Station 17 and 18)
513 are observed (Fig. 3), and agree with high $d\text{Nd}$ concentrations observed previously in

514 this region (Rickli et al., 2010). Based on Nd-isotope evidence, the high dNd
515 concentration was attributed to local decomposition of Fe-Mn oxides in the water
516 column, or in shelf sediments, under low oxygen conditions (Rickli et al., 2010). This
517 interpretation is consistent with more recent dFe and dMn observations, which are
518 also high in coastal surface waters (Noble et al., 2012).

519

520 Dissolved REE enrichment is also observed in the OMZ (Fig. 3). This enrichment is
521 similar, albeit of smaller magnitude, to the enrichment observed at the oxic/anoxic
522 interface in the water column in anoxic basins. It has been shown to be caused by the
523 desorption of REEs upon reductive dissolution of Fe-Mn oxides (e.g., de Baar et al.,
524 1988; German and Elderfield, 1989; German et al., 1991a; Sholkovitz et al., 1992;
525 Schijf et al., 1995). The close association between $dREEs$ and the redox cycling of Fe
526 and Mn in the OMZ along the CoFeMUG section is demonstrated by the significant
527 positive correlation between $dREEs$ (including the Ce anomaly) and dFe , or dMn ,
528 observed for the data at stations in the OMZ ($dO_2 < \sim 60 \mu M$) at ~ 400 m (a quasi-
529 isopycnal layer with density of $\sim 27.0-27.1$) (Fig. 9). No such correlation is visible in
530 data from the same depth from stations located outside the OMZ.

531

532 The close association between REEs, Fe and Mn in the OMZ is also reflected in the
533 REE patterns (Fig. 10). Seawater $dREE$ concentrations at ~ 400 m were normalized to
534 the mean $dREE$ concentrations averaged across all CoFeMUG samples at ~ 1000 m to
535 better reveal small variations in $dREE$ patterns. Compared to seawater outside the
536 OMZ (Station 1–9), seawater influenced by the OMZ shows REE patterns
537 characterized by pronounced $dLREE$ enrichment and weak negative or positive Ce
538 anomalies (Fig. 10a). These features are consistent with reduction of Fe-Mn oxides

539 because these particles display typical LREE-enriched patterns with prominent Ce
540 excess (e.g., de Baar et al., 1988; German and Elderfield, 1989; Sholkovitz et al.,
541 1994; Bayon et al., 2004; Freslon et al., 2014) (Fig. 10b).

542

543 The seawater REE patterns provide evidence for *in-situ* release of *d*REEs from
544 reduction of Fe-Mn oxides in the water-column of the OMZ. Lateral transport of
545 *d*REEs released from sediments on the African shelf may also occur, but if lateral
546 transport were the dominant REE source, one would have expected a progressive
547 depletion of *d*LREEs relative to *d*HREEs with increasing distance from shore due to
548 continuous scavenging, and progressive development of a negative Ce anomaly
549 towards that of seawater outside the OMZ. More pronounced *d*LREE enrichment and
550 positive Ce anomalies observed at Station 15 and 17 relative to the REE pattern found
551 at Station 18, however, clearly contradicts the expected trend, suggesting *in-situ*
552 regeneration of *d*REEs (Fig. 10a). This observation is consistent with that in the
553 eastern North Atlantic (~20°N), where Nd isotopes also indicate major release of
554 scavenged Nd from particles in the OMZ off the Mauritanian shelf (Stichel et al.,
555 2015). Our data indicate a local *d*O₂ threshold of ~25 μM (i.e., observed at Station 17
556 and 15) that enables reductive release of *d*REEs from Fe-Mn oxides. This value is
557 slightly higher than that reported for the OMZ in the northwest Indian Ocean (*d*O₂ <
558 ~15 μM) where recycling of *d*REEs from particles occurs (German and Elderfield,
559 1990), but the observation in the OMZ in the eastern North Atlantic demonstrates that
560 desorption of *d*REEs from particles can happen at even higher *d*O₂ concentrations
561 (~40 μM) (Stichel et al., 2015).

562

563 In contrast, secondary concentration maxima are absent in *d*Nd profiles at water

564 depths corresponding to the OMZs in the eastern equatorial Pacific, southeast Pacific
565 and Arabian Sea where local dO_2 concentrations can be $<15 \mu\text{M}$ (Grasse et al., 2012;
566 Jeandel et al., 2013; Goswami et al., 2014). It remains unclear whether these previous
567 observations truly reflect a lack of $d\text{Nd}$ enrichment in OMZs due to the relatively low
568 spatial and depth resolution of available data. Enrichment or depletion of an element
569 may only become apparent when individual profiles are considered in the context of
570 its distribution at the basin scale, as demonstrated by $d\text{Yb}$ from the CoFeMUG
571 section, whose enrichment in the OMZ is not visible from any individual profile
572 (Supplemental Material, Fig. S2), but is clearly suggested by an east–west
573 concentration gradient at ~ 400 m across the section (Fig. 3). Alternatively, the
574 contrasting observations indicate that, besides dO_2 contents, multiple parameters,
575 including regional REE input, particle dynamics and hydrographic conditions
576 collectively determine the REE cycling in OMZs.

577

578 **5.2. The dominance of preformed $d\text{REEs}$ in Atlantic deep waters**

579

580 Concentrations of $d\text{REEs}$ in deep-waters of the central Atlantic are dominantly
581 controlled by mixing of the major Atlantic water masses ($>75\%$), rather than by
582 geochemical processes operating during transit of these waters from their source
583 regions (Fig. 7). Deviations from purely conservative mixing for the $d\text{REEs}$ are up to
584 a maximum of 25%. The dominance of the preformed component in setting deep-
585 water $d\text{REE}$ concentrations explains why these concentrations resemble the general
586 water mass structure of the South Atlantic (Fig. 2 and 3). For example, higher $d\text{REE}$
587 concentrations in the deep Brazil Basin than those observed in the deep Angola Basin
588 is largely related to the presence of AABW in the Brazil Basin.

589

590 Preformed d REEs are particularly important in setting observed d REE concentrations
591 in the deep Brazil Basin (Fig. 7), where ~95% of the observed d Yb, and ~90% of d Nd,
592 can be explained by conservative water-mass mixing. A slightly higher percentage of
593 preformed d Yb than that of preformed d Nd is consistent with the general behaviour of
594 REEs in the ocean that HREEs are less particle-reactive than LREEs (e.g., Wood,
595 1990; Sholkovitz et al., 1994).

596

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

604

605 Our results indicate that the linear d REE– d Si relationship in the deep tropical Atlantic
606 results mostly from water mass mixing due to dominantly conservative behaviour of
607 these elements, rather than from local biogeochemical processes coupling the two
608 elements. This conclusion contrasts with studies that have suggested a direct link
609 between the cycling of d Nd and d Si in the high-latitude Southern Ocean based on the
610 observed linear relationships between the two elements (e.g., Stichel et al., 2012a;
611 Garcia-Solsona et al., 2014; Hathorne et al., 2015). A possible explanation that
612 reconciles our results with these previous studies relies on the large contrast in opal
613 fluxes between our study region and the Southern Ocean. High opal fluxes in the

614 Southern Ocean may facilitate strong local regeneration of d REEs from dissolution of
615 biogenic silica in deep waters in this specific region. In addition, this d REE
616 regeneration could be further promoted by strong vertical mixing in certain areas of
617 the Southern Ocean. After deep-water d REEs and d Si are exported from the Southern
618 Ocean into the sub-tropical and tropical South Atlantic where opal flux is low, their
619 distributions are no longer controlled by a coupled REE and opal cycle, but
620 essentially governed by water mass mixing. A coupled REE–Si cycle was proposed to
621 explain general concentration profiles of d REEs in the ocean (Akagi, 2013), our
622 results, however, demonstrate that such a coupling is not necessarily true on a global
623 scale.

624

625 **5.3. Suggested REE sources from sedimentary Fe oxides and remineralization of** 626 **calcite**

627

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

634

635 Addition of d REEs (\sim 10% for d Nd and \sim 5% for d Yb) is observed in AABW in the
636 deep Brazil Basin ($>$ \sim 4000 m), and can be explained by release of d REEs from *in-situ*
637 remineralization of particles, or by accumulation of remineralized d REEs along the
638 flow path of AABW from \sim 40°S. More significant REE addition (up to \sim 25%) is seen

639 on the eastern side of the section, in the Angola Basin, with Nd excess seen at two
640 depths (~1500 m and below ~4000 m), and Yb excess at all depths below ~1500 m
641 (Fig. 6 and 7). The different distribution of ΔNd and ΔYb in the Angola Basin may
642 result from different particle reactivity between LREEs and HREEs. Because HREEs
643 are less particle-reactive than LREEs in seawater (e.g., Wood, 1990; Sholkovitz et al.,
644 1994), signals of Yb addition are expected to survive longer in the water column, so
645 that they can be mixed or advected from their source. In contrast, Nd is more quickly
646 scavenged by particles, so that signs of its addition are likely to be more restricted
647 spatially.

648

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

662

663 There is no noticeable development of less pronounced negative Ce anomaly

664 associated with the REE excess below ~4000 m (Fig. 3), suggesting that a different
665 processes must be responsible for this deep REE excess. This 4000 m d REE excess
666 occurs just below the calcite saturation depth (CCD) (Feely et al., 2004), suggesting
667 that dissolution of calcite might release REEs scavenged from shallower depths back
668 to seawater. Carbonates commonly show seawater-like negative Ce anomalies
669 (Palmer, 1985; Haley et al., 2005; Akagi et al., 2011), rather than positive Ce
670 anomalies typically associated with Fe-Mn oxides and organic matters (Bayon et al.,
671 2004; Freslon et al., 2014), so that dissolution of calcite might explain the absence of
672 a Ce anomaly associated with the increased trivalent REEs below ~4000 m.

673

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

682

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

689 regenerated *d*REEs as compared to the Brazil Basin.

690

691 **5.4. Scavenging of *d*LREEs above the mid-Atlantic ridge (MAR)**

692

693 Recent results have clearly indicated that mid-ocean ridges can represent significant
694 sources of dissolved trace metals, such as Fe, to the water, and metals released from
695 hydrothermal vents can transport over hundreds to thousands of kilometers away from
696 the source (e.g., Klunder et al., 2012; Nishioka et al., 2013; Saito et al., 2013;
697 Fitzsimmons et al., 2014; Hatta et al., 2015; Resing et al., 2015). Such addition has
698 also been seen for *d*Mn and *d*Fe in the CoFeMUG section (Noble et al., 2012; Saito et
699 al., 2013). These new field observations, together with increased recognition of
700 organic metal-binding ligands in hydrothermal fluids (e.g., Sander et al., 2007;
701 Bennett et al., 2008; Toner et al., 2009; Sander and Koschinsky, 2011), have
702 overturned the previous assertion that mineral precipitation and scavenging
703 quantitatively remove Fe from hydrothermal plumes (e.g., German et al., 1991b).

704

705 Measurements of this study do not indicate any similar release of *d*REEs to the water-
706 column (Fig. 3). The deconvolution results also confirm this conclusion, and instead
707 quantify removal of *d*Nd above the mid-ocean ridge rather than addition. The lack of
708 *d*REE addition may be surprising, given that hydrothermal fluids are enriched in
709 *d*REEs by several orders of magnitude compared to ambient seawater (e.g.,
710 Klinkhammer et al., 1994; Mitra et al., 1994; Bau and Dulski, 1999; Douville et al.,
711 1999; Craddock et al., 2010; Schmidt et al., 2010), but is consistent with previous
712 studies indicating quantitative scavenging of *d*REEs in hydrothermal plumes (e.g.,
713 German et al., 1990; Mitra et al., 1994; Bau and Dulski, 1999). The removal of

714 LREEs observed here is also consistent with previous studies that have demonstrated
715 preferential scavenging of LREEs on Fe-Mn particles during dispersion of particles in
716 neutrally buoyant hydrothermal plumes (German et al., 1990; Rudnicki and Elderfield,
717 1993; Mitra et al., 1994).

718

719 **5.5. Apparent decoupling between Ce and Mn in the Angola Basin**

720

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

729

730 A similar decoupling between Ce and Mn, albeit of much smaller magnitude, was
731 previously observed in the northwest Indian Ocean (German and Elderfield, 1990).
732 This decoupling was attributed to a delicate environment where $d\text{O}_2$ concentrations
733 are sufficiently high to allow for the oxidative precipitation of Mn at the sediment–
734 seawater interface during diffusion of Mn from reduced sediments, but insufficient to
735 cause oxidative removal of Ce from the same sedimentary source. This explanation,
736 however, seems inconsistent with high $d\text{Fe}$ concentrations observed at ~1500 m at the
737 CoFeMUG section (Noble et al., 2012). Because the standard redox potential follows
738 the sequence $\text{Fe} < \text{Mn} < \text{Ce}$ (Lu et al., 2010), if reduced sediments on the continental

739 margin serve as a local source of these metals to the water column, enrichment of dFe
740 and dCe at ~1500 m, but not dMn , is inconsistent with the redox chemistry of these
741 elements during their diffusion out of sediments. A possible explanation for this
742 apparent inconsistency is that Mn content in sediments along the African continental
743 margin is much lower relative to Fe (Bremner and Willis, 1993), so that the supply of
744 Mn from the reduced sedimentary source would be intrinsically low. In addition, Ce
745 may be present as cerium oxides, or be mostly associated with Fe oxides in sediments,
746 rather than being associated with Mn oxides, as demonstrated previously by data from
747 pore waters off Peru and California margins (Haley et al., 2004).

748

749 **6. CONCLUSIONS**

750

751 This study presents $dREE$ concentrations along a full-depth, zonal section at ~12°S in
752 the tropical South Atlantic. High $dREE$ concentrations in surface waters and OMZ
753 (~400 m) near the Angolan coast are likely to result at least partially from
754 decomposition of Fe-Mn oxides in the water column.

755

756 The contribution of water mass mixing to $dREE$ concentrations in deep waters (>1000
757 m) was quantified using a multi-parameter end-member mixing model. Results show
758 that >75% of the $dREE$ concentrations are preformed. This explains the observed
759 strong correlation between $dREEs$ and dissolved Si in the deep Brazil Basin; both
760 elements behave almost conservatively in deep-waters of the Atlantic. The
761 deconvolution also reveals $dREE$ addition of up to ~10% in AABW in the deep Brazil
762 Basin, which reflects remineralization of particulates *in-situ* or along the flow path
763 from ~40°S. More significant $dREE$ addition of up to 25% was found at ~1500 m and

764 below ~4000 m in the Angola Basin near the continent–ocean interface, the upper
765 associated with increased Ce anomalies values and the deeper not. The shallow plume
766 is attributed to release of *d*REEs from dissolution of sedimentary Fe oxides on the
767 continental margin, and the deep one to remineralization of calcite. The higher
768 percentage of *d*REE addition in the Angola Basin compared to that in the Brazil Basin
769 may reflect the higher particulate fluxes, together with older water masses and a more
770 sluggish circulation in the Angola Basin that permit accumulation of more non-
771 conservative *d*REEs during water mass advection from source regions. These
772 observations suggest that processes responsible for the boundary sources of REEs
773 differ significantly with region.

774

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

779

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781

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790

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

7

8 **Fig. 2.** (A) Dissolved silicate (dSi) along the CoFeMUG section (Noble et al., 2012),
9 and depth ranges of major water masses according to characteristic neutral density
10 surfaces (Vanicek and Siedler, 2002). TSW–Tropical Surface Water; SACW–South
11 Atlantic Central Water; AAIW–Antarctic Intermediate Water; UCDW–Upper
12 Circumpolar Deep Water; NADW–North Atlantic Deep Water; AABW–Antarctic
13 Bottom Water. Numbers above section are CoFeMUG station numbers (Fig. 1). (B)
14 Dissolved O_2 showing the OMZ on the Angolan margin (Noble et al., 2012).

15

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

20

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

23

24 **Fig. 5.** Results of modelled mixing fractions of UCDW, NADW (combined UNADW
25 and LNADW) and AABW along the CoFeMUG section. Plotted results are the

26 arithmetic average of 250,000 Monte Carlo perturbation experiments. Figures were
27 created using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2015).

28

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

34

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

39

40 **Fig. 8.** Probability distribution characterizing the stability of the spatial patterns of
41 ΔNd and ΔYb . The white dashed line shows the probability equal to 1/3 – the limit of
42 statistical significance. Figures were created using Ocean Data View (Schlitzer, R.,
43 Ocean Data View, odv.awi.de, 2015).

44

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

48

49 **Fig. 10.** REE patterns normalized against the average of REE concentrations at
50 ~1000 m at the CoFeMUG section. (A) Seawater measurements from this study from

51 ~400 m, with samples outside the OMZ shaded in grey. Note the LREE and Ce
52 enrichment for samples in the OMZ, consistent with release of REEs from Fe-Mn
53 oxides. (B) Fe-Mn leachate from sediments in the Angola Basin (Bayon et al., 2004),
54 demonstrating expected patterns of REEs from dissolution of Fe-Mn oxides.

55

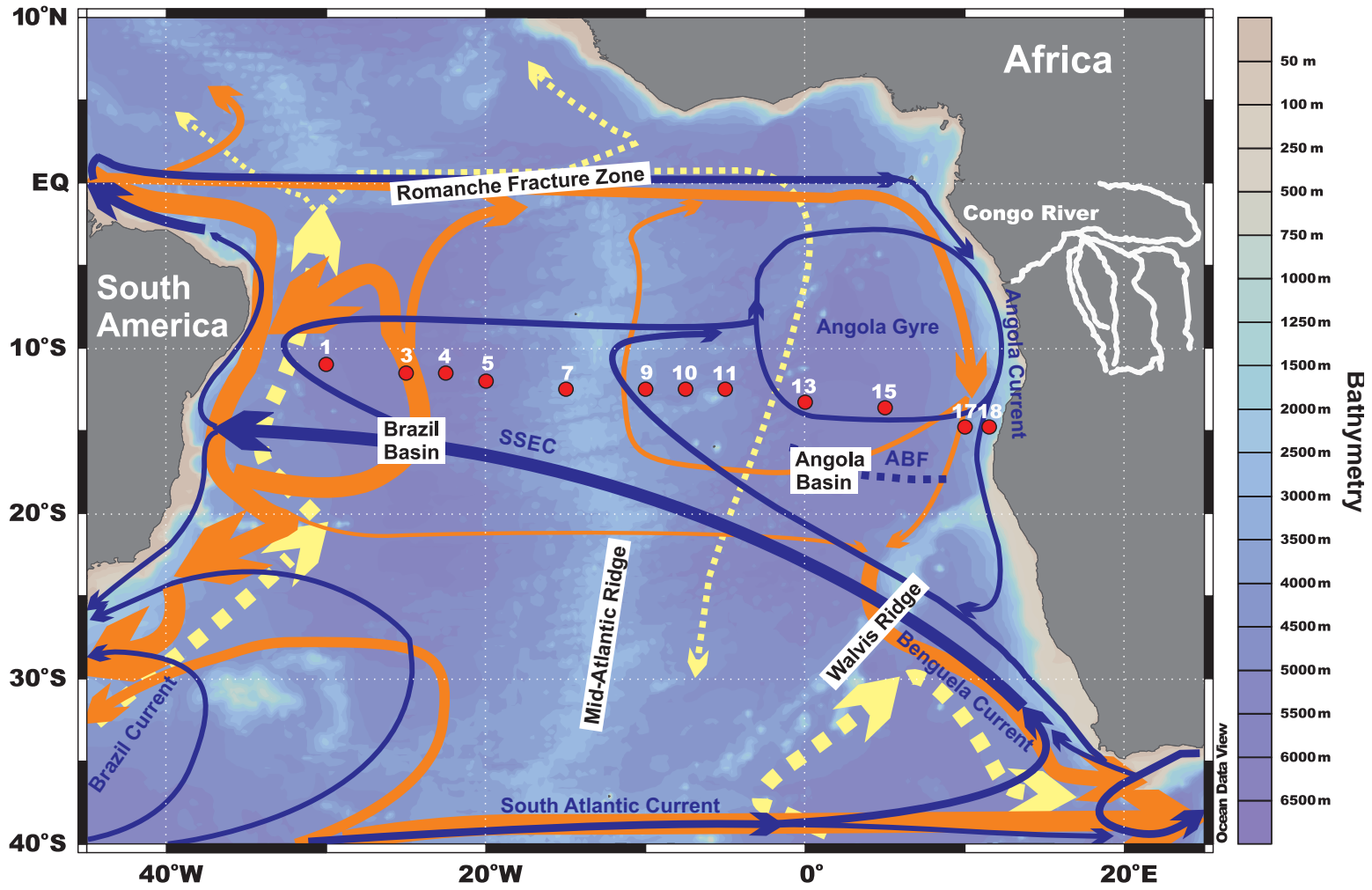
56 **Fig. 11.** Deep-water (>2000 m) $d\text{REE}-d\text{Si}$ relationship in the Brazil and Angola
57 Basin.

Table 1. Characteristics of each tracer in the 4 pre-defined end-member water types

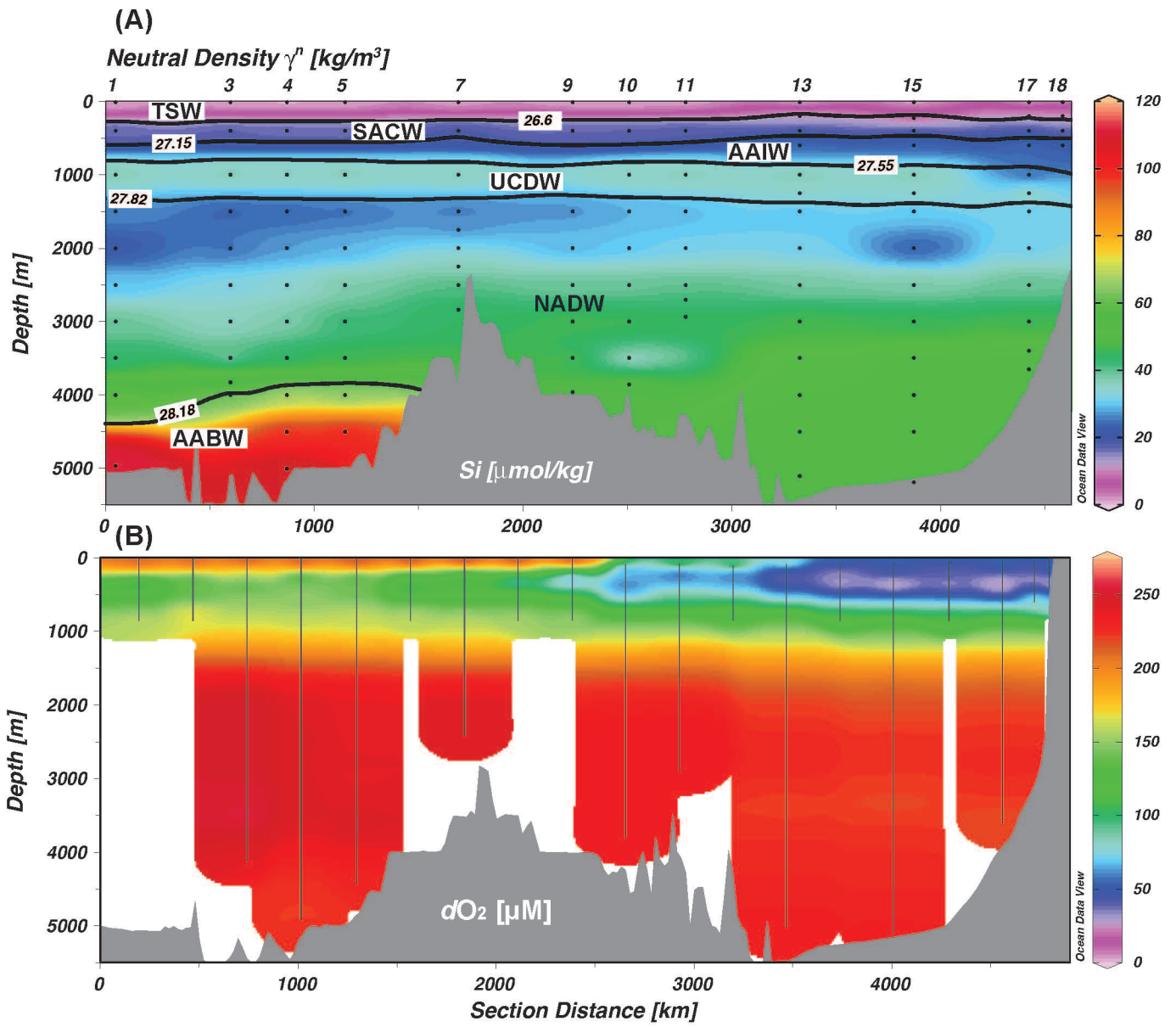
		T (°C) ¹	S ¹	Silicate (μmol/L) ¹	Phosphate (μmol/L) ¹	dNd (pmol/kg) ¹	dYb (pmol/kg) ¹
UCDW		3.32 ± 0.52	34.51 ± 0.10	44.57 ± 8.84	2.22 ± 0.11	12.09 ± 0.96	5.37 ± 0.37
NADW	UNADW	4.21 ± 1.38	35.02 ± 0.22	12.01 ± 1.82	1.14 ± 0.06	16.89 ± 5.07	4.50 ± 0.41
	LNADW	2.61 ± 0.38	34.93 ± 0.03	24.94 ± 10.66	1.26 ± 0.16	19.17 ± 5.59	4.98 ± 0.53
AABW		0.49 ± 0.51	34.71 ± 0.04	113.47 ± 14.40	2.14 ± 0.14	32.20 ± 4.85	7.86 ± 0.98

¹ see text for details on how end-member values were defined and on references cited.

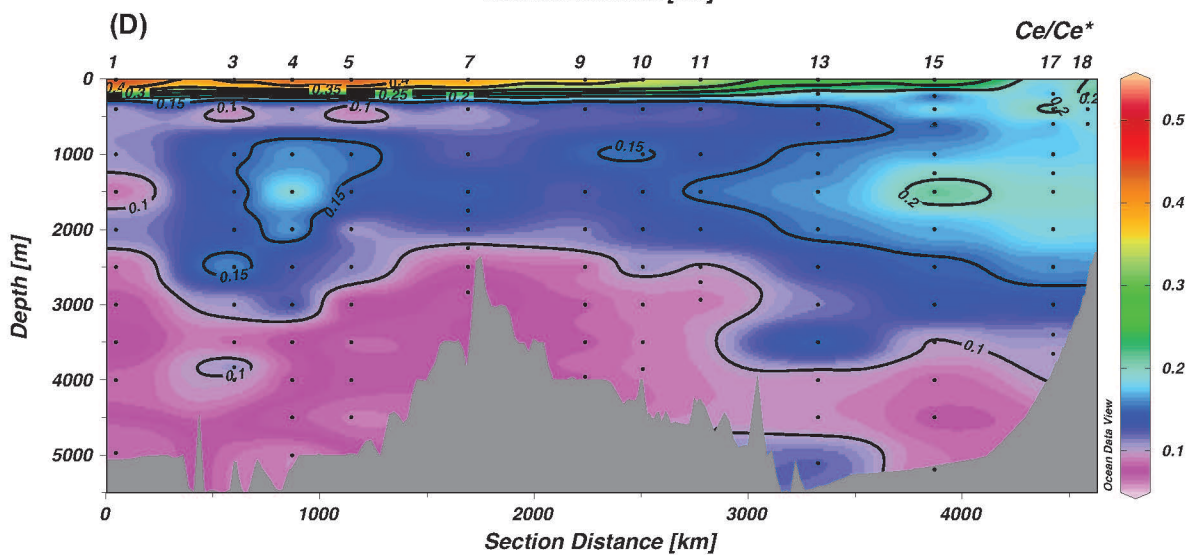
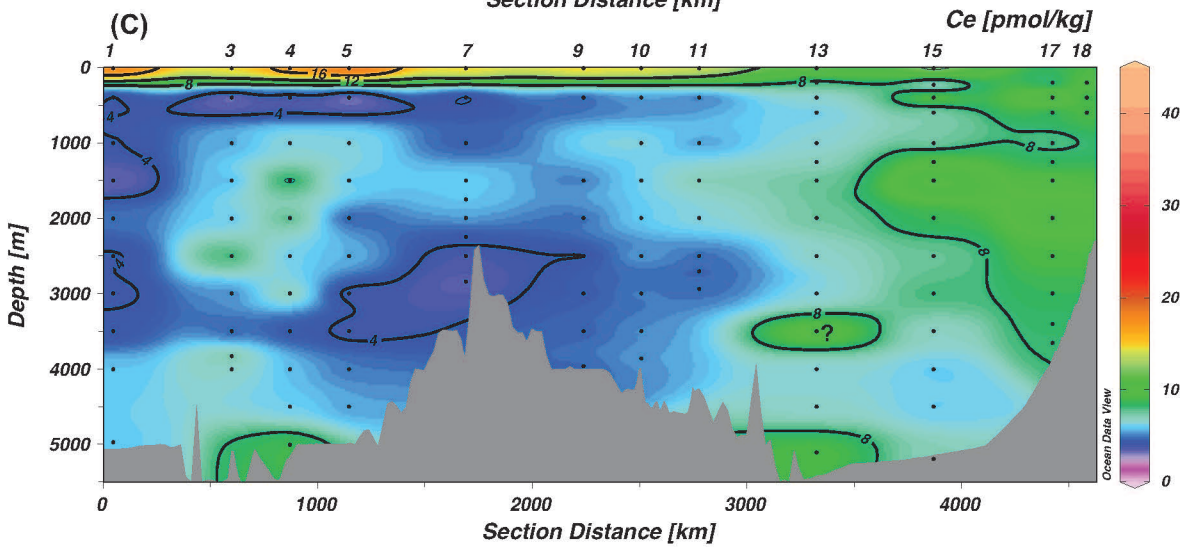
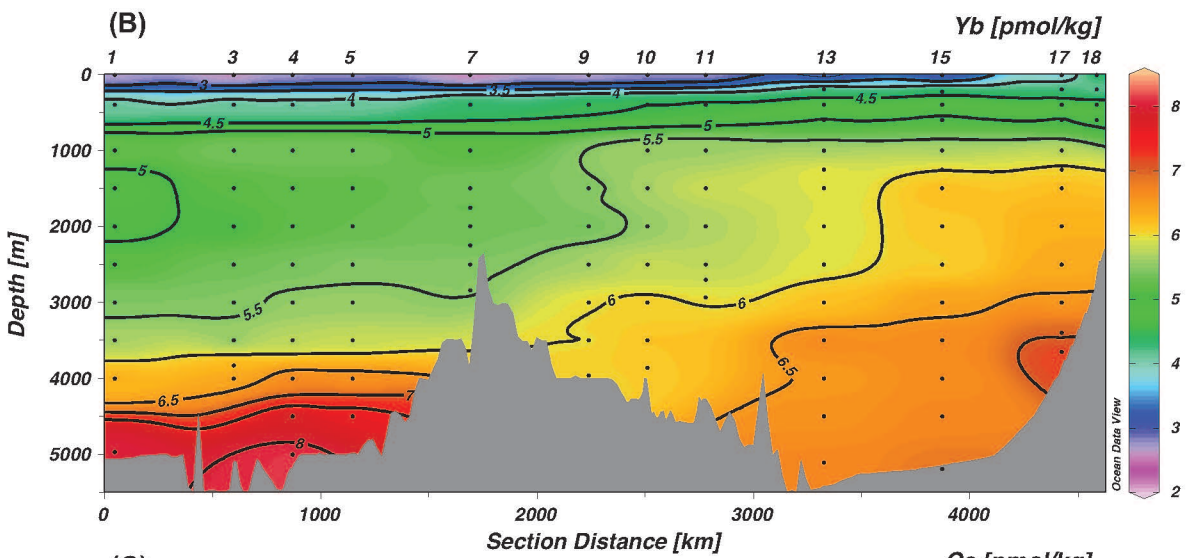
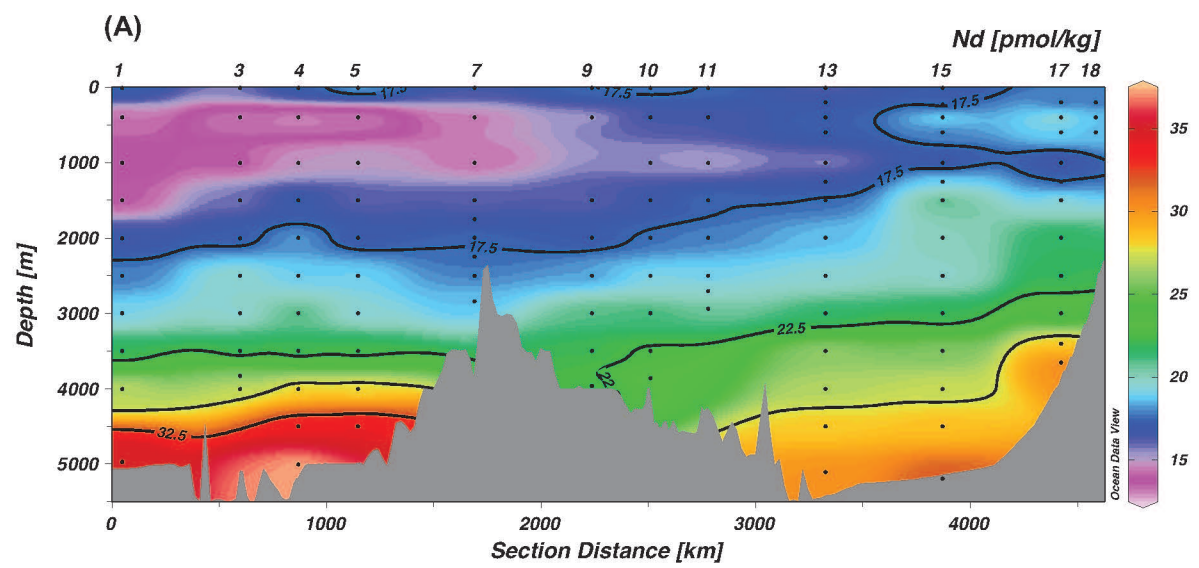
Figure_01



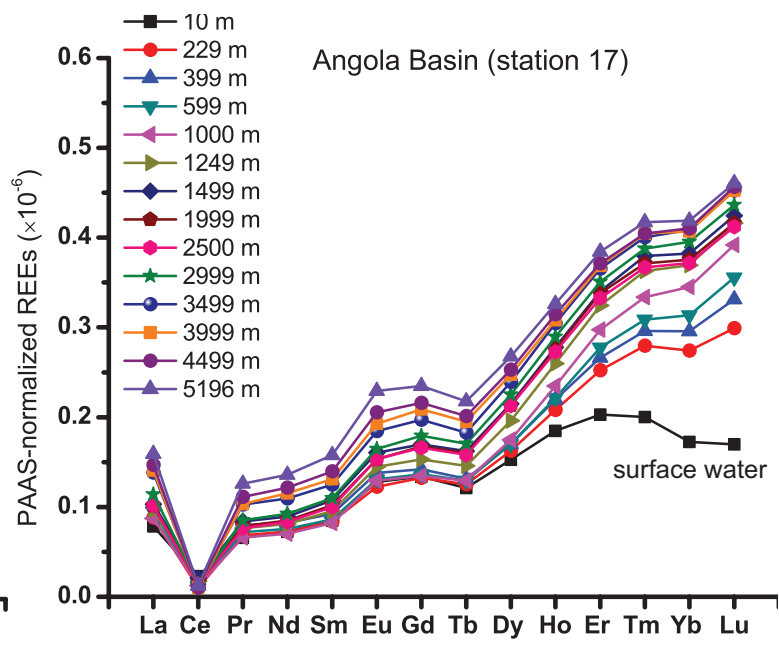
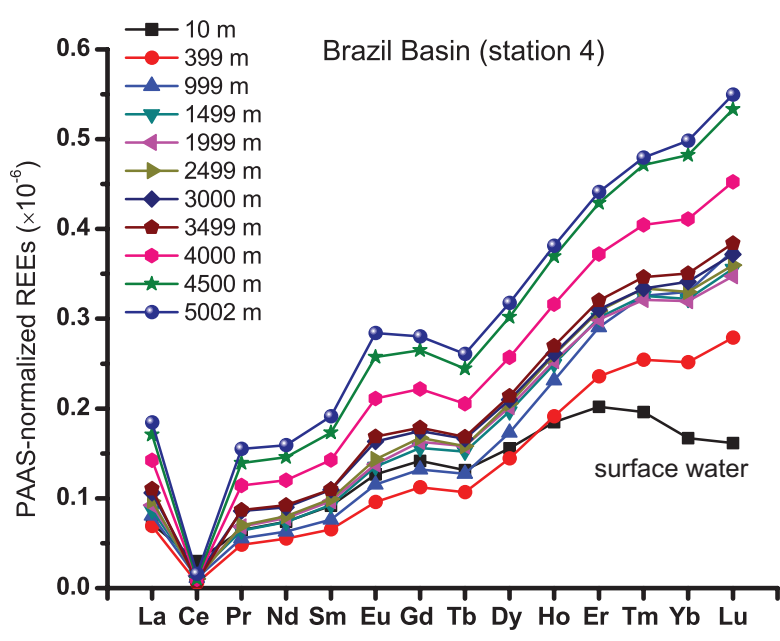
Figure_02



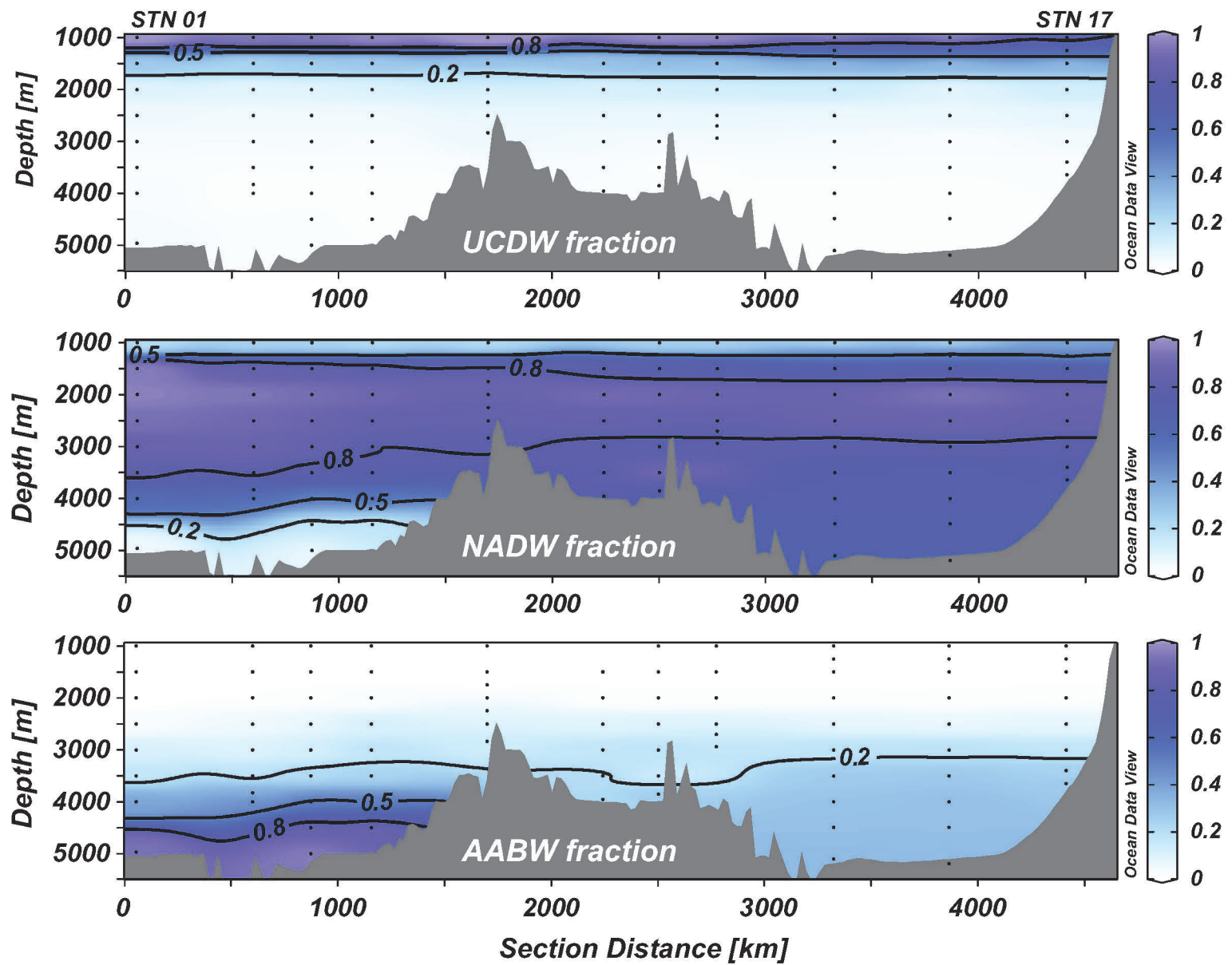
Figure_03

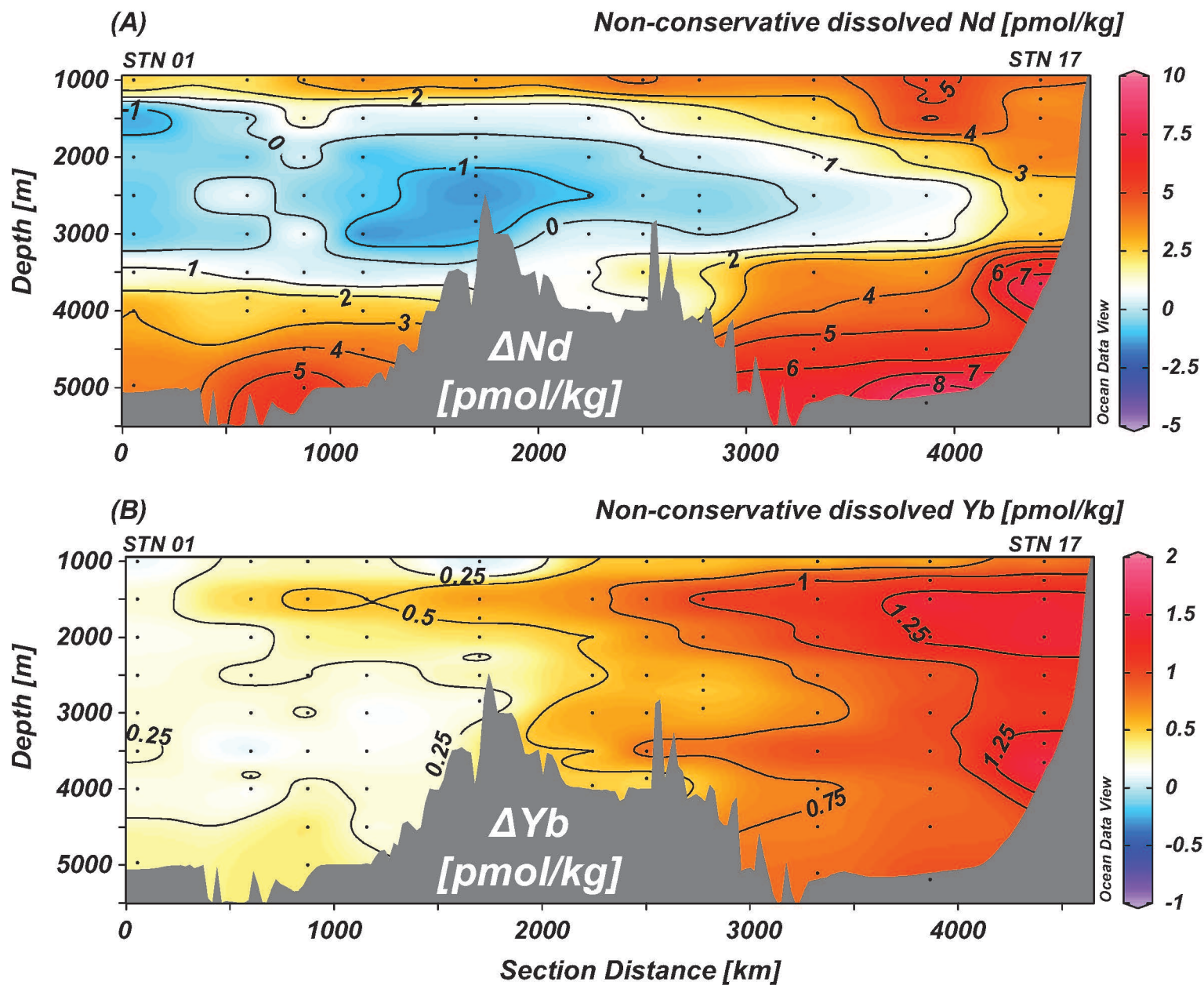


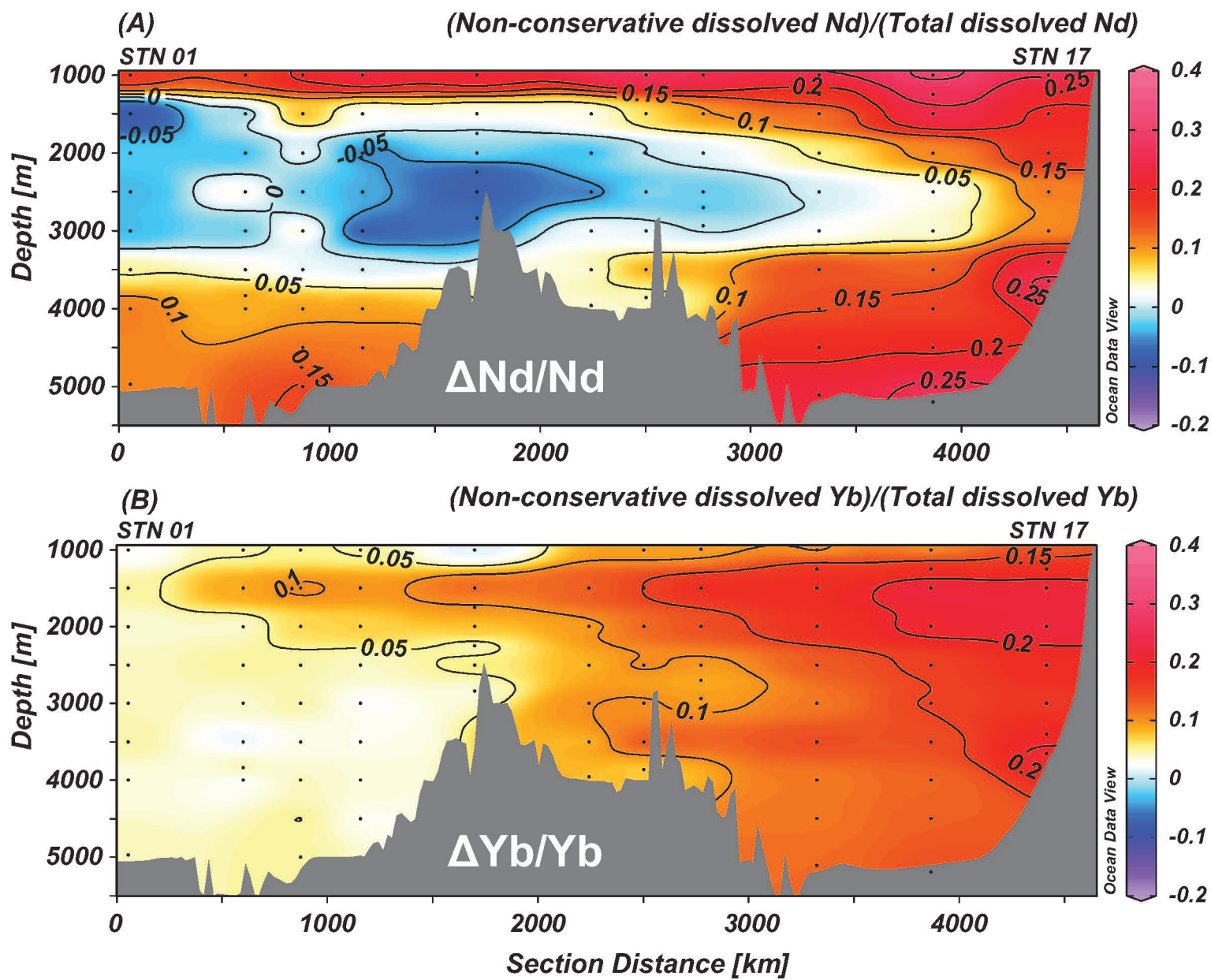
Figure_04

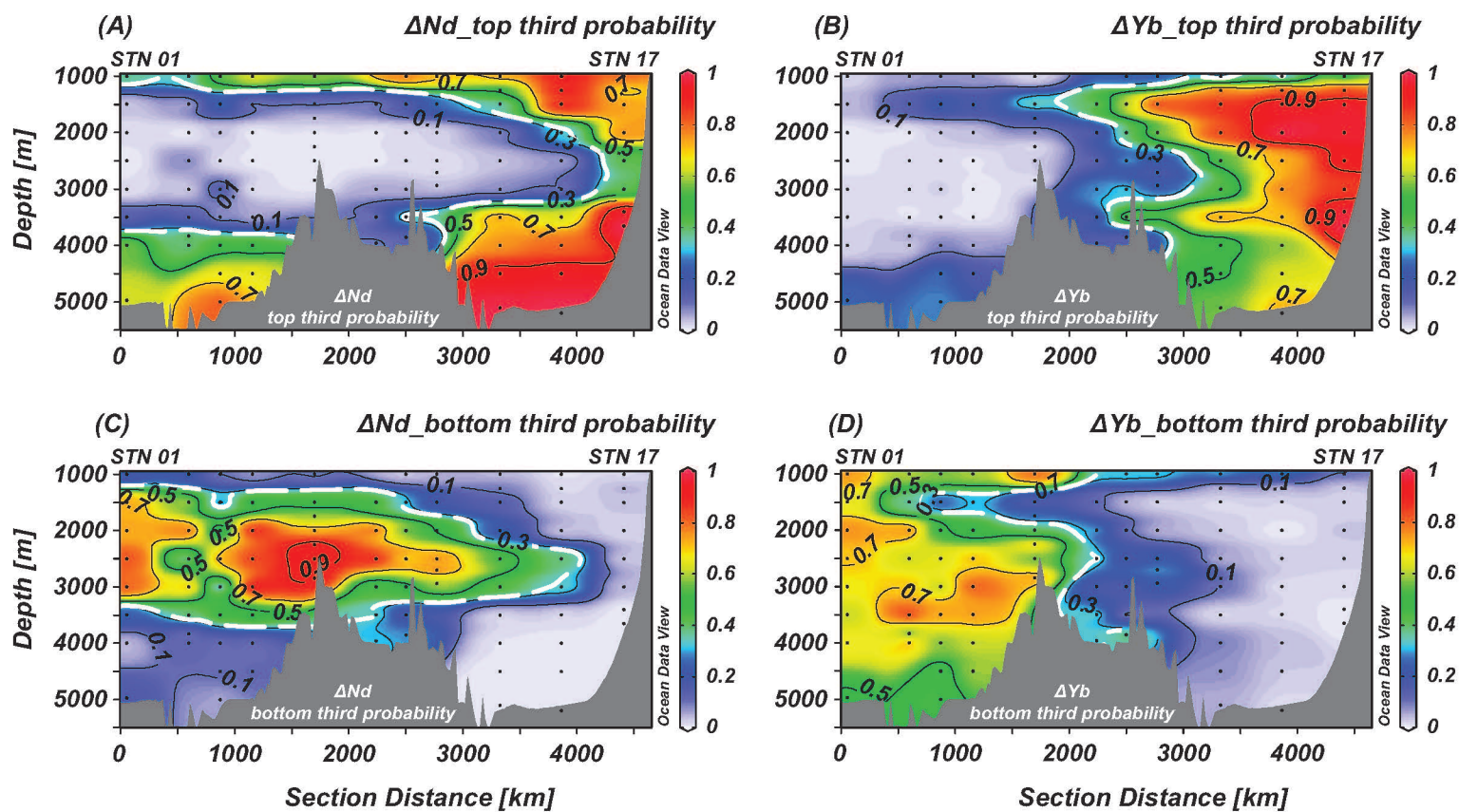


Figure_05_revised

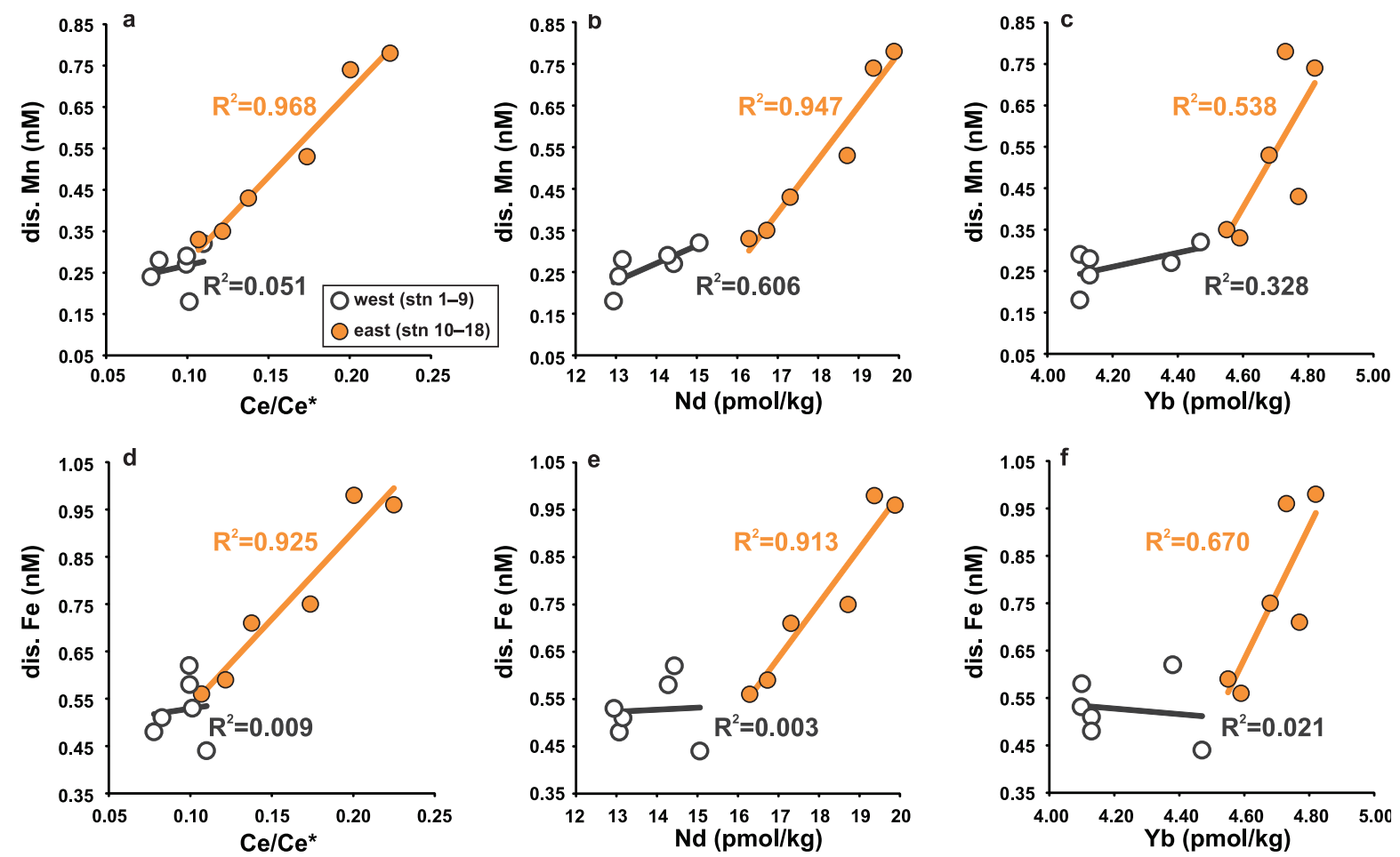


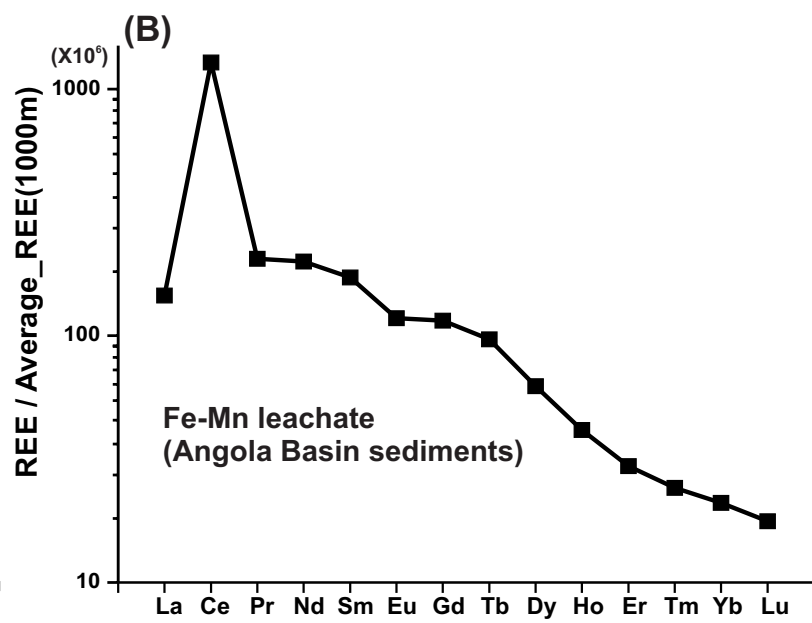
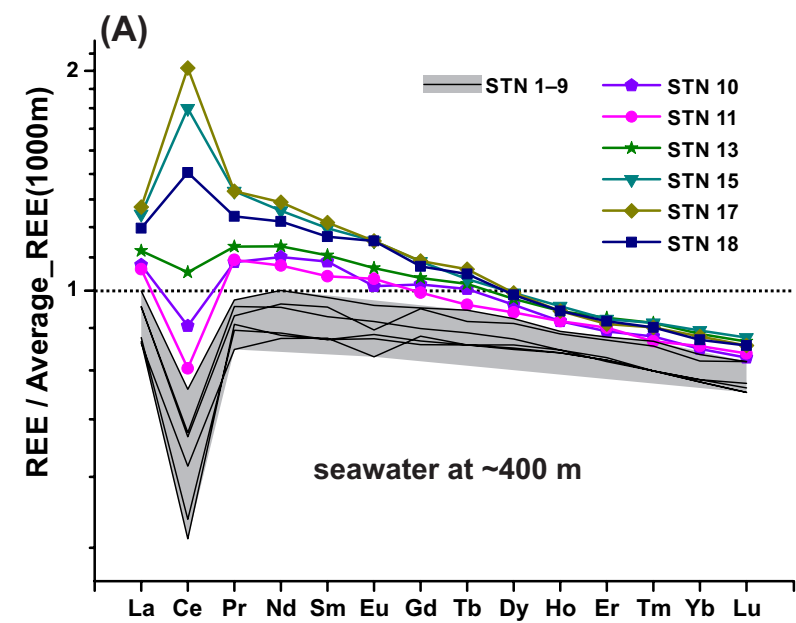




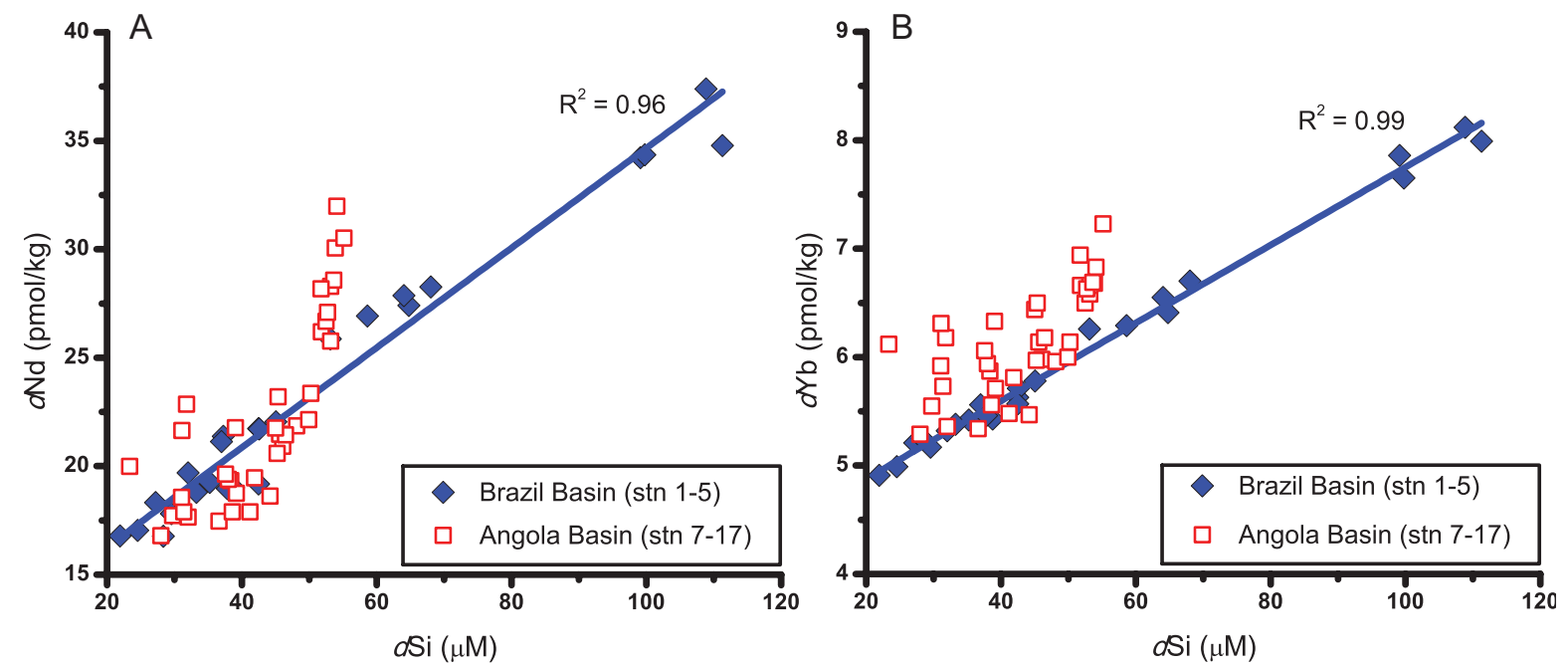


Figure_09





Figure_11



Appendix Table A1 (data table)

[Click here to download Appendix: Table A1_CoFeMUG REE.xlsx](#)

Supplemental Material_revised

[Click here to download Appendix: CoFeMUG_Supplemental Material_revision.pdf](#)