Marine Chemistry 177 (2015) 172–183

Contents lists available at ScienceDirect

Marine Chemistry

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

Rare earth element distribution in Caribbean seawater: Continental inputs versus lateral transport of distinct REE compositions in subsurface water masses

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ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form 2 March 2015
Accepted 3 March 2015
Available online 21 March 2015

Keywords:
Caribbean
Orinoco
Gulf of Mexico
Rare earths
Ocean circulation
Water masses

ABSTRACT

The rare earth element (REE) concentrations of full water column profiles from ten stations in the Caribbean, the Gulf of Mexico, and the Florida Straits, as well as of surface waters close to the mouth of the Orinoco River have been analyzed. The results show a high concentration of REEs in surface waters, in particular close to the mouth of the Orinoco, and a middle-REE-enrichment that is strongest in the south and east of the study area suggesting that fluvial inputs are the main sources rather than REEs supplied by Saharan dust. The surface waters close to the Orinoco are heavy REE enriched compared to the potential fluvial sources, emphasizing the importance of processes in the estuaries and the surface ocean that preferentially remove light- and middle-REEs. Relatively small heavy-REE enrichments in near-bottom water samples at the mouth of the Orinoco may be the result of preferential release of light REEs from river-transported sediments. The REE patterns of distinct subsurface water masses are largely coherent across the Caribbean basin, suggesting that the lateral transport of preformed compositions is not significantly influenced by vertical processes of scavenging and release. In particular, low Dy/Er molar ratios are associated with Antarctic Intermediate Water and have most likely been advected into the Caribbean from the Southern Ocean. In contrast, deep waters in the Caribbean are enriched in light and middle REEs compared to incoming Upper North Atlantic Deep Water suggesting that release from sinking particles or from sediments is an important source of these REEs in the deep ocean, in particular when deep water residence times are long.

1. Introduction

The rare earth elements (REEs) are a closely related group with similar chemical behavior (Elderfield, 1988). Dissolved REEs in seawater are supplied to the oceans from the continents but typically show a heavy-REE (HREE) enriched pattern compared to the average continental crust (De Baar et al, 1985; Elderfield and Greaves, 1982; Elderfield, 1988; Klinkhammer et al., 1983; Taylor and McLennan, 1985). As REEs are not considered to be biologically important, the seawater pattern has instead been attributed to differing solid/solution partition coefficients (Byrne and Kim, 1990). With the exception of Ce(IV) and Eu(II), the REEs are trivalent and show an increasing tendency for complexation as atomic number rises (Cantrell and Byrne, 1987; De Baar et al, 1991). Affinities can be predicted from experiments and show that light-REEs (LREEs) are adsorbed to most surfaces, whereas HREEs are more strongly complexed by ligands and thus preferentially stay in solution (Byrne and Kim, 1990; Cantrell and Byrne, 1987). Much of the preferential removal of LREEs from river water entering the ocean occurs at low salinities and may be driven by salt induced coagulation of river-borne colloids (Elderfield et al, 1990; Goldstein and Jacobsen, 1988; Sholkovitz, 1976, 1992, 1993, 1995; Sholkovitz and Elderfield, 1988). There is also evidence for preferential release of HREEs at higher salinities in estuaries, which would further increase the HREE enrichment in seawater relative to the average composition of continental rocks (Sholkovitz and Szymczak, 2000). Vertical processes in the water column under full marine conditions, such as particle scavenging and release, are also important in modifying the concentrations of REEs relative to one another (Byrne and Kim, 1990; Elderfield and Greaves, 1982; Sholkovitz et al., 1994). Consistent with the residence time of the light trivalent REEs on the order of several 100 years (e.g. Rempfer et al., 2011) and a most likely even longer residence time of the heavy REEs, a further important factor influencing the distribution of REE compositions in seawater is lateral advection of pre-formed compositions, which has led to the suggestion that REE patterns can be used as water mass tracers (German et al., 1995; Haley et al., 2014; Molina-Kescher et al., 2014; Piepgras and Wasserburg, 1982; Zhang and Nozaki, 1996).

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http://dx.doi.org/10.1016/j.marchem.2015.03.013

The Caribbean and the Gulf of Mexico (GOM) provide a unique setting to examine the relative importance of vertical and horizontal processes on the REE composition of seawater. The surface ocean in the Caribbean is likely to have been strongly affected by inputs from the Amazon, Orinoco and Magdalena Rivers, which together comprise approximately 20% of the global fluvial discharge (Hu et al., 2004; Müller-Karger et al., 1989). Further inputs of REEs are expected from the Mississippi River as well as from Saharan dust (Prospero and Mayol-Bracero, 2013), similar to observations in the Southeast Atlantic (Bayon et al., 2004). Vigorous circulation channels large volumes of Atlantic water through surface and intermediate depths in the Caribbean (28 Sv, Johns et al., 2002), whereas turnover in the deep Caribbean is limited by a maximum sill depth of ~1800 m and is very slow (0.2 Sv, Fratantoni et al., 1997; Joyce et al., 1999; MacCready et al., 1999; Stalcup et al., 1975; Sturges, 1975; Worthington, 1955). A companion paper has shown that all of these factors, in particular additions and/or exchange with the sediments, significantly alter the radiogenic isotope composition of the REE Nd in deep waters of the Caribbean (Osborne et al., 2014). Here we examine if and how the dissolved REEs in seawater are transformed during passage through the Caribbean and the GOM.

1.1. Hydrographic setting

The hydrography of the study area and sampling stations has been presented in detail in Osborne et al. (2014). In brief, seawater channeled through the Caribbean is an important part of the Western Boundary Current, which forms the upper, northward-flowing limb of the Atlantic Meridional Overturning Circulation (Schmitz and McCartney, 1993; Schmitz and Richardson, 1991). The Caribbean, Loop and Florida Currents transport thermocline waters through the Caribbean and the GOM into the Western North Atlantic (Fig. 1). Caribbean Water (CW, 0–80 m) is a mixture of Atlantic and Orinoco water, with seasonally varying amounts of Amazon River water delivered via the Guyana Current (Müller-Karger et al., 1989). Subtropical Under Water (SUW) originates in the tropical and subtropical Atlantic gyres and is transported into the Caribbean via the Northern Equatorial Current (Johns et al., 2002; Wüst, 1964). Eighteen Degree Water (EDW) (Worthington, 1959, 1976) is present in the northern part of the Caribbean basin, having formed in the western North Atlantic subtropical gyre (Forget et al., 2011), otherwise the water mass directly below SUW is North Atlantic Central Water (NCW). Low salinity Antarctic Intermediate Water (AAIW) is found between ~400 and 1000 m and is more prominent in the southern and eastern parts of Caribbean (Wüst, 1964). The deepest water entering the Caribbean is restricted by the maximum depth of the sill connecting it to the Atlantic and thus the deep Caribbean is filled with Upper North Atlantic Deep Water (UNADW) to a depth of ~1800 m (Wüst, 1964).

2. Methods

Samples were taken during Meteor Cruise 78, Leg 1 in February and March 2009 (Fig. 1). Surface water samples at Sites 226-3 and 249-1 were collected using an acid cleaned 20 L polycarbonate cylindrical plastic vessel, deployed in the upper meters using a clean nylon/polymer recovery tether. All other samples were collected in Niskin bottles attached to the shipboard CTD-rosette. Approximately 20 L of seawater was recovered at each sampling depth and was filtered through 0.45 μm Millipore® cellulose acetate filters and acidified to pH ~ 2 with double distilled concentrated HCl within a few hours of collection. The samples

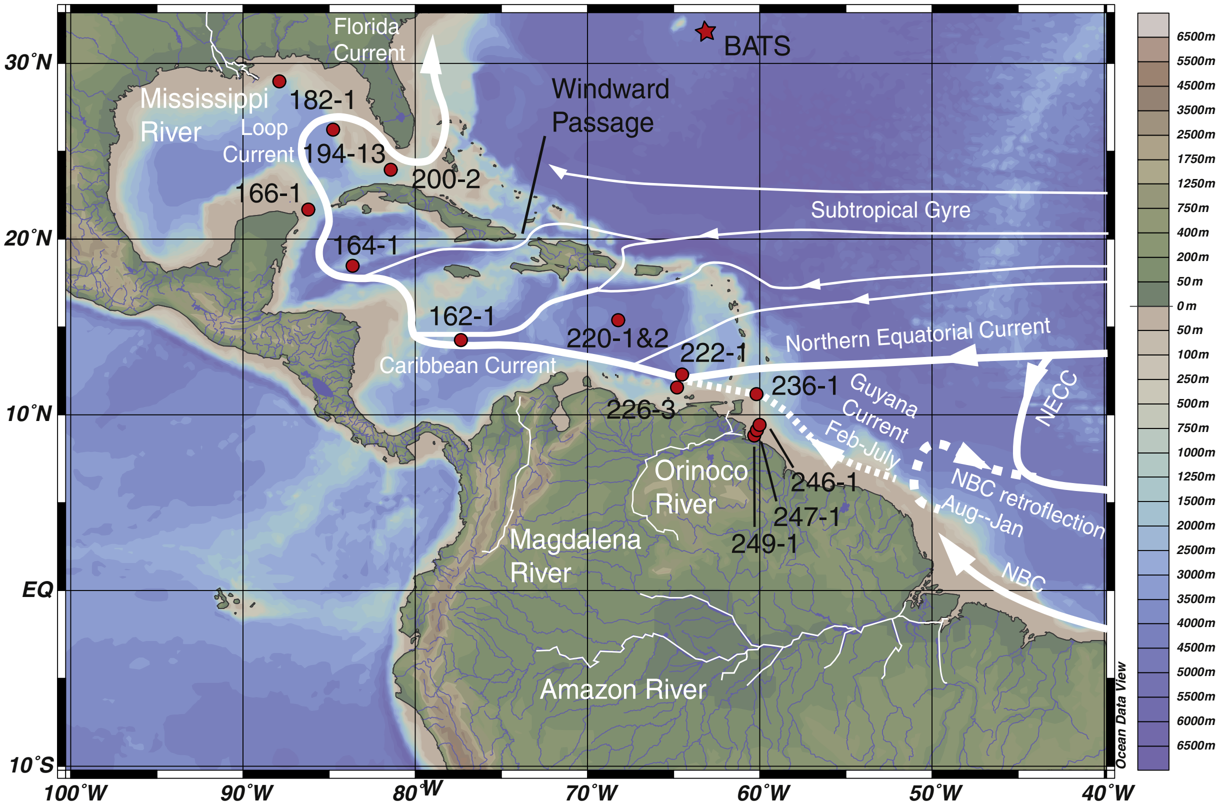

Fig. 1. Location map. Sampling stations occupied during RV Meteor cruise M78/1 (red circles) and the BATS site (red star, Van de Flierdt et al., 2012). Also shown are major rivers and surface ocean currents, modified from Osborne et al. (2014) following Hellweger and Gordon (2002), Jouanno et al. (2008), Lumpkin and Garzoli (2005), Schott et al. (2002) and Steph et al. (2006). NBC, North Brazil Coastal Current; NECC, Northern Equatorial Counter Current. The figure was produced using Ocean Data View (Schlitzer, 2011).

were stored in acid cleaned polyethylene bottles and the pH was rechecked prior to measurement.

REE concentrations for all samples were determined using a seaFAST online pre-concentration system (Elemental Scientific Inc., Nebraska, USA) directly connected to an Agilent 7500ce ICP-MS at GEOMAR. All samples were initially measured following the procedures detailed in Hathorne et al. (2012). External reproducibility was monitored by repeated measurements of the GEOTRACES inter calibration sample BATS (15 m) (van de Flierdt et al., 2012) and was between 6 and 22% (2σ), except for Sm which was 30% owing to a Sm blank originating from the buffer solution during one of the measurement sessions (Hathorne et al., 2012). Since the first measurements in 2011 significant improvements have been made to the seaFAST technique and selected samples were re-measured using two important modifications of the original method, which also included measuring concentrations of Y together with the REEs. The main modifications of the method were the use of an 8 mL sample loop, rather than 4.2 ml, and the preparation of calibration standards with a mixed REE solution of a seawater-like composition in a natural seawater matrix. Trace metals, including the REEs, were removed from this seawater matrix by FeOOH co-precipitation and the REE concentrations in the resulting emptied seawater are indistinguishable from 2% HNO_3 blanks or 0.1% HCl. Although no shipboard procedural blanks were taken during this cruise, comparable shipboard blanks obtained during other cruises by our lab using very similar methods were <0.16 pM for La and Ce and below detection for other elements. The accuracy and precision of the analyses were assessed by repeated analysis of GEOTRACES BATS reference seawater samples (Table S1). The best 2σ reproducibilities between 1 and 15% for all REEs were obtained by time resolved analysis (TRA), a recent adaption to the data collection that allows the elution peak to be sampled at the highest frequency. Table S1 and Fig. S1 (Supplementary material) shows that all three modifications of the method reproduce within the uncertainties of the GEOTRACES inter-calibration values (van de Fierdt et al, 2012).

3. Results

Results are presented in Supplementary Table S2 and in Figs. 2 and 3. For those samples that were re-measured using the modified method (Stations 162-1, 166-1, 200-2 and 236-1), the results from the TRA method are reported here. All other results have been obtained using the method of Hathorne et al. (2012).

Surface waters of the Caribbean and GOM stations (0–11 m) are enriched in REEs compared to the sub-surface layer (~100–200 m), for example La concentrations range from 17.3 to 21.7 pM around a mean of 20.1 pM in the uppermost samples, decreasing to a range from 15.4 to 19.6 pM around a mean of 16.9 pM in the sub-surface concentration minimum (Fig. 2). After an initial drop in the subsurface waters most LREEs and middle-REEs (MREEs) increase again in concentration below ~200–400 m to values similar to or, in the case of La, greater than those of the surface waters (the average La concentration of samples between 500 and 1000 m water depth is 22.9 pM, with a range

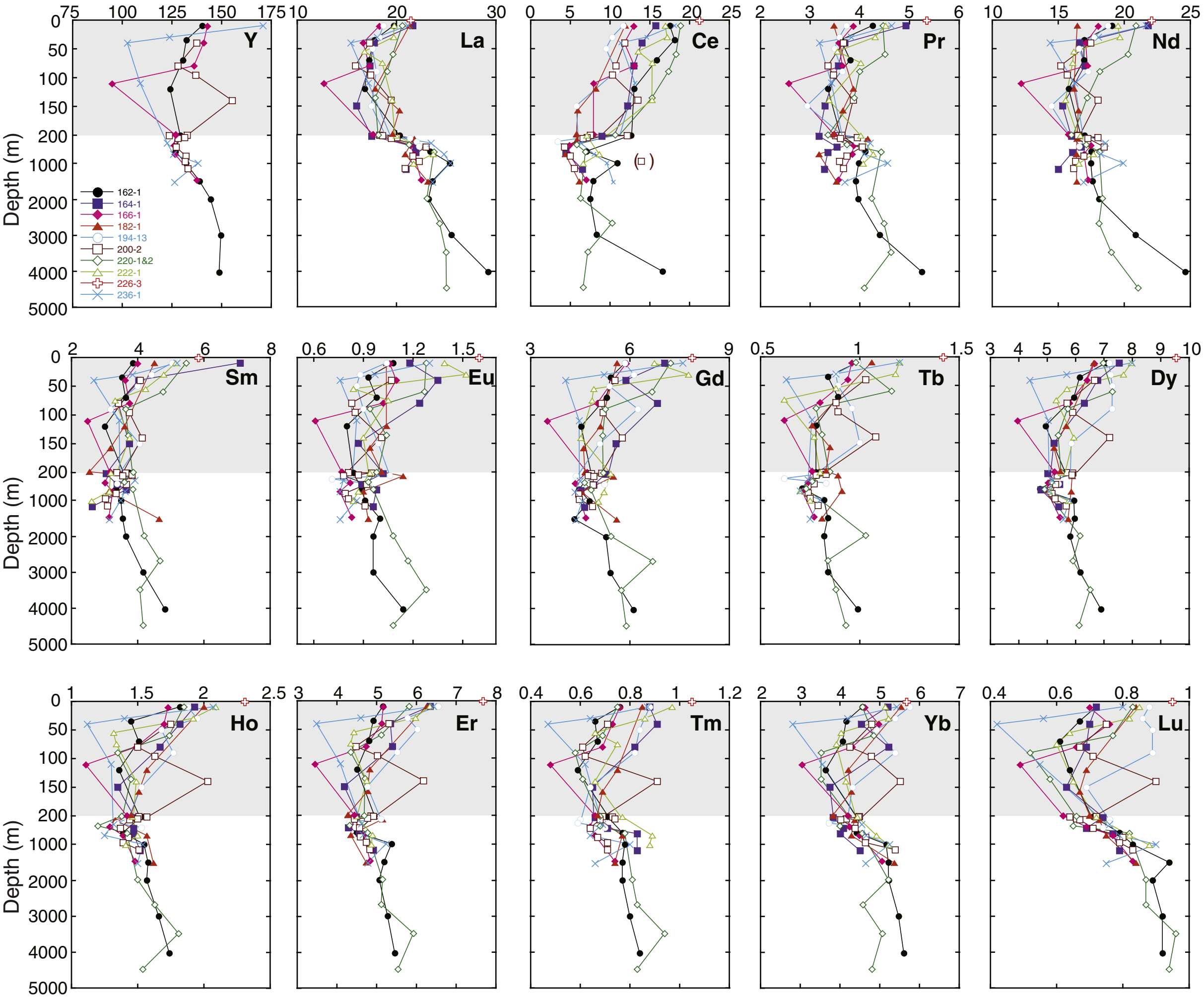

Fig. 2. REE profiles. Water column profiles of the REEs in all except the Orinoco plume stations. Also shown are the Y concentration profiles for those stations measured using the TRA method. All concentrations are in pM.

from 20.9 to 25.4 pM). Ce, in contrast, remains depleted below the surface layer (surface sample Ce concentrations range from 11.7 to 21.2 pM around a mean of 15.7; between 500 and 1000 m water depth Ce concentrations range from 4.3 to 13.9 pM around a mean of 6.8 pM). The sample at 950 m from Station 200-2 in the Florida Straits has significantly higher Ce concentrations than other samples at similar depths and samples above and below in the same profile. Despite repeat measurements confirming this high Ce concentration, this data point at Station 200-2, 950 m is considered suspect and will not be discussed further. Whereas most LREEs and MREEs show a moderate increase in concentration continuing into the deep ocean (e.g. La concentrations below 1000 m water depth range from 20.9 to 29.2 pM around a mean of 23.7 pM), the HREE concentrations remain relatively constant below ~1000 m (e.g. Lu concentrations below 1000 m water depth range from 0.8 to 1.0 pM around a mean of 0.9 pM). Station 200-2 in the Florida Strait does not follow this general pattern and instead shows a subsurface maximum in REE concentration at 140 m water depth. The hydrographic profile at this station is also different from the Caribbean sites and will be discussed in detail below.

REE concentrations at Station 249-1, closest to the mouth of the Orinoco (Fig. 1), are two to three times higher than all other surface water samples in this study (mean La concentration is 52.4 pM). Surface seawater REE concentrations at nearby Stations 247-1 (La = 21.6 pM) and 246-1 (La = 23.1 pM) are slightly elevated compared to the Caribbean stations and are also higher than the concentrations at 30 m and 50 m depth in the same profiles (La concentrations range from 15.5 to 19.5 pM around a mean of 17.4 pM).

Fig. 3 shows the REE patterns for each station normalized to Post-Achaean Australian Shale (PAAS) (Taylor and McLennan, 1985) on both linear and log scales. The amount of preferential Ce removal relative to its lanthanide neighbors is displayed by the 'Ce-anomaly', Ce/Ce*, defined as the PAAS normalized (Taylor and McLennan, 1985) Ce concentration divided by the average of the PAAS normalized Pr and Nd concentrations (Fig. 4). Lower Ce/Ce* values indicate a stronger Ce removal relative to La and Pr. The Ce-anomaly is significantly less pronounced in the surface waters of Orinoco Station 249-1 (Ce/Ce* is 0.7) than at all other surface water samples (Ce/Ce* ranges from 0.32 to 0.47 around a mean of 0.40).

Common to all REE patterns (Fig. 3) is a systematic enrichment from Ce to Er, most pronounced in surface and sub-surface samples. There is a large variability, however, in the abundances of the HREEs, which will be discussed in more detail below.

4. Discussion

4.1. Surface water REE distribution

All surface water REE concentrations of this study are elevated compared to the open Atlantic Ocean (BATS 15 m, van de Flierdt et al., 2012) and the highest REE concentrations are found in the stations closest to the Orinoco River mouth (249-1, 247-1 and 246-1, Figs. 1, 3 and 5). All surface samples show the typical PAAS-normalized seawater REE pattern of progressive enrichment with increasing atomic mass and peaks at Er–Tm, similar to the BATS 15 m sample (van de Flierdt et al., 2012) (Fig. 5a). However, normalizing the surface water samples to seawater (BATS 2000 m, van de Flierdt et al., 2012) reveals a broad MREE-enrichment that is most prominent in the surface waters near the Orinoco mouth (Fig. 5b). A distinct MREE-enrichment is also clearly present at Station 226-3, which is located in the coastal upwelling region of the southern Caribbean (Rueda-Roa and Muller-Karger, 2013), and moderate MREE-enrichments are present at the other two stations from the southeastern Caribbean (236-1 and 222-1). This spatial distribution of the strongest MREE-enrichments supports an Orinoco/Amazon source of REEs to the surface ocean. No dissolved REE data are available for Orinoco River water itself but Orinoco sedimentary organic matter has a broad MREE-enriched pattern (Freslon et al., 2014) (Fig. 5a). Amazon River water is also MREE-enriched, with a distinct peak in Gd (Goldstein and Jacobsen, 1988; Elderfield et al, 1990; Sholkovitz, 1993) (Fig. 5a). The MREE-enrichment at Stations 247-1 and 246-1 near the Orinoco mouth is centered on Tb and is somewhat different from the station nearest to the Orinoco (249-1), which shows a broad, flat MREE-enrichment from Sm to Tb (Fig. 5b). Although no Tb concentrations were measured for Amazon River water (Barroux

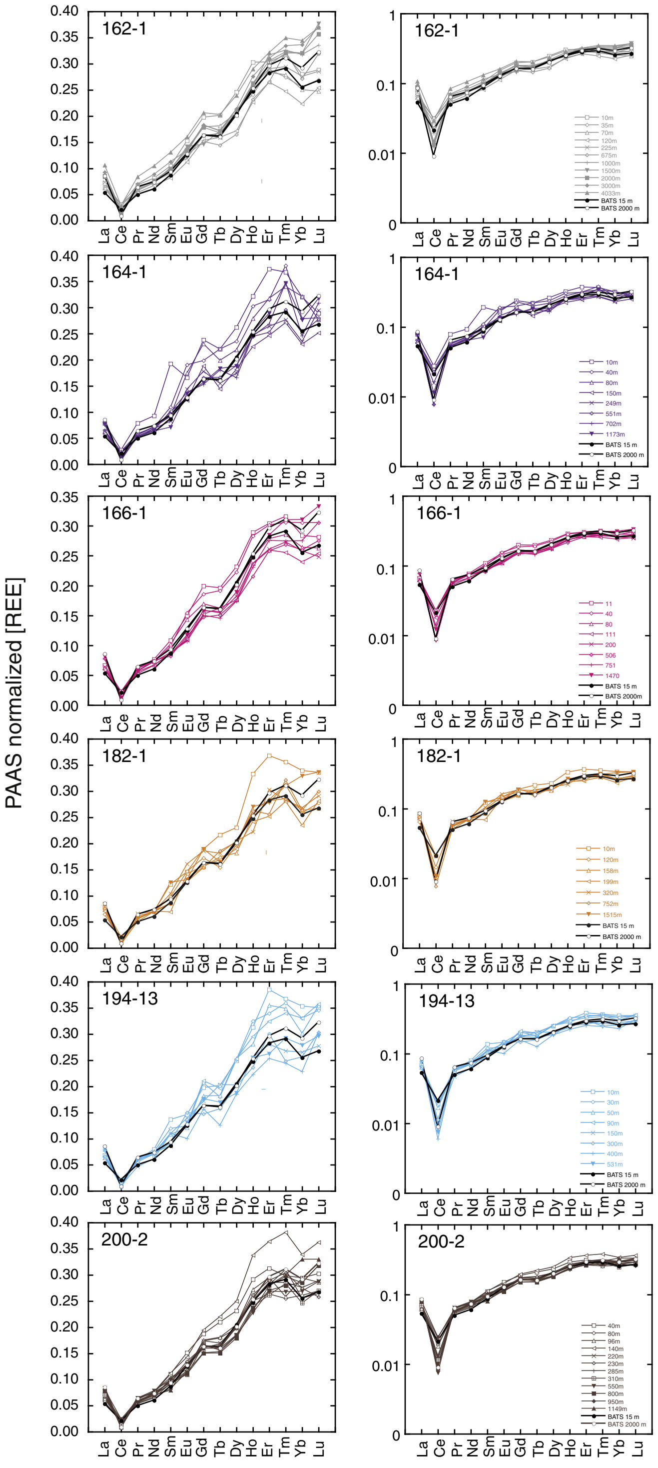

Fig. 3. REE patterns. REE patterns for each station normalized to Post-Achaean Australian Shale (PAAS) (Taylor and McLennan, 1985), plotted on both linear and log scales. The BATS 15 m and BATS 2000 m compositions (van de Flierdt et al., 2012) are shown in each panel for comparison.

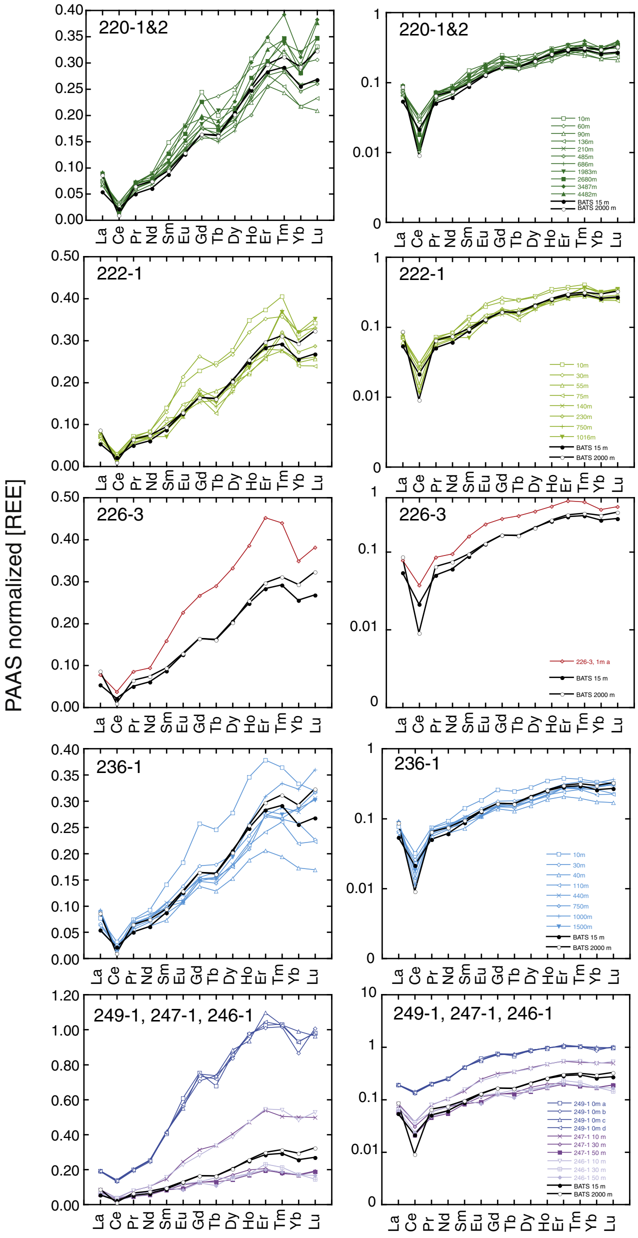

Fig. 3 (*continued*).

et al., 2006; Elderfield et al., 1990; Gerard et al., 2003), the relatively radiogenic Nd isotope composition of the surface waters at Stations 247-1 and 246-1 (~−10 ε_{Nd}) compared to Station 249-1 (−13.6 ε_{Nd}) (Fig. 6) suggests the admixture of Amazon plume water (Osborne et al., 2014). Future sampling of the Amazon River and Amazon plume will show whether Tb is indeed enriched in this source.

Another potential source of REE to the surface Caribbean is Saharan dust, which is delivered in large quantities to the Caribbean by the trade winds resulting in monthly mean atmospheric dust concentrations of up to 45 μg m^{-3} (Prospero and Lamb, 2003). It has been shown that dust can be a significant source of REEs in seawater (Bayon et al., 2004). As Saharan dust also has a broad MREE-enrichment (Pourmand et al., 2014) (Fig. 5a), which is released upon dissolution in seawater (Greaves et al., 1994) (Fig. 7), it is not possible to distinguish between the dust and fluvial sources on the basis of REE patterns alone. However, evidence from the Nd isotopic compositions of surface waters in the Caribbean, which range from −9.4 to −11 ε_{Nd} (Fig. 6, Osborne et al., 2014), supports a dominant supply of REEs to Caribbean surface waters

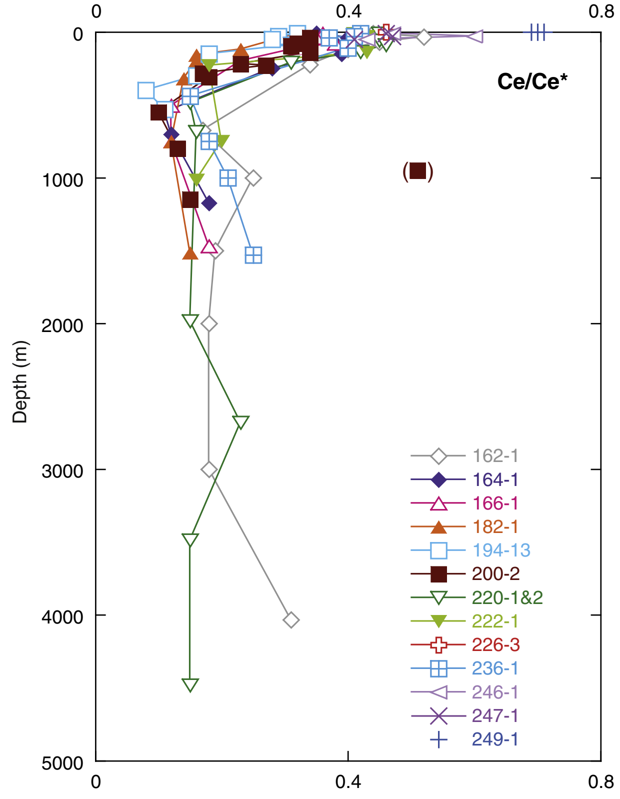

Fig. 4. Ce/Ce*. Water column profiles of Ce/Ce* for all stations. Ce/Ce* is defined as PAAS normalized (Taylor and McLennan, 1985) Ce concentration divided by average of the PAAS normalized Pr and Nd concentrations.

via mixed Amazon/Orinoco River water transported by the Guyana Current, as the Guyana Current has a more radiogenic Nd isotope composition (~−10 ε_{Nd}, Osborne et al., 2014) than Saharan dust (−10 to −14.1, the majority of samples being less radiogenic than −11, Pourmand et al., 2014).

Finally, the Mississippi may be expected to contribute REEs to the GOM and Florida Straits (Fig. 1). Mississippi River water has a seawater-like REE pattern, which has been attributed to the formation of stable carbonate complexes in the mildly alkaline river water (Shiller, 2002). This means that it is difficult to distinguish REEs supplied by the Mississippi from that already in surface seawater. However, the relatively high HREE/LREE ratio of Mississippi water (Table S2, defined as Yb_N/Nd_N, where $_N$ denotes normalization to PAAS, Taylor and McLennan, 1985) may well contribute to the higher HREE/LREE measured at Station 182-1 (4.85) close to the Mississippi mouth and at Florida Straits Stations 194-13 (4.43) and 200-2 (3.96) compared to the lower values of other Caribbean surface waters (3.15 to 3.80).

4.2. Removal and addition of REE close to the Orinoco River mouth

Plotting HREE/LREE versus MREE/MREE* (defined as average of Gd_N and Dy_N/average of Yb_N and Nd_N) emphasizes the clear distinction between potential REE sources and the surface water compositions, even close to the Orinoco River mouth (Fig. 7). All potential sources have HREE/LREE < 2 and MREE/MREE* between 1 and 2 (Barroux et al., 2006; Elderfield et al., 1990; Freslon et al., 2014; Gerard et al., 2003; Greaves et al., 1994; Pourmand et al., 2014), whereas the surface water samples (colored symbols, Fig. 7) have HREE/LREE > 2 and MREE/MREE* between 1 and 1.5. Most of the surface water samples fall on a mixing line between the potential sources and the BATS 15 m sample (van de Flierdt et al., 2012). There are, however, some exceptions, which will be discussed below.

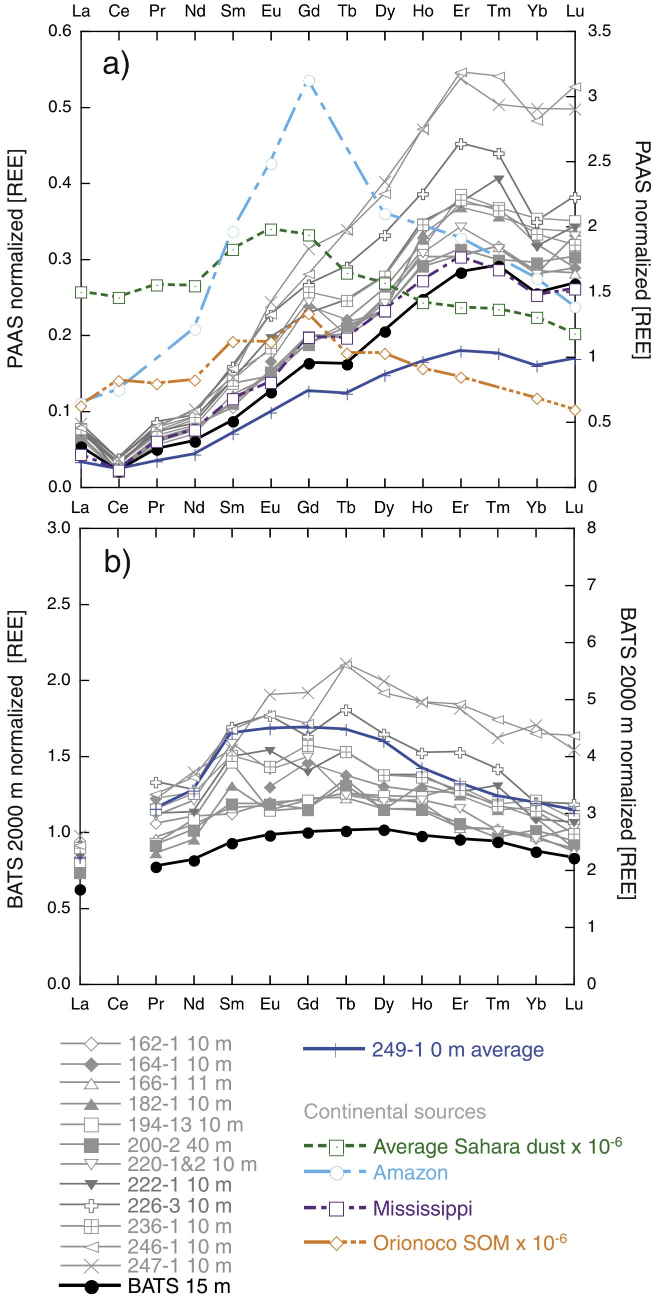

Fig. 5. Surface water REE patterns. a) PAAS normalized (Taylor and McLennan, 1985) REE concentration patterns of the surface waters and the BATS 15 m GEOTRACES intercomparison sample (van de Flierdt et al., 2012) (left y-axis), and Station 249-1 and potential sources to the surface ocean (right y-axis) (average Sahara dust, Pourmand et al., 2014; Amazon River water, Elderfield et al., 1990; Mississippi River water, Shiller, 2002; Orinoco sedimentary organic matter (SOM), Freslon et al., 2014). b) Surface water and BATS 15 m GEOTRACES intercomparison sample normalized to BATS 2000 m (van de Flierdt et al., 2012). Station 249-1 concentrations are plotted on the right y-axis.

In HREE/LREE versus MREE/MREE* space (Fig. 7), our Orinoco River-mouth samples from Station 249-1 (29.6 psu, Schönfeld et al., 2011) plot close to the data of the Amazon plume (6 to 36 psu) from the Amazon River mouth transection of Sholkovitz (1993). Only those samples with salinities < 1 in the Sholkovitz (1993) study are indistinguishable from the field of the Amazon River water (Barroux et al., 2006; Elderfield et al., 1990; Gerard et al., 2003) (Fig. 7). Orinoco River water is rich in organic material and it has been suggested that organic molecules are major carriers of REEs in the colloidal size fraction (e.g. Tang and Johannesson, 2003; Pourret et al., 2007a, 2007b; Bau et al., 2013).

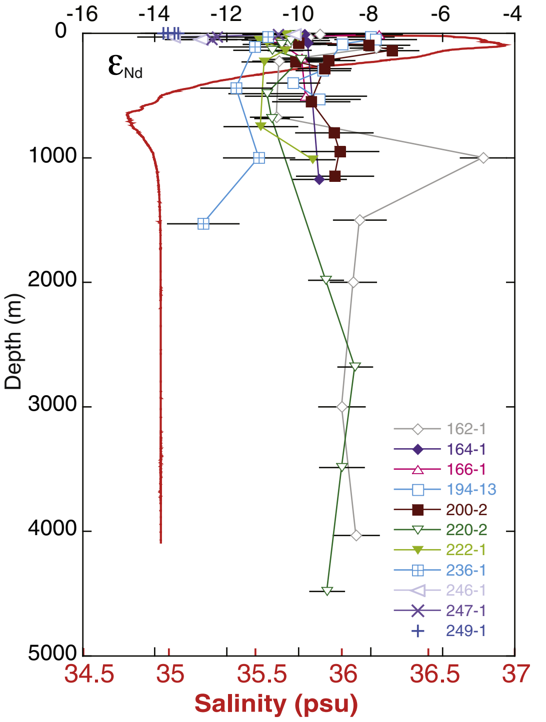

Fig. 6. ε_{Nd}. Water column profiles of ε_{Nd} (with 2 sigma error) from samples obtained during the same cruise (M78/1), and the salinity profile for Station 162-1 (Osborne et al., 2014).

Further evidence is found when considering that the dissolved REE concentrations measured in river water depend strongly on the choice of filtration or ultrafiltration pore size (Sholkovitz, 1995). For example, samples of Connecticut River water, from which the colloids were removed through ultrafiltration at <50 kD and <5 kD, are much more HREE-enriched than samples only filtered at 0.22 μm (Sholkovitz, 1995). The salt induced coagulation of river-borne colloids is thought to be the major process removing REEs from estuaries and occurs at low salinities (Elderfield et al., 1990; Goldstein and Jacobsen, 1988; Sholkovitz, 1976, 1992, 1993, 1995; Sholkovitz and Elderfield, 1988). Therefore large-scale removal of organic colloids, which are enriched in LREE and MREE (Bau et al., 2013; Haley et al, 2014; Pourret et al, 2007b), would contribute to the high HREE/LREE in Station 249-1 (Fig. 7).

Our data also suggest that additional processes involving the removal and addition of REEs maybe be of local importance close to the Orinoco River mouth. The surface samples at Stations 246-1 and 247-1 have amongst the highest HREE/LREE ratios in the study area (4.81 to 4.85, Fig. 7). As previously discussed, the relatively radiogenic Nd isotope composition of these samples (~− 10 ε_{Nd}, Osborne et al., 2014, Fig. 6) suggests the admixture of Amazon plume water. High particle density and/or productivity may be responsible for the pronounced removal of LREE from the dissolved load during advection of these surface waters. Interestingly, the underlying waters at 30 and 50 m at the two stations, which are already below the distinct halocline, have much lower HREE/LREE ratios and also a much less radiogenic ε_{Nd} signature (~− 13, Osborne et al., 2014, Fig. 6). While the ε_{Nd} signature would be consistent with both an Atlantic seawater and an Orinoco River source (Goldstein and Jacobsen, 1987; Huang et al., 2014; White et al., 1985), the low HREE/LREE ratio indicates preferential release of LREEs from riverine particles (Sholkovitz, 1995), or release of REEs from organic matter (Freslon et al., 2014), and is thus more consistent with an Orinoco source. This supports the idea that sediments deposited near river mouths may supply LREEs to seawater (Sholkovitz, 1993; Sholkovitz and Szymczak, 2000).

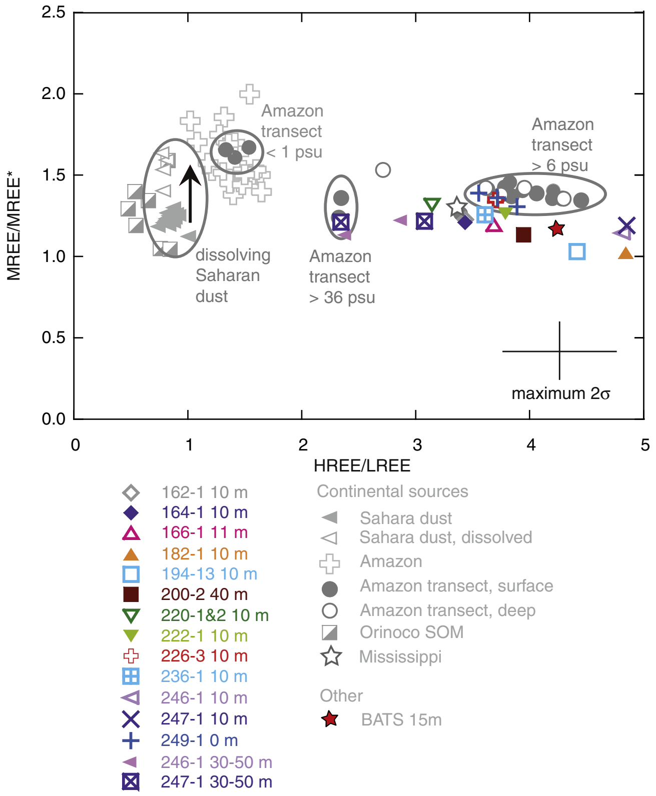

Fig. 7. HREE/LREE versus MREE/MREE*. Surface water samples and literature values plotted as PAAS normalized (Taylor and McLennan, 1985) HREE/LREE (Yb/Nd) vs. MREE/MREE* (average of Gd and Dy/average of Yb and Nd). The ratios have been defined in this way in order to include the maximum amount of literature values, as studies using isotope-dilution methods were unable to measure the concentrations of mono-isotopic REEs (Pr, Tb, Ho and Tm). Continental sources are Sahara dust (Greaves et al., 1994; Pourmand et al., 2014), dissolved Sahara dust (Greaves et al., 1994); Amazon River water (Barroux et al., 2006; Elderfield et al., 1990; Gerard et al., 2003), transection of the Amazon estuary (Sholkovitz, 1993), Orinoco sedimentary organic matter (SOM) (Freslon et al., 2014), and Mississippi River water (Shiller, 2002). Also shown for comparison is BATS 15 m (van de Fierdt et al, 2012).

In summary, surface water REE concentrations in the Caribbean–GOM are higher than in the open Atlantic Ocean (BATS 15 m, van de Flierdt et al., 2012) and show a MREE-enrichment which is strongest in the south and east of the study area. This indicates that REE supply to the surface ocean is dominated by inputs from the Amazon and, locally, the Orinoco, consistent with the distribution of ε_{Nd} compositions (Osborne et al., 2014, Fig. 6). Relatively low HREE/LREE ratios in near-bottom water samples at the mouth of the Orinoco may be the result of preferential release of LREE from river-transported sediments.

4.3. Subsurface and intermediate water REE patterns

Below the surface waters, the REE concentration profiles (Fig. 2) show nutrient-like behavior, with removal from the dissolved phase in the upper water column and release at depth, in particular for the LREEs. However, categorizing the seawater samples into different water masses based on temperature and salinity (Osborne et al., 2014) and plotting the REEs normalized to BATS 2000 m (van de Flierdt et al., 2012) (Fig. 8) reveals a large degree of consistency within the subsurface and intermediate water masses. The REE patterns of SUW, EDW and NCW at all stations have similar shapes characterized by a small MREE enrichment and a progressive HREE depletion relative to BATS 2000 m, and these patterns are consistent across the basin. The small MREE enrichment hints at a contribution from either dust or the fluvial input, however a better characterization of the incoming water masses at each of these depths is required to assess whether this signal was acquired within or outside of the study area. Despite the input of REEs to the surface ocean, the underlying water masses are largely unaffected during passage through the Caribbean itself. The Nd isotope compositions of the same samples were shown to have Atlantic-like surface and intermediate water ε_{Nd} compositions in the Caribbean, consistent with ε_{Nd} behaving as a quasi-conservative water mass tracer (Osborne et al., 2014, Fig. 6). Rapid transport of these water masses through the basin with average current speeds of 30 to 40 cm s^{-1} (Fratantoni, 2001), is likely to limit the interaction with REEs supplied from the surface ocean and is probably mainly responsible for the conservative behavior of both REE patterns and ε_{Nd}.

One sub-surface water mass, however, does have a distinctly different REE pattern. Samples taken from the relatively low salinity, high oxygen waters between 50 and 150 m water depth at Stations 194-13 and 200-2, close to Florida, (Figs. 1 and S2) have elevated MREEs and HREEs that are more similar to surface water concentrations (Fig. 2, Table S2). At Station 200-2, this layer is located between SUW above and EDW below. The distinct REE patterns (Fig. 8b), hydrographic properties and relatively radiogenic ε_{Nd} compositions (Osborne et al., 2014, Fig. 6) all point to these samples having a source different from other sub-surface waters. The ε_{Nd} signature is not consistent with the admixture of Mississippi water (Goldstein et al., 1984; Osborne et al., 2014) and the REE patterns are also not similar to those at near-Mississippi Station 182-1 at any depth (not shown). The hydrographic properties, however, are similar to those of subsurface waters entering via the Windward Passage (Fig. 1) (Roemmich, 1981; Schmitz and Richardson, 1991). Other studies have shown before that some distinct REE patterns, such as Eu and Gd anomalies, can be traced laterally over larger distances (e.g. Grenier et al., 2013). If the distinct REE pattern at Stations 194-13 and 200-2 has indeed been transported laterally, either a contribution from a distinct source with elevated MREE and HREE concentrations must be responsible for this pattern, perhaps in the Windward Passage itself, or these waters are derived from an area with high particle fluxes and pronounced LREE removal.

4.4. The subsurface minimum Dy/Er ratio as a tracer for AAIW in the Caribbean Sea and other areas of the global ocean

The REE patterns of samples taken within AAIW are similar across the basin and the concentrations of Dy and Er in particular show very little scatter (Fig. 8e). A distinct vertical minimum in the Dy/Er ratio coincides with the depth of the local salinity minimum (Fig. 9). Although most of the change in Dy/Er is close to the 2σ uncertainty, the minimum is clearly present at the same depths at all stations where AAIW is present and we therefore conclude that this is a robust feature of the REE compositions. This conclusion is supported by a statistical evaluation of the Dy/Er ratio versus error and is presented in the Supplementary material and Fig. S3. Zhang and Nozaki (1996) were the first to suggest that ratios within the HREEs could be suitable as water mass tracers. Once a water mass has acquired its HREE compositions, this may be preserved as a result of similarities in complexation efficiency of the HREEs (Cantrell and Byrne, 1987), perhaps driven by similar covalences (Tanaka et al., 2008), resulting in negligible alteration of the ratios between Dy, Ho, and Er during vertical processes of scavenging and release (Zhang and Nozaki, 1996). We show here that the low Dy/Er ratio is an advected feature, characteristic of AAIW.

The Dy/Er minimum is found in all basins influenced by AAIW. For example, Zhang and Nozaki (1996) showed that Dy/Er ratios < 1 were found between 500 and 1500 m in the southwest Pacific. Data from more recent studies also show that the Dy/Er minimum can be identified in the Equatorial Pacific and in the Pacific sector of the Southern Oceans (Grenier et al., 2013; Molina-Kescher et al., 2014). The Dy/Er minimum is less pronounced in the southeast Atlantic (German et al, 1995) and in the southwest Indian Ocean (Bertram and Elderfield, 1993) compared with data in the South Pacific. This difference in signal

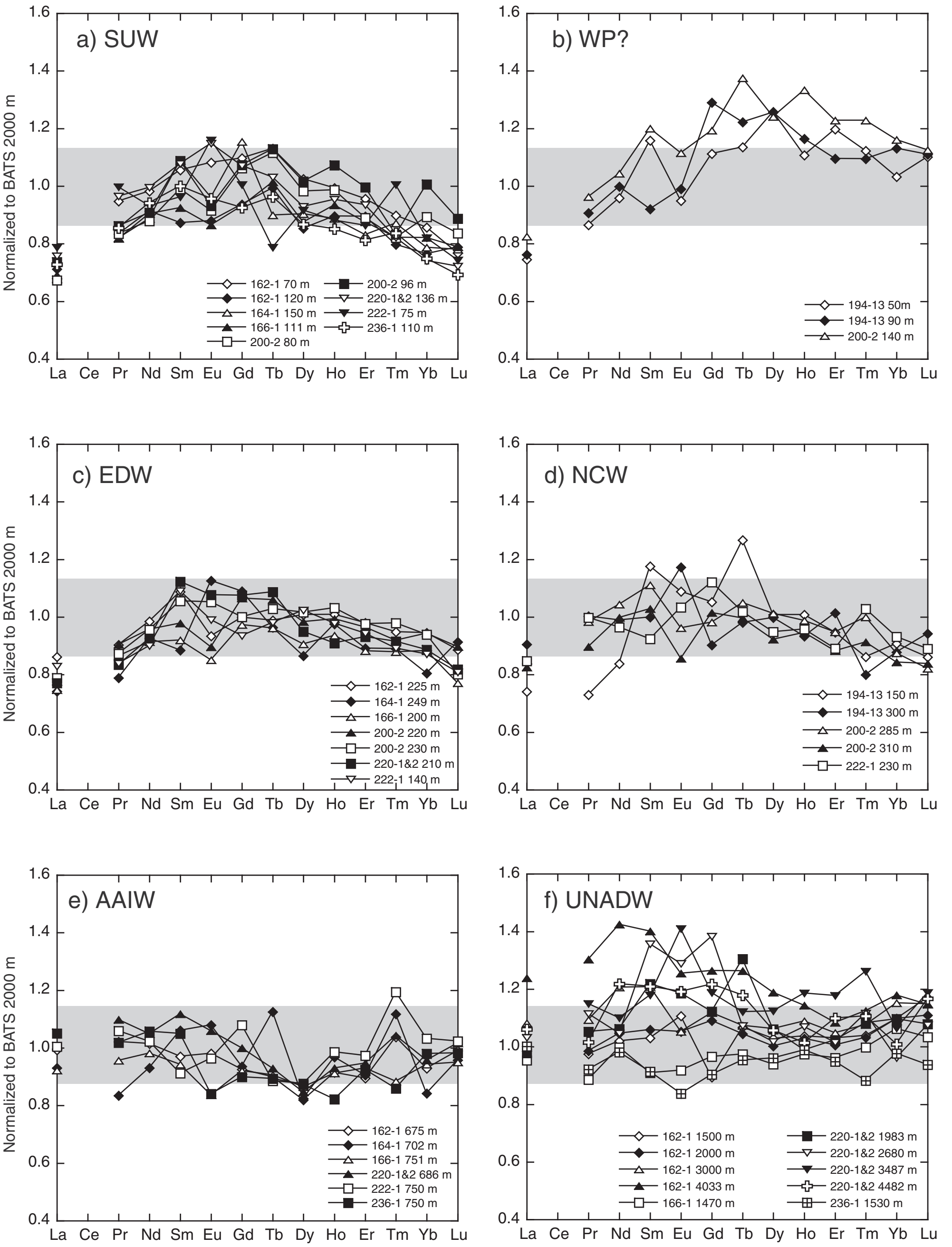

Fig. 8. Sub-surface water mass REE patterns. The data are grouped according to hydrographic properties (Osborne et al., 2014) and normalized to BATS 2000 m (van de Flierdt et al, 2012). The gray bars indicate a range of ± 14% corresponding to the largest 2 sigma uncertainties of the measurements (apart from Sm). WP? denotes water samples with a distinct REE pattern, possibly acquired during transport through the Windward Passage.

strength between basins in the Southern hemisphere may reflect basic differences in the formation history of Pacific-type and Atlantic-type intermediate waters. The minimum Dy/Er is less pronounced in the North Atlantic (Elderfield and Greaves, 1982; Pahnke et al., 2012; Sholkovitz and Schneider, 1991, Greaves et al, 1991), consistent with progressive mixing and erosion of the original core of AAIW. Furthermore, the Dy/Er ratio in water masses of the North Atlantic is generally too high to explain the Dy/Er minimum in the Caribbean samples supporting a Southern Ocean source.

A global compilation of dissolved seawater Dy and Er data (Fig. 10a) shows that some of the lowest seawater Dy/Er ratios are found in the Southern Ocean (Fig. 10c, d). By following the geographical evolution of the low Dy/Er ratios for all samples within the 27.2 and 27.4 isopycnals that bracket AAIW (Fig. 10b), the Dy/Er minimum can be traced almost to the surface (Fig. 10c) in the area between the Subantarctic and Polar Front (Fig. 10a–c).

While the low Dy/Er ratios from our Caribbean samples can be traced to the formation regions of AAIW, it is not clear how AAIW inherits its low Dy/Er ratio in the first place. A detailed investigation of possible sources of low Dy/Er in AAIW is beyond the scope of this study and we can only offer a tentative explanation here. AAIW is formed by mixing of waters from three distinct sources: subtropical waters flowing southwards towards the Subantarctic Front, Antarctic Surface Waters (AASW) moving northwards to the polar front, and some version of Upper Circumpolar Deep Water (UCDW) through subsurface mixing (see Carter et al., 2014). The Dy/Er ratio of subtropical waters is clearly too high and cannot account for the low AAIW Dy/Er signal (Fig. 10c, d). The dataset south of the polar front is too sparse to

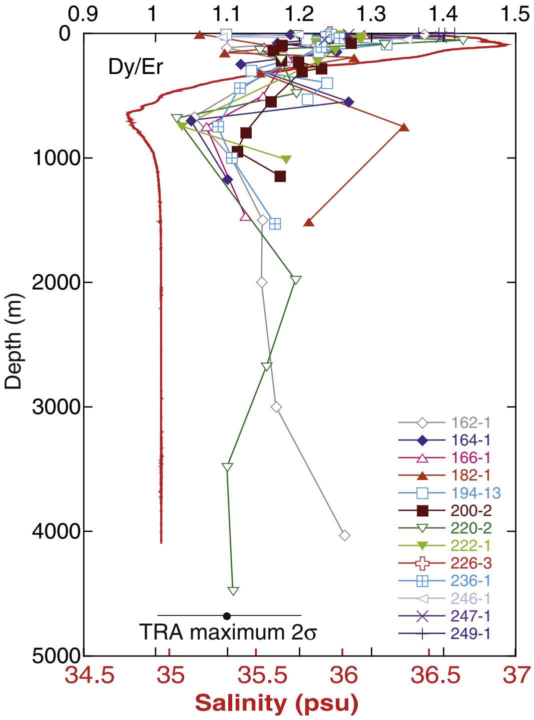

Fig. 9. Dy/Er. Water column profiles of Dy/Er for all stations. The reported values are molar ratios and the error bar represents the maximum 2σ uncertainty of 7% for those samples measured using the TRA method (Stations 162-1, 166-1, 200-2 and 236-1). The significance of the Dy/Er signal versus error is discussed more fully in the Supplementary material. Also shown is the salinity profile for Station 162-1 (Osborne et al., 2014).

unambiguously determine the Dy/Er of AASW, but Fig. 10a–c indicates that the few AASW samples available located south of the polar front (upstream of AAIW from the perspective of the AASW end-member) and with densities between 27.2 and 27.4 have Dy/Er ratios that are greater than 1 (Fig. 10c). A few surface samples with low Dy/Er values exist in the Southern Ocean (Fig. 10c), but it is not clear how these surface waters would maintain their low Dy/Er signal during the northward migration and evolution of AASW towards the polar front, as the AASW samples just south of the polar front apparently have a higher Dy/Er than AAIW. We emphasize though that this will need to be re-evaluated as the Southern Ocean REE dataset grows. However, since local lithogenic (dust, or rivers) or volcanic sources are negligible in the formation regions of AAIW and are thus unlikely to be the source of the local low Dy/Er ratio in AAIW, by elimination, subsurface mixing with some form of UCDW ought to be the likely cause of the low Dy/Er ratio in AAIW.

Pacific-type UCDW is different from Atlantic-type UCDW (Talley et al., 2011). In the Pacific, the water mass that is the equivalent to UCDW in the Atlantic in terms of density is older and tainted by Pacific Deep Water, while in the Atlantic UCDW is younger and contains a greater fraction of Labrador Sea Water and NADW. The circulation of Pacific Deep waters between 1500 and 3000 m is also more sluggish than in the Atlantic (Talley, 2008) and Pacific Deep waters interact strongly with some of the most intense hydrothermal ridges worldwide. This combination of slow circulation and high venting results in the observed accumulation of large primordial helium concentrations in the South and Equatorial Pacific (Bianchi et al., 2010). This prominent primordial helium signature is not observed in other basins (see Bianchi et al., 2010 and references therein). The deep Pacific hydrothermal primordial helium signal can be traced to the Southern Ocean, where it upwells. The primordial isotopic helium signal quickly equilibrates with atmospheric helium, however, such that the signature of primordial helium does not persist in AAIW. There are, however, data from the plume of the East Pacific Rise (EPR) showing systematically extremely low Dy/Er ratios (Fig. 10c, d, Klinkhammer et al., 1983). Particulate samples from the EPR hydrothermal pool conversely have relatively high Dy/Er ratios (1.6 ± 0.1, Sherrell et al., 1999). We consequently suggest that processes related to the hydrothermal activity in the Equatorial and South Pacific imprint a low Dy/Er signature to deep Pacific waters and that this low Dy/Er ratio ultimately contributes to the low Dy/Er ratio of AAIW; given more data, the Dy/Er ratio could become a valuable geochemical tracer helping to understand the formation mechanisms of AAIW.

We are not able to provide a mechanisms to explain how hydrothermal processes imprint a low Dy/Er on the deep waters of the South Pacific, but our preliminary study suggest 1) that the Dy/Er is sensitive to these processes, 2) that the deep low Dy/Er ratios likely forms in the Equatorial and South Pacific, possibly because of the combination of slow circulation with intense and temporally consistent venting there, and 3) that the Dy/Er ratio shows promise as a tracer to evaluate the contribution of subsurface mixing of UCDW for the formation of AAIW and to help distinguish between Pacific-type AAIW and Atlantic-type AAIW.

4.5. Accumulation of LREE and MREE in the deep Caribbean

Upper North Atlantic Deep Water can only enter the Caribbean via the Anegada–Jungfern and Windward Passages (Johns et al., 2002), where it overflows to fill the deep Caribbean to a depth of ~1800 m (Wüst, 1964). The REE profiles (Fig. 8f) show that the increase in REE concentration with depth is more pronounced for LREEs and MREEs than for HREEs, confirming that the composition of UNADW is transformed at depth within the Caribbean basin by the preferential release of LREE and MREE. This is consistent with the findings of Osborne et al. (2014), who showed that the isotopic composition of Nd in Caribbean deep waters is offset to more radiogenic values compared to the incoming UNADW (Fig. 6). The offset was attributed to the long residence time of deep waters within the basin allowing the seawater Nd isotope composition to shift towards that of the sediments and particles within the Caribbean as Nd is added to the dissolved phase (Osborne et al., 2014). The REE data presented here suggest that addition at depth is also important for Pr, Sm, Eu and Gd, with concentrations increasing by as much as 40%, if BATS 2000 m (van de Flierdt et al., 2012) is taken to represent incoming UNADW. There is also some heterogeneity in the composition of the deepest waters. For example there is a distinct Eu peak at 3487 m water depth in the Venezuela Basin (Station 220-1&2) that is not present in the other deep samples. Osborne et al. (2014) found that significant exchange of Nd with the sediments was necessary in order to balance the isotopic composition observed in the deep waters. Further deep, bottom and pore water samples are required to investigate the rate of release and/or exchange of REEs between sediment and seawater in order to better understand the magnitude of the inputs originating from this source to the deep Caribbean but also other areas of the ocean and how this may change under different hydrographic conditions, for example in a more acidified ocean.

5. Conclusions

Surface seawater REE concentrations in the Caribbean and GOM are elevated relative to the immediately underlying waters and are highest in the region of the Orinoco River mouth. The spatial distribution of the largest MREE-enrichments in the surface waters supports a dominant contribution of REEs from the Amazon/Orinoco rather than from Saharan dust. The REE composition of surface waters close to the Orinoco is HREE-enriched compared to the likely composition of Orinoco River water (Freslon et al., 2014). This is consistent with previous studies, which found that rapid scavenging processes in the estuaries and the surface ocean preferentially remove LREE and MREE from the dissolved

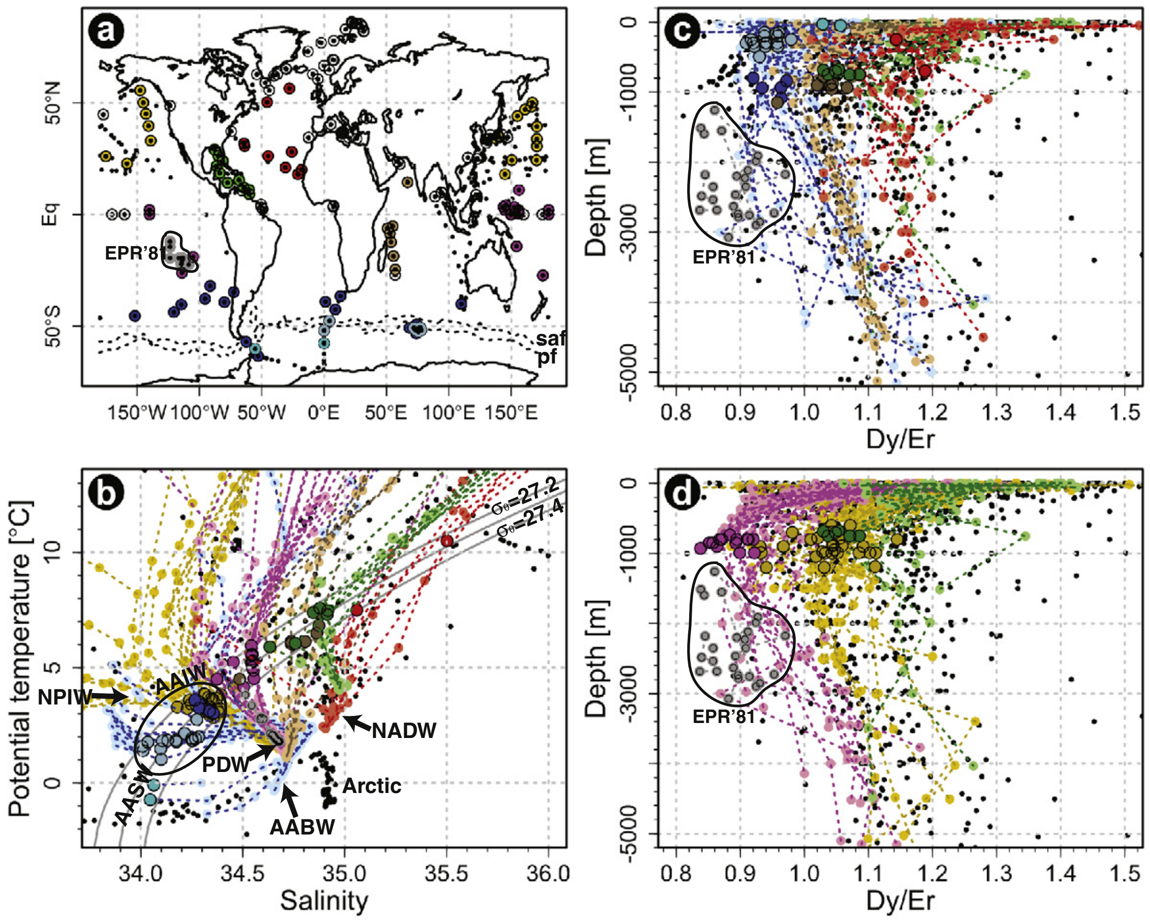

Fig. 10. Global Dy/Er. a) Map showing the locations of stations in a global compilation (Plancherel et al., in preparation, references for data sources in Table S3) of Dy/Er measurements (black dots). Stations containing more than one sample are circled in black. Data used in panels (b) to (d) are colored according to this map. The Subantarctic (SAF) and Polar Front (PF) are shown as black dotted lines (Orsi et al., 1995). Hydrothermal plume data from the East Pacific Rise 1981 Vulcan expedition (Klinkhammer et al., 1983) are marked as EPR'81 and drawn in gray in all panels. b) T/S diagram of the data. Potential temperature and salinity values for all samples were interpolated from the annual gridded World Ocean Atlas 2005 climatology (Antonov et al., 2006; Locarnini et al., 2006). Main water masses are marked: North Atlantic Deep Water (NADW), Antarctic Bottom Water (AABW), Antarctic Surface Water (AASW), Antarctic Intermediate Water (AAIW), North Pacific Intermediate Water (NPIW), and Pacific Deep Water (PDW). The 27.2, 27.3 and 27.4 isopycnals are shown as gray contours. Dy/Er vs. depth profiles for c) the Southern Ocean (blue), North Atlantic (red), Indian (brown) and the Caribbean (green, this study) and d) the South and equatorial Pacific (magenta), the North Pacific (yellow) and the Caribbean (green, this study). In panels (b) to (d), data points within the range 27.2 ≤ σ_θ ≤ 27.4 are drawn with larger symbols, darker shades and circled in black.

phase. Preferential release of LREE from river-transported sediments may be responsible for the low HREE/LREE ratios in near-bottom water samples at the mouth of the Orinoco. Sub-surface and intermediate waters largely retain their REE patterns across the Caribbean and GOM basins, suggesting that horizontal advection of REEs and their patterns is more important than vertical processes of scavenging and release. In particular, AAIW has a distinctly low Dy/Er ratio, which appears to have been transported laterally from the AAIW formation regions in the Southern Ocean, although the origin of the low Dy/Er signal itself requires further investigation. UNADW in the deep Caribbean is enriched in LREE and MREE relative to the incoming waters by as much as 40%, suggesting that the addition of these REEs at depth through release from particles or sediments may be important for local and global REE budgets.

Database linking

Table S2 will be available via the PANGAEA database (www.pangaea.de) — further details tbc.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marchem.2015.03.013.

Author contributions

A.O. processed the data; B.H., E.H. and A.O. analyzed the samples; Y.P. provided the global seawater REE compilation. Together A.O., B.H., E.H., Y.P. and M.F. discussed and interpreted the data and wrote the paper.

Acknowledgments

Thank you to the Captain and crew of the R/V Meteor. We also thank two anonymous reviewers for their constructive comments and the Guest Editors for editorial handling. This work was funded through an Alexander von Humboldt Fellowship (A.O.). Y.P. acknowledges support from NERC via the UK GEOTRACES consortium.

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