



# Particulate Rare Earth Element behavior in the North Atlantic (GEOVIDE cruise)

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10 **Abstract.** Particulate concentrations of the fourteen Rare Earth Elements (PREE), yttrium and 232-thorium have been measured in two hundred samples collected in the epipelagic (ca 0-200 m) and the mesopelagic (ca 200-1000 m) zones of the North Atlantic, during the GEOVIDE cruise (May/June 2014, R/V Pourquoi Pas ?, GEOTRACES GA01). Particulate cerium (PCe) concentrations vary from 0.2 pmol.L<sup>-1</sup> to 16 pmol.L<sup>-1</sup>, particulate neodymium (PNd) ones from 0.09 pmol.L<sup>-1</sup> to 6.1 pmol.L<sup>-1</sup> and particulate ytterbium (PYb) ones from 0.01 pmol.L<sup>-1</sup> to 0.5 pmol.L<sup>-1</sup>. PREE concentrations are higher close to  
15 the Iberian margin and on the Greenland shelf, where PREE concentrations normalized to Post Archean Australian Shale (PAAS) display a positive Ce anomaly between 0.3 and 3, and a light REE (LREE) enrichment compared to heavy REE (HREE) illustrated by high PNd<sub>N</sub>/PYb<sub>N</sub> ratios (normalized to PAAS). The lithogenic fraction of the particulate REE concentration is closely related to the margin morphology and the hydrodynamic context: off the Iberian margin, up to 100% of the PREEs are lithogenic and this lithogenic input spreads westward along isopycnals as intermediate nepheloid layers (INL)  
20 up to 1700 km<sup>2</sup>. Lithogenic inputs are also observed along the Greenland and Newfoundland margins, although the circulation stacks them along the coasts. PREE distributions are also controlled by the biological uptake in the surface layers and remineralization processes deeper. Low surface concentrations and some normalized REE patterns displaying a negative Ce anomaly and HREE enrichment indicate freshly formed biogenic particles. A significant relationship between biogenic silica (BSi) and PHREE is also observed in the diatom blooms occurring in the Labrador and Irminger seas. PHo/PY ratio was  
25 calculated in order to identify processes independent of the ionic radius. However, we could not firmly assess the role of the iron hydroxides in the scavenging prates of these elements.

## 1 Introduction

Marine particles are the main way to transfer chemical species to the deep ocean together with the convection of water masses. Particles are abundant in the upper ocean, where dust inputs or massive blooms occur (up to 1000 µg.L<sup>-1</sup>), but their  
30 concentration decrease with depth (5 to 60 µg.L<sup>-1</sup> on average in the subsurface and deep ocean, (McCave and Hall, 2002; Stemann et al., 2002). However, particles are up to 1000 times more concentrated in elements than the dissolved phase (Lam



et al., 2015), and especially in trace elements. For example, in the subpolar North Atlantic (GEOTRACES GA01 cruise, the section studied here), particulate Fe (PFe) concentration can reach  $50 \text{ nmol.L}^{-1}$  when dissolved Fe (DFe) does not exceed  $2.5 \text{ nmol.L}^{-1}$  (Gourain et al., 2019; Menzel Barraqueta et al., 2018; Tonnard et al., 2018). The size spectra between the particulate and the dissolved phase is continuous and the separation between both pools is operational, depending on the porosity of the filters used to discriminate the two phases, usually  $0.4 \mu\text{m}$  (Planquette and Sherrell, 2012). Concentrations then depend on the choice of this limit, even if the vertical flux is mostly due to the large, dense, sinking particles, in opposition to the smaller and less dense particles that are in suspension in the water column. However, these small suspended particles represent over 80% of the total particle mass (Lam et al., 2015 and references therein). In addition, their higher surface to volume ratios make suspended particles the main drivers of dissolved-particulate exchanges.

In the ocean, three main sources of particles are distinguishable. The first one is lithogenic, with inputs from the rivers, dust deposits, ice melting and resuspension of deposited sediments. The second one is biogenic, and related to the production of fresh organic matter by photosynthetic activity followed by zooplankton grazing, and the following life cycle. The last one consists in authigenic processes such as red clays, oxides and hydroxides precipitation and formation. All these sources and processes lead to a very heterogeneous pool, in time, space and composition, evolving throughout their stay in the ocean and control the density of particles and consequently their fate in the water column. Then, exchanges between the particle and dissolved phases determine the chemistry of seawater and the residence time of the chemical species. They also determine the transfer rate of elements such as carbon and micro-nutrients between the upper layers and the deep ocean, where they are stored for times going from the global circulation scale (500 – 1000 years) to geological ones.

Oceanic tracers such as rare earth elements (REE) are truly adapted to the study of these exchanges (Jeandel et al., 1995; Kuss et al., 2001; Tachikawa et al., 1999). Physical and geochemical processes such as aggregation-disaggregation, dissolution, complexation, sorption, mineralization and scavenging lead to a fractionation along the REE series, depending on their origin and intensity. Thus, measuring the distribution of REEs between the solid and dissolved phases can help tracing and quantifying these processes.

The North Atlantic is a key region of the global ocean, as it is the highest oceanic sink of anthropogenic  $\text{CO}_2$  (Khatiwala et al., 2013). Indeed, it is together i) a major place of deep water formation, mainly by convection, which drives the Atlantic meridional overturning circulation (AMOC), and ii) a productive area, representing up to 18% of the global oceanic primary production (Sanders et al., 2014).

In this context, we present the first basin scale section of PREE concentrations and fractionation patterns obtained for suspended particles collected in the North Atlantic (SPNA), along the GEOVIDE section (GA01 GEOTRACES cruise), from the surface to 1500 m. We will specifically discuss processes affecting the PREE distribution such as lithogenic inputs from the margins, influence of biological activity and the role of ionic radius on their fate in the water column.



## 2 Methods

### 2.1 Study area: hydrographical and biogeochemical context

Samples **have been** collected in the epipelagic and mesopelagic zones (0 m – 1500 m) during the GEOVIDE cruise (16th of May 2014 to 30th of June 2014, R/V Pourquoi Pas ?) along the transect presented in Fig. 1. This figure also presents the main surface currents, as described in details (Zunino et al., 2017) and (García-Ibáñez et al., 2018), together with the three main biogeochemical provinces identified by Longhurst (1995) and described in details by Lemaitre et al. (2018). The position of the stations where PREEs were sampled (Fig. 1) were chosen to be representative of the diversity of biogeochemical provinces and water masses (Fig. 2).

Warm and salty waters coming from the tropical Atlantic are advected toward the Arctic by the North Atlantic Current (NAC, see Table 1 for abbreviations list). In response to air-sea exchanges and mixing with polar waters, surface waters become colder and fresher, but more importantly, denser. They **tend thus** to mix with underlying waters, particularly during **convecting** events triggered by storms. In the Nordic Seas (between 65°N and 80°N), the water column can be ventilated down to the bottom, while convection never exceeds 2000 m in the subpolar gyre. The freshly formed deep water then returns southward mainly via western boundary currents.

The North Atlantic Subtropical (NAST) province is characterized by warm and salty waters (García-Ibáñez et al., 2018; Longhurst, 1995; Reygondeau et al., 2018; Zunino et al., 2017). This province is depleted in nutrients, yet under influence of margin inputs, displayed a declining bloom of cyanobacteria during the cruise (Lemaitre et al., 2018). Stations #1 and #13 were sampled in the NAST. The North Atlantic Drift region (NADR) is located between the NAST and the Reykjanes ridge, with higher nutrient concentrations than in the NAST (Longhurst, 1995). A strong bloom of coccolithophorids, with a maximum intensity in the Icelandic basin, occurred during the cruise, generating the highest primary production rate observed on GEOVIDE (1740 molC.m<sup>-2</sup>.d<sup>-1</sup>, station #26, Fonseca-Batista et al., 2019) and high carbon export (up to 80 molC.m<sup>-2</sup>.d<sup>-1</sup>, station #32, Lemaitre et al., 2018). Four open ocean stations were sampled in this province: in the northern branch of the NAC (station #21), at the Subpolar front (station #26), in the northern branch of the NAC (station #32) and on the Reykjanes Ridge (station #38).

West of the Reykjanes Ridge, the Irminger and Labrador Seas (Fig. 1) are rich in nutrients, and belong to the Arctic region (ARCT). Large blooms of diatoms occurred in this area, **which a** maximum intensity at the end of May, **in other words** three weeks before GEOVIDE sampling in the Labrador Sea and one month before the sampling in the Irminger Sea. The western part of the ARCT region is under the influence of the Newfoundland margin. In this province, station #44 was sampled in the middle of the gyre of the Irminger Sea, station #51 in the BGC and station #53 on the Greenland shelf. In the Labrador Sea, station #64 is in the West Greenland Current (the **continuity** of the EGCC after it **passed** Cape Farewell) and station #69 is in the area of formation of LSW, where strong convection events occurred the winter before GEOVIDE (García-Ibáñez et al., 2018; de Jong and de Steur, 2016). Westward, **the** station #77 is close to the Newfoundland margin (ca 300 km).



## 2.2 Sampling at sea

Two sampling systems **have been** deployed during GEOVIDE to collect suspended particles: a standard CTD rosette equipped with 12 L Niskin bottles and a clean CTD rosette equipped with 12 L GO-FLO bottles. The standard rosette was used to collect samples dedicated to the concentration analyses of dissolved and particulate **barium in excess** ( $Ba_{xs}$ ), dissolved and particulate REEs (including Nd isotopic composition) as well as ancillary parameter analyses.  $Ba_{xs}$  and PREE chemical treatment and analyses were conducted on the same samples:  $Ba_{xs}$  was first measured at the Royal Museum for Central Africa (Tervuren, Belgium), then PREEs were later analyzed at LEGOS (Toulouse, France; this work). Ba and  $^{232}\text{Th}$  concentrations were measured at both places, allowing us to compare ~~our procedures~~. Regarding the samples collected with the clean rosette, Ba,  $^{232}\text{Th}$  and Y (with the latter belonging to REEs, named YREEs when Y is included) were also measured. Ba and  $^{232}\text{Th}$  were used to compare the data obtained with the standard and clean rosette procedures (as done for  $Ba_{xs}$  by Lemaitre et al., 2018, with comparable results:  $r^2= 0.61$ ,  $p < 0.01$ , Fig. S1 in supplementary) distinguishable by the sampling systems, filtration method, chemistry performed on filters and analysis. The **comparison of Y concentrations** from the two procedures validated the use of our standard rosette to sample YREEs, less prone to contamination than trace metals, as shown by van de Flierdt et al. (2012).

Sampling method and sample preparation for water collection with the standard rosette for  $Ba_{xs}$  and PYREE analyses described here follow those of Lemaitre et al. (2018). Sampling was focused on the epipelagic and mesopelagic zones (0 m – 1500 m). On board, four to eight liters were filtered using clean **slightly** pressurized containers. Bottles were shaken three times as recommended in the GEOTRACES cookbook, to avoid the loss of particles by sticking to the walls or settling at the bottom of the bottle. Seawater was then poured in the Perspex containers at the base of which polycarbonate filters of 0.4  $\mu\text{m}$  porosity (Nuclepore®, 47 mm or 90 mm of diameter) were mounted. After sample filtration, the container was **rinsed with  $\leq 5$  mL of ultra-pure water (Milli-Q; 18.2 M $\Omega$ .cm)** to remove the maximum of sea salt deposited on the membranes. Finally, filters were removed using plastic tweezers and were dried under a laminar flow hood at ambient temperature before being stored in clean **petri** dishes.

Regarding samples collected with the clean rosette, sampling method and samples preparation are described in Gourain et al. (2019).

## 2.3 Sample preparation and analysis

Filters were first cut in two parts using a ceramic blade. One half was archived, while the other half was placed in a clean Teflon vial (Savillex®). The filter was then digested with a strong acid solution made of 1.5 mL HCl, 1 mL HNO<sub>3</sub> and 0.5 mL HF, all concentrated (Merck® Suprapur Grades). Vials were **subsequently** left on hot plates at 90°C overnight. The PREE concentrations were measured on 2 mL of the archived solutions, which were placed in clean 5 mL polypropylene tubes and doped with a solution containing In and Re (ca 100 ppt of both tracers) in order to correct matrix effects and sensitivity shifts during analysis. In addition to REEs, Y, Ba and  $^{232}\text{Th}$  concentrations were measured in the same **leaching**



130 solution. Analyses were performed at the Observatoire Midi Pyrénées (Toulouse, France) using a high-resolution inductively  
coupled plasma mass spectrometer (SF-ICPMS, Element XR, Thermo Fischer Scientific®) coupled to a desolvating nebulizer  
(Aridus II, CETAC Technologies®) to minimize oxides and hydroxides production rates and thus (hydr)oxides interferences  
(Aries et al., 2000). Oxide production rates were determined at the beginning and the end of every session using a ~~mono-~~  
~~elementary~~ Ce solution ( $\text{CeO} < 0.03\%$ ). Other REE (hydr)oxides rates were then determined using the constant proportionality  
135 factor between them (Aries et al., 2000), previously determined with the same analytical configuration. Interferences represent  
0.001% to 1% of the signal except for Eu (0.3% to 10%).

A five points calibration curve was established with a multi elemental standard at the beginning, the middle and the end of the  
analysis, while a standard solution concentrated with  $20 \cdot 10^{-12} \text{ g} \cdot \text{g}^{-1}$  of REE was measured every 5 samples. The certified  
reference material SLR-1 (NRC Canada) was systematically analyzed with the samples and their concentrations are within  
140 the error bar of the consensual values published by Yeghisheyan et al. 2013, with a smaller error (see Figure S1 in  
supplementary). Reproducibility was assessed by measuring two or three times several samples from the same leaching  
solution, and varied from 0% to 20%, like the error.

Procedural blanks have been estimated by conducting the chemistry on clean, unused filters. The average chemical blank ( $n =$   
8) represents 0.01% to 5% of the sample concentrations, except for Y and Lu for which the contribution of the blank was  
145 generally higher (between 1% and 30%).

Uncertainty of each concentration, estimated from error propagation was between 20% and 30% (and can be up to 40% for  
Eu) of the concentration. In addition to the mass spectrometry standard deviation the other sources contributing to the final  
error bar of the concentrations are: the proportion of filter analyzed, the volume of leachate and the volume taken in the archive  
for the analysis. For details on errors, see Fig. S2 in supplementary.

150 Thus the hypothesis of homogeneity is assumed, in the light of the apparent consistency of suspended particles on filters.  
The same digest solutions were also analysed at the Royal Museum for Central Africa (Tervuren, Belgium) mainly for  
determining Ba and some other element concentrations, including  $^{232}\text{Th}$ . It was conducted using an inductively coupled plasma  
quadrupole mass spectrometer (ICP-QMS; X Series 2 Thermo Fischer®). Ba, Y and  $^{232}\text{Th}$  were also measured in clean rosette  
samples. The digestion procedure and analytical method are detailed in Gourain et al. (2019). Concentrations of Ba and  $^{232}\text{Th}$   
155 are consistent between the analysis conducted in Brest and the PREE analysis in Toulouse. “Toulouse” Ba concentrations vs.  
“Tervuren” Ba concentrations give a regression slope of 0.87 ( $r^2=0.90$ ,  $n=198$ ). For  $^{232}\text{Th}$ , “Toulouse” concentrations vs.  
“Tervuren” concentrations give a slope of 1.05 ( $r^2=0.98$ ,  $n=198$ ), which is also very comparable. Ba and Y analyses were used  
to compare the clean rosette and standard rosette procedures. Consistent Ba concentrations were found when compared to the  
results of Lemaitre et al. (2018;  $r^2=0.61$ ,  $n=66$ ). Y concentrations measured in Toulouse on samples collected with the standard  
160 rosette match the concentrations obtained in Brest on the clean samples, with a regression slope of 0.93 ( $r^2=0.82$ ,  $n=78$  points  
at same depths). Thus both procedures are suitable for PREE analysis. In addition, these validations allow us to discuss the  
PREE concentrations with the trace metal ones from Gourain et al. (2019).



### 3 Results

The data set of PYREE, PBa and P<sup>232</sup>Th concentrations is compiled in Table 2. For sake of clarity, we only displayed PCe, PNd and PYb concentrations (Fig. 2 and 3), these three REEs representing the light REEs (Nd), heavy REEs (Yb) and a specific behavior (Ce). LREEs and HREEs are supposed to react to different processes during dissolved-particulate exchanges. Ce has a IV oxidation state in addition to the III oxidation state common to all REEs and its oxidation onto particles prevent desorption. The Ce (III)/Ce(IV) distribution is therefore a proxy of redox and desorption processes.

PCe (Fig. 2) concentrations are higher than PNd (Fig. 3 and B) concentrations, which are higher than PYb concentrations (Fig. 3 C and D), in agreement with their respective natural abundance and reactivity.

#### 3.1 Cerium

Particulate Ce concentrations (PCe, Fig. 2) vary between 0.2 pmol.L<sup>-1</sup> (station #64) and 16.3 pmol.L<sup>-1</sup> (station #32; Fig. 2). They are higher close to the Iberian margin (station #1: 1 pmol.L<sup>-1</sup> < PCe < 9.4 pmol.L<sup>-1</sup>) and on the Greenland shelf (station #53: 5.7 pmol.L<sup>-1</sup> < PCe < 14.6 pmol.L<sup>-1</sup>). In the NAST (for station #13) and the NADR regions, vertical profiles present a surface or subsurface maximum at all stations. Below 200 m depth, PCe concentrations decrease and reach a value of 2 pmol.L<sup>-1</sup> in the mesopelagic zone. PCe concentrations are higher to the east of the polar front (stations #13 and #21) compared to the west (stations #26, #32 and #38). A second maximum is observed at greater depth at station #13 and in the NADR region (except close to the subarctic front, at station #26). In the ARCT region, surface PCe concentrations are lower and increase at the bottom of the epipelagic zone for all open-sea stations (PCe > 1 pmol.L<sup>-1</sup>). Maximum concentrations are observed at the bottom of the epipelagic zone at stations #44, #64 and #69. PCe concentrations are more variable in the mesopelagic zone of the ARCT region than in the NADR region, and higher than the ones observed at the surface except at station #69 where they are about within the same range (1 pmol.L<sup>-1</sup> < PCe < 2 pmol.L<sup>-1</sup>). PCe profiles differ from that of PNd and PYb at two stations only: station #38, where peaks of PCe are observed at 100 m and 800 m, that are not observed for the other PREE profiles; station #44, where PCe concentrations are more variable in the epipelagic zone than PNd and PYb, with maxima at 120 m and 160 m that are not observed for other PREEs.

#### 3.2 Neodymium

As for PCe (and other PREEs, see supplementary information), PNd concentrations are the highest close to the Portugal and Greenland margins with values up to 4.5 pmol.L<sup>-1</sup> in the upper 100 m (Fig. 3 a and B). Concentrations decrease as the distance to margins increases, as seen at stations #13 where PNd hardly reaches 1 pmol.L<sup>-1</sup>. Low PNd values were also measured at station #77, although this station is relatively close to the Newfoundland margin, but located out of the continental shelf.



### 3.3 Ytterbium

Distributions of PNd and PYb (Fig. 3) differ on several points: three stations (#13, #44 and #69) display a maximum in subsurface for PYb that is not observed for PNd, whereas a local maximum in PNd is identified at 160 m at stations #64 and #69, but not for PYb. In the open ocean, at stations #21, #26, #32 and #38, concentrations are higher in the surface layer (from 0 m to 200 m). The highest concentrations were determined in the NADR region, which was the most productive during the cruise (Fonseca-Batista, 2018). Concentrations then decrease with depth to become constant, except at station #38 where they increase again in the mesopelagic zone. In the ARCT region, surface concentrations of PNd are lower at 100 m compared to 250 m, similar to station #1 while the contrary is observed in the NADR region.

### 3.4 PNd<sub>N</sub>/PYb<sub>N</sub> ratios

To highlight a possible fractionation between LREE and HREE, the PNd<sub>N</sub>/PYb<sub>N</sub> ratio is calculated from concentrations normalized to PAAS, in order to get rid of the natural abundance effect of the REEs. Results are presented in Fig. 4, interpolated along the section. This ratio presents a high variability, changing from 0.01 to 4.3. Higher ratios (> 1) are observed along the margins, decreasing as the distance to the coast increases. PNd<sub>N</sub>/PYb<sub>N</sub> is lower at the surface (< 0.7) except at stations #1, #38 and #53, and increases in the subsurface layers (0.7 < PNd<sub>N</sub>/PYb<sub>N</sub> < 1) in the open ocean. The strongest ratio value is observed in the core of the epipelagic zone at station #21 (Fig. 4C), where high concentrations of PLa, PCe, PPr and PNd are also observed. However, for other stations with a similar enrichment, no high PNd<sub>N</sub>/PYb<sub>N</sub> ratio are observed.

## 4 Discussion

### 4.1 Comparison with other studies



PREE data in suspended particles are very scarce in the literature. To our knowledge, for the North Atlantic, only one other set of concentrations was published by Kuss et al. (2001), who measured PREEs in samples centrifuged from several m<sup>3</sup> of water at a depth of 7 m, collected along the 20°W meridian between 30°N and 60°N. These authors observed PCe concentrations ranging between 0.2 pmol.L<sup>-1</sup> and 4.9 pmol.L<sup>-1</sup> with higher concentrations close to the margins especially near the European one, consistent with our data. Their PNd concentrations of about 0.5 pmol.L<sup>-1</sup> to the east of the NADR are also consistent with ours. PNd and PYb concentrations reported by Tachikawa et al. (1999) at a station located in a mesotrophic zone of the north-east tropical Atlantic, directly influenced by Saharan dust (6 g.m<sup>-2</sup>.yr<sup>-1</sup> to 15 g.m<sup>-2</sup>.yr<sup>-1</sup>, Rea, 1994), are higher than those reported here (PNd = 2.6 pmol.L<sup>-1</sup> and PYb = 0.94 pmol.L<sup>-1</sup> at 10 m). Contrastingly, these authors observed lower concentrations than ours at the oligotrophic site of their study, where the dust flux is lower than at the mesotrophic site (4-5 g.m<sup>-2</sup>.yr<sup>-1</sup>, Rea, 1994) but higher than that found during the GEOVIDE cruise (2 ng.m<sup>-3</sup> to 500 ng.m<sup>-3</sup>, Shelley et al., 2017). However, these author's PCe concentrations are similar to those reported in this study, and that for both the mesotrophic and



220 oligotrophic sites. The difference of concentrations observed for the other PREEs can be explained by the high particle  
concentrations **characterizing the compared** to the tropical **one**, even if dust inputs are higher **on** the later (Gehlen et al., 2006).  
PREE are found both in the lithogenic and authigenic phases of **the** particles. Schematically, particles are often represented  
with a “lithogenic core” coated by authigenic material (Bayon et al., 2004; Sholkovitz et al., 1994). The lithogenic has an  
external origin, product of **the** continental weathering transported by **the** winds or discharged by **the** rivers on the margins. The  
225 authigenic phase is of internal origin, major phases being biogenic matter (particulate organic matter POM, biogenic silica  
BSi, calcium carbonate CaCO<sub>3</sub>) and metal oxides and hydroxides such as MnO<sub>2</sub> and Fe(OH)<sub>3</sub>. REEs in the authigenic phase  
are **scavenged** by organic coatings **and** for iron and manganese oxides and hydroxides that are known to be the main carrier of  
REEs, **scavenged** by adsorption during their precipitation (Bau, 1999; Bau and Koschinsky, 2009). REEs could also be  
absorbed in inorganic planktonic tests (CaCO<sub>3</sub>, Palmer, 1985 and BSi, Akagi, 2013) or biogenic byprod **as** barite  
230 (Ba<sub>xs</sub>, Guichard et al., 1979). LREEs would be more sensitive to oxide phases of Fe and Mn, while HREEs, more soluble, could  
react preferentially with biogenic phases (Akagi, 2013; Bertram and Elderfield, 1992; Grenier, 2018; Pham et al., 2019). Their  
distribution coefficients **are also varying** with depth and the nature of the particle phases (Schijf et al., 2015).  
Thus, differentiating the distribution of the REEs in the two phases allows us to estimate the fraction implied in scavenging  
processes by the authigenic phase, while the lithogenic **one enables to picture** continental inputs. The high PREE concentrations  
235 observed in Fig. 3 close to the Portugal margin and on the Greenland shelf suggest that particulate material is released by the  
margins to the water column. Lithogenic REE fraction can be quantified using conservative lithogenic tracers such as Al, Th  
or Ti (Gourain et al., 2019; Tachikawa et al., 1997). These authors used Al as a lithogenic tracer, but here we chose to use  
<sup>232</sup>Th. Indeed, the lithogenic fractions calculated from particulate Al (PAI) concentrations were often higher than 100% in  
surface waters close to the margins, revealing that a fraction of the total **PaI** is likely in the authigenic phase (Lerner et al.,  
240 2018; Van Beueskom et al., 1997). In addition, Al being more prone to contamination was sampled with the clean rosette  
(Gourain et al., 2019), while <sup>232</sup>Th used for calculation was measured in the same samples as PREEs, collected with the standard  
rosette. The concentration of the lithogenic PREE fraction in particles is calculated by multiplying the <sup>232</sup>Th concentration in  
a given sample by the ratio of the considered REE on <sup>232</sup>Th in the upper crust (Rudnick and Gao, 2014, Eq. (1)).

$$[REE]_{litho} = [^{232}\text{Th}] \times \left( \frac{[REE]}{[^{232}\text{Th}]} \right)_{UCC} \quad (1)$$

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$$\%REE_{litho} = \frac{[REE]_{litho}}{[REE]} \quad (2)$$

$$REE_{authi} = REE_{total} - REE_{litho} \quad (3)$$

These PREE lithogenic concentrations are then divided by the total PREE concentrations to obtain the percentage of particulate  
250 REE with a lithogenic origin (Eq. (2)). The authigenic concentrations are then obtained by subtraction of the lithogenic  
concentrations **to** the total concentrations (Eq. (3)).





The percentage of lithogenic PNd along the section is represented in Fig. 5. Then we chose to represent the average value of the lithogenic fractions of the remaining PREEs for the LREE, **excepted for PCe on one hand** and for HREE on the other hand. Profiles of five selected stations (#1, #26, #51, #53 and #77) are shown in Fig. 5. These stations are representative of the three  
255 different distributions observed along the section. Error bars represent the standard deviation of the resulting averages, the contribution of the error on the concentrations being negligible compared to the **laters**. For some points at station #1 and at 160 m at stations #13 and #32, the calculated lithogenic proportion exceeds 100%, suggesting an excess of  $^{232}\text{Th}$  in the particles, likely authigenic, or a difference between the adsorption kinetics of  $^{232}\text{Th}$  and REE, as reported by Hayes et al. (2015). In these cases, we capped the lithogenic proportion to 100%.

260 PREE concentrations are normalized to Post-Archean Australian shale, PAAS (Rudnick and Gao, 2014). This normalization allows i) a better diagnostic of the fractionation between PREEs and ii) comparison with patterns in the literature. As shown by the flat PAAS-normalized patterns of the lithogenic fractions (Fig. S3 in supp. mat.), PAAS is a valuable reference to represent the lithogenic material. In addition, it does not present any significant difference in REE composition with shales and loess from Europe, North America and China (Rudnick and Gao, 2014). Normalization to atmospheric depositions has  
265 been put aside as these inputs were low during the cruise (Shelley et al., 2017) and normalization to dusts led to patterns depleted in Eu and Gd, and enriched in Tb, Dy, Ho and Er (data from Patey et al., 2015, on dusts collected close to Cape Verde; Fig. S3), less representative of lithogenic inputs than PAAS. Patterns normalized to PAAS are presented in **Fig.5** for selected stations. To facilitate readability, patterns of each sample are averaged by **layers** displaying similar values. Error bars represent the standard deviation of the concentration series, the errors on PAAS concentrations **being negligible compared to it**. A REE  
270 pattern obtained in the Atlantic seawater at 12°S (Zheng et al., 2016) is also represented together with station #26 patterns, for comparison.

#### 4.2 Lithogenic supply **by the margins**

The high concentrations of PREEs (Fig. 3) at stations #1 and #53 reflect lithogenic inputs from the margins. At these stations, the lithogenic PREE fractions range between 50% and 100%, the highest **ones** being observed at station #1 (Fig. 5). The  
275 relatively flat patterns displayed at these stations for total PREE indicate a weak fractionation of PREEs, with a little enrichment in LREEs due to their **lower solubility** compared to the HREEs. These maxima can be seen beyond the **Subpolar** Front until station #32, spreading along the isopycnals 27.05 and 27.4 over 2500 km from the Iberian margin (Fig. 6). Similar maxima have been reported by (Gourain et al., 2019, Fig. 6 B) for lithogenic PFe and PMn), lithogenic PMn being taken by these authors as tracer of sediment resuspension.

280 Above the Greenland shelf, at station #53, the proportion of lithogenic PREE is also high, only slightly lower than at station #1 (median contributions of 59% for PLREE and 83% for PHREE; Fig. 5). Unlike what is observed to the eastern end of the section, these lithogenic particles remain on the shelf and do not spread offshore. Except at the surface for LREE, the lithogenic proportion **are** lower than 50% at stations #51 and #64 in the Irminger Sea and in the Labrador Sea respectively. This containment of particles along the shelf is explained by the circulation. Indeed, the East Greenland Irminger Current (EGIC)



285 is a strong narrow current **bypassing** Greenland **along its** shelf ( $23.4 \pm 1.9$  Sv, Danialt et al., 2016), likely preventing exchanges between the Irminger Subpolar Mode Water (IrSBPMW) and waters of the Greenland shelf, transported by the EGCC current which flows parallel to the coast (green and orange arrows around the Greenland southeastern tip in Fig. 1). Our observations are consistent with that of Lacan and Jeandel, 2005, who showed that the Nd isotopic signatures ( $\epsilon\text{Nd}$ ) of SPMW transported by the EGIC do not vary significantly along the Greenland shelf. In the same way, the lithogenic influence is moderate at  
290 station #77, land-ocean exchanges being reduced **due to the EGCC again** ( $1.5 \pm 0.2$  Sv, Danialt et al., 2016). While the lithogenic fraction is still relatively high at this station ( $50\% < \text{REE}_{\text{litho}} < 80\%$  below 150m), the fractionated patterns indicate that other processes are at play.

High lithogenic proportions are also observed at station #69 but not to the east of the Labrador Sea (station #64; Fig. 5). In contrast with the Iberian margin, no intermediate enriched layers are observed (Figs. 2 and 3) and the lithogenic fraction is less  
295 important and remains roughly constant below 200 m at stations #51 (about 45%) and #77 (around 60%, Fig. 5). Normalized total concentrations display fractionated PREE patterns, underlining authigenic processes likely at play in this area.

Comparable lithogenic percentages have been reported by Garcia-Solsona et al. (2014) between South Africa **and Antarctic**, from 0% at the surface to 80% deeper, with higher lithogenic proportions for HREE than for LREE. Using PAI as a lithogenic tracer, Tachikawa et al. (1999) evaluated the lithogenic proportion to be between 50% and 80% at the different Eumeli sites  
300 in the east tropical Atlantic.

Gourain et al. (2019) reported similar results than ours for PFe and PMn at the same stations along GEOVIDE. These authors observed strong lithogenic contribution from the Iberian margin spreading until station #32, lower contribution along the Newfoundland margin and no particular lithogenic contribution along the Greenland margin, in agreement with our observations. Using lithogenic PMn as a tracer of sediment resuspension, they observe that 100% of PMn is originating from  
305 sediment resuspension at station #1 between 250 m and 1000 m (their Fig. 4). Interestingly, Le Roy et al. (~~comm. pers.~~) observed an unexpected maximum of  $^{227}\text{Ac}$  activity at 500 m at stations #1 and #21, indicating a strong sediment source, again consistent with the PREE data. At station #13 at 200 m, however, no lithogenic maximum is identified. This could result from the compression of isopycnals, leading to the merging of the two maxima observed eastward (Fig. 4). Unfortunately, the different sampling resolutions for PREE and  $^{227}\text{Ac}$  do not permit to further compare data between these tracers except at the  
310 surface of station #1, where a maximum of  $^{227}\text{Ac}$  is consistent from the lithogenic PREE signal.

These layers highly enriched in lithogenic particles could be attributed to the formation of intermediate nepheloid layers (INL) at 250 m and 500 m along the Iberian margin, ~~similarly~~ to those revealed slightly north by McCave and Hall (2002). A contribution of the Mediterranean Water (MW) to these high concentrations and lithogenic proportions cannot be excluded too, but the lack of data in the core of the MW (1000 m to 1500 m, García-Ibáñez et al., 2018) prevents us from further  
315 investigations.

A highly energetic process is needed to enhance such strong resuspension of lithogenic matter. It may be due to the friction and energetic excitation of internal waves along the continental slope (Cacchione, 2002). Another source can be the erosion of the coast by the strong current (from  $0.05 \text{ m}\cdot\text{s}^{-1}$  to  $0.1 \text{ m}\cdot\text{s}^{-1}$ ) coming out from Gibraltar and flowing northward along the Iberian



margin (Gourain et al., 2019; McCave and Hall, 2002; Zunino et al., 2017). Our observations could also result from a  
320 combination of both, with generation of internal waves south of station #1 generating sediment resuspension, those particles  
being advected northward by the current.

To sum up, margins can provide significant amounts of particulate lithogenic material to the ocean; nevertheless, occurrence  
and magnitude of these inputs are depending on the morphology of the margin and the hydrodynamical forcing, leading (or  
not) to nepheloid layer formations.

### 325 4.3 REE fractionation: Ce anomalies

Ce is the only REE having a (IV) oxidation state in the water column. When adsorbed onto particles together with other REEs,  
oxidation (biotic or abiotic) makes it less prone to desorption than other REEs, leading to Ce enrichment of the particulate  
phase (Byrne and Kim, 1990; Elderfield, 1988; Moffett, 1990, 1994; Tachikawa et al., 1999). This oxidation is thought to  
occur for authigenic Ce adsorbed on Fe(OH)<sub>3</sub> and MnO<sub>2</sub> (Bau, 1999; Bau et al., 1996). This P<sub>Ce</sub> enrichment is commonly  
330 quantified by the ratio of the P<sub>Ce</sub> concentration on the theoretical P<sub>Ce</sub> concentration calculated using its neighbors P<sub>Nd</sub> and  
P<sub>Pr</sub> and expressed as Ce\*, following Bolhar et al. (2004):

$$\frac{Ce}{Ce^*} = \frac{[Ce]}{2 * [Pr] - [Nd]} \quad (4)$$

In the present set of data, this ratio is always larger than one (positive anomaly) except at stations #26, #32, #51 and #77  
335 between the surface and ca. 100 m, where P<sub>Ce</sub> is depleted compared to other P<sub>REEs</sub>, as already discussed above. This surface  
minimum is followed by a pronounced (Ce/Ce\*>3) positive anomaly down to 200 m. At greater depth, the anomaly is relatively  
higher in the NADR region compared to the NAST and ARCT regions.

These results indicate that Ce oxidation occurs after particles left the surface, leading to a subsurface maximum. At greater  
depths, remineralization rates are high in the ARCT region, moderate in the NAST region and low in the NADR region  
340 (Lemaitre et al., 2018). It is likely that lower remineralization rates conduct to higher net fluxes from the dissolved phase  
toward the particulate phase, associated with a strong and irreversible scavenging of Ce by adsorption and oxidation, while a  
fraction of the other trivalent REEs are released by desorption from the particles (Bau, 1999; Tachikawa et al., 1999). A  
stronger anomaly could also reflect higher particle concentrations offering higher surface reactive areas, but particle mass  
remains unknown at those depths and beam transmissiometry does not allow identifying higher particle concentrations.

345 To compare P<sub>Ce</sub> to Mn and Fe (hydr)oxides, particulate Fe(OH)<sub>3</sub> and MnO<sub>2</sub> concentrations are calculated with the formula of  
Lam et al. (2017, Figure S6) using P<sub>Mn</sub>, P<sub>Fe</sub> and P<sub>Al</sub> data from Gourain et al. (2019). The observed decoupling between Ce  
anomaly and MnO<sub>2</sub> distributions indicates that more processes are at play than the biologically mediated oxidation that would  
lead to similar distributions of the two tracers (Moffett, 1990). Different complexation conditions between these two elements  
likely prevent the occurrence of a good correlation. The positive Ce anomaly is not observed when the residence time of  
350 particles is short, which is the case in the NADR and the ARCT regions where the export is strong (stations #51 and #77,  
Lemaitre et al., 2018). CaCO<sub>3</sub> formation can explain the observed negative anomalies at station #26 and #32 (Garcia-Solsona



et al., 2014; Haley et al., 2005; Sholkovitz and Shen, 1995). However, this hypothesis does not hold at station #21 where  $\text{CaCO}_3$  concentration is high while the PCe anomaly is positive (Fig. S4 in supplementary). A surface photoreduction could explain the surface weak anomalies by reducing Ce(IV) in Ce(III) that can be desorbed from particles. The  $\text{MnO}_2$  depletion in the surface waters of NADR region would support this hypothesis, although this  $\text{MnO}_2$  depletion reaches 500 m (ie below the euphotic layer, Fig S6A in supplementary). In the NAST region, a  $\text{MnO}_2$  surface minimum occurs too, but does not correspond to a PCe/Ce\* minimum.

#### 4.4 The influence of biological activity on the REE distributions

##### 4.2 The influence of biological activity on the REE distributions

360 The surface of open-sea stations (all of them except #1 and #53) are characterized by a higher lithogenic proportion for LREEs than for HREEs, meaning that the expected relative enrichment of the authigenic phase in LREE -due to their lower solubility- is not observed (see the vertical profiles reported in Fig. 5). Thus, an uncommon enrichment of the authigenic material in HREEs is observed in these samples, also shown in the total PREE patterns (Fig. 5 and Fig. S4 in supplementary). Indeed, these patterns display a negative Ce anomaly on the first hundred meters and enrichment in HREEs characterized by high PYbN/PNdN ratios ( $>1$ , Fig. 4) that can reach 1000 m. Such kind of pattern is classically observed for dissolved REEs, more rarely for PREEs. Suspended PREEs displaying such “dissolved-type” pattern suggest that they have been likely formed through absorption than adsorption processes, the latter leading to fractionation between the REEs, which is not the case during the uptake of REEs in the carbonate planktonic shells (Palmer and Elderfield, 1986). The negative PCe anomaly (Fig. 7) suggests recently formed particles on which Ce oxidation leading to positive PCe anomaly have not occurred yet. All these stations are subject to a strong primary production (Fonseca-Batista et al., 2019), so the preferential transfer of HREEs from the dissolved phase to the authigenic particulate one likely occurs when the biological stripping is active. However, this transfer is more important in the ARCT region than in the NADR region, leading to stronger HREE enrichments, while the highest bloom activity was observed in the NADR region with a maximum at station #26. The high prevalence of coccolithophorids characterizing this bloom (Lemaitre et al., 2018) could explain the relatively low HREE enrichment, except at station #26. In the NADR region, the patterns flatten with depth to present a quasi-lithogenic signature under 60 m, suggesting that particles with a strong organic signature have not reached this depth yet. In the ARCT region, the bloom was dominated by diatoms, still active at station #51 and declining at the others (Fonseca-Batista et al., 2019; Lemaitre et al., 2018). This declining bloom leads to a strong export, but high remineralization rates decrease the biological signature proportion in favor of the lithogenic one at depth (Fig. 5). Even if the characterization of the authigenic phase leans on  $^{232}\text{Th}$  and the assumption that REEs and  $^{232}\text{Th}$  behave similarly from the original lithogenic source, it is thus very likely that biological uptake appears to have a strong effect on the total REE patterns observed.

A relationship between HREEs and biogenic matter, mostly BSi, have been suggested by Akagi (2013) following thermodynamic calculations. According to this work, 10% to 20% of REEs are forming a  $\text{REE}(\text{H}_3\text{SiO}_4)_2^+$  complex with silicic acid, this proportion being more important as the atomic number is low and with depth. Complexation of REE with



385 silicates was further confirmed by Patten and Byrne (2017), although these authors estimated lower complexation constant, thus a less important fraction of REEs complexed by silica. In addition, significant correlations were observed between dissolved Si and dissolved HREE by Bertram and Elderfield (1992; western Indian Ocean), Akagi et al. (2011, North Pacific Ocean); Stichel et al. (2012) and Garcia-Solsona et al. (2014), both in the Atlantic sector of Southern Ocean), Grenier et al. (2018; Kerguelen Islands) and Pham et al. (2019; Solomon Sea). Contrastingly in other areas, the correlation between SiOH<sub>4</sub> and REEs ~~present a curvature~~ or is ~~absent~~ (Patten and Byrne, 2017, their Fig. 7; Zheng et al., 2016, their Fig. 11). Even if the causes of such relationships are not clear, the **PYbN/PNdN ratio in the authigenic phase is the highest between the surface and 50 m** in the Irminger Sea and the Labrador Sea, where **BSi concentrations are also the highest** (Sarhou et al., 2018), reflecting a bloom dominated by diatom species (Fig. S5A and B in supplementary material). Although the correlation between BSi and PHREEs stays weak (from R<sup>2</sup>=0.06 for Ho to R<sup>2</sup>=0.4 for Lu), this correlation coefficient rises with the atomic mass number (Fig. S5C), showing that BSi has a significant **influence** on authigenic PREE distributions from Tb to Lu that does not appear for lighter REEs. These correlations may show that **in some areas the HREE distributions are linked to the biogeochemistry of silicate**, and not only to a conservative mixing as shown by Zheng et al. (2016) and de Baar et al. (2018). This relationship would depend on the abundance and the nature of particles (the occurrence of diatoms), and on the speciation of REEs in the dissolved phase as shown by de Baar et al. (2018). Akagi, (2013) and Akagi et al. (2011) proposed an incorporation of the silica-REEs complexes during the frustules construction, but the mechanism under this enrichment during diatom blooms remains to be clarified. Linking it to ~~usual~~ complexation and adsorption processes is not straightforward since this would imply a sharp break between LREE and HREE affinities with BSi, which has ~~still~~ to be demonstrated. In addition, an effective relationship between BSi and PHREE can be blurred by other scavenging processes ~~implying~~ particulate Mn and Fe (hydr)oxides, also known to influence the **slope between** LREE and HREE.

#### 405 **4.5 The PAAS-normalized particulate Ho/Y ratio: a proxy of processes independent of the ionic radius**

Yttrium (Y) and the lanthanide holmium (Ho) are characterized by about the same ionic radius and identical charge, making them “geochemical twins” (Bau, 1999). The PAAS-normalized particulate ratio (PHoN/PYN) highlights differences in their distributions, and therefore allows identifying radius-independent fractionation processes affecting YREE in seawater. We choose to normalize PHo/PY measured in our particulate samples to the PAAS ratio to reveal any relative loss or enrichment compared to continental material (Fig. 8). Due to differences of electron configuration, Ho is more prone to establish ionic bounds, and then to be preferentially scavenged by adsorption onto (hydr)oxides as FeOH<sub>3</sub> and MnO<sub>2</sub>. In comparison, Y is preferentially scavenged when covalent bounds are established (Censi et al., 2007; Bau, 1999; Bau et al., 1995). Along the GEOVIDE section, PHoN/PYN ratio varies between 0.4 and 1.5, with most of the values less than 1 (i.e. depleted compared to PAAS), which **does not support the expected preferential scavenging of Ho**. Moreover, PHoN/PYN relationship with FeOH<sub>3</sub> and MnO<sub>2</sub> doesn't fit to any pattern (Fig. 9). PHoN/PYN is higher when [Fe(OH)<sub>3</sub>] > 10-2 µg.L<sup>-1</sup>, while there is **no evidence of a higher HoN/YN ratio when MnO<sub>2</sub> content increases**. However, while there is a pronounced east-west gradient in the



Fe(OH)<sub>3</sub> distribution, the PHoN/PYN ratio (Fig. S6 in supplementary) is low (<0.6) in Labrador Sea surface waters (station #69), the Irminger Sea (stations #44 and #51) and from the surface to 750 m in the NADR region (stations #21, #26 and #32). These locations are depleted in both MnO<sub>2</sub> and Fe(OH)<sub>3</sub> (Fig. S6 in supplementary), leading to a weak adsorption of Ho. All along the section, low ratios are observed at the surface and until 800 m in the areas of marked biological productivity (stations #26, #32, #69), although they are directly linked to primary production intensity. This suggests a preferential scavenging of Y during the formation of biogenic matter, as reported by Censi et al. (2007), and not through simple adsorption which would support preferential scavenging of Ho. In the NADR region, at depths between 200 m and 600 m that are characterized by strong and positive PCe anomaly and a persistent PHREE enrichment, a PHo depletion is observed at stations #26 and #21. The low remineralization rates observed in this area could make persistent the PY enrichment formed at the surface, when the positive PCe anomaly suggests that a dynamic scavenging occurs. The difference between those two elements can be explained by a preferential scavenging of LREE compared to HREE during adsorption processes. The PHo enrichment at station #32 between 350 m and 600 m goes with the most important Ce positive anomaly, indicating intensive exchanges by adsorption with the dissolved phase, and then a stronger scavenging of REEs. In the ARCT region, slightly lower ratios are observed at station #69 than for others, and this station is characterized by a lower primary production and the higher remineralization rates along the section (Lemaitre et al., 2018). Ho, more adsorbed than Y is then more prone to be released, leading to a lower signal due to the Y enrichment of the covalent part of the particles, less easily remineralized. The higher ratios at other ARCT stations indicate scavenging by particles, although the Ce anomaly is lower than in the NADR region. Thus, our results show that high PHoN/PYN ratio not only reflects sorption processes driven by the occurrence of Fe(OH)<sub>3</sub> and to a lesser extent MnO<sub>2</sub> but all processes favoring outer-sphere complex formation, which would promote Ho and other REEs scavenging compared to Y. The relationship with particle production, particle residence time and remineralization rates is not clear indicating the influence of other parameters not identified yet.

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**Table 1: List of region, water masse and current abbreviations.**

<b>Regions</b>	
<b>SPNA</b>	Subpolar North Atlantic
<b>NAST</b>	North Atlantic Subtropical
<b>NADR</b>	North Atlantic drift
<b>ARCT</b>	Arctic
<b>Water masses</b>	
<b>ENACW</b>	East North Atlantic Central Water
<b>MW</b>	Mediterranean Water
<b>SPMW</b>	Subpolar Mode Water
<b>IrSPMW</b>	Irminger Subpolar Mode Water
<b>LSW</b>	Irminger Subpolar Mode Water
<b>Currents</b>	
<b>NAC</b>	North Atlantic Current
<b>ERRC</b>	East Reykjanes Ridge Current
<b>IC</b>	Irminger Current
<b>EGIC</b>	East Greenland Irminger Current
<b>EGCC</b>	East Greenland Coastal Current

620 **Table 2: Particulate REE, Y, Ba and <sup>232</sup>Th concentrations with the corresponding 2σ error.**

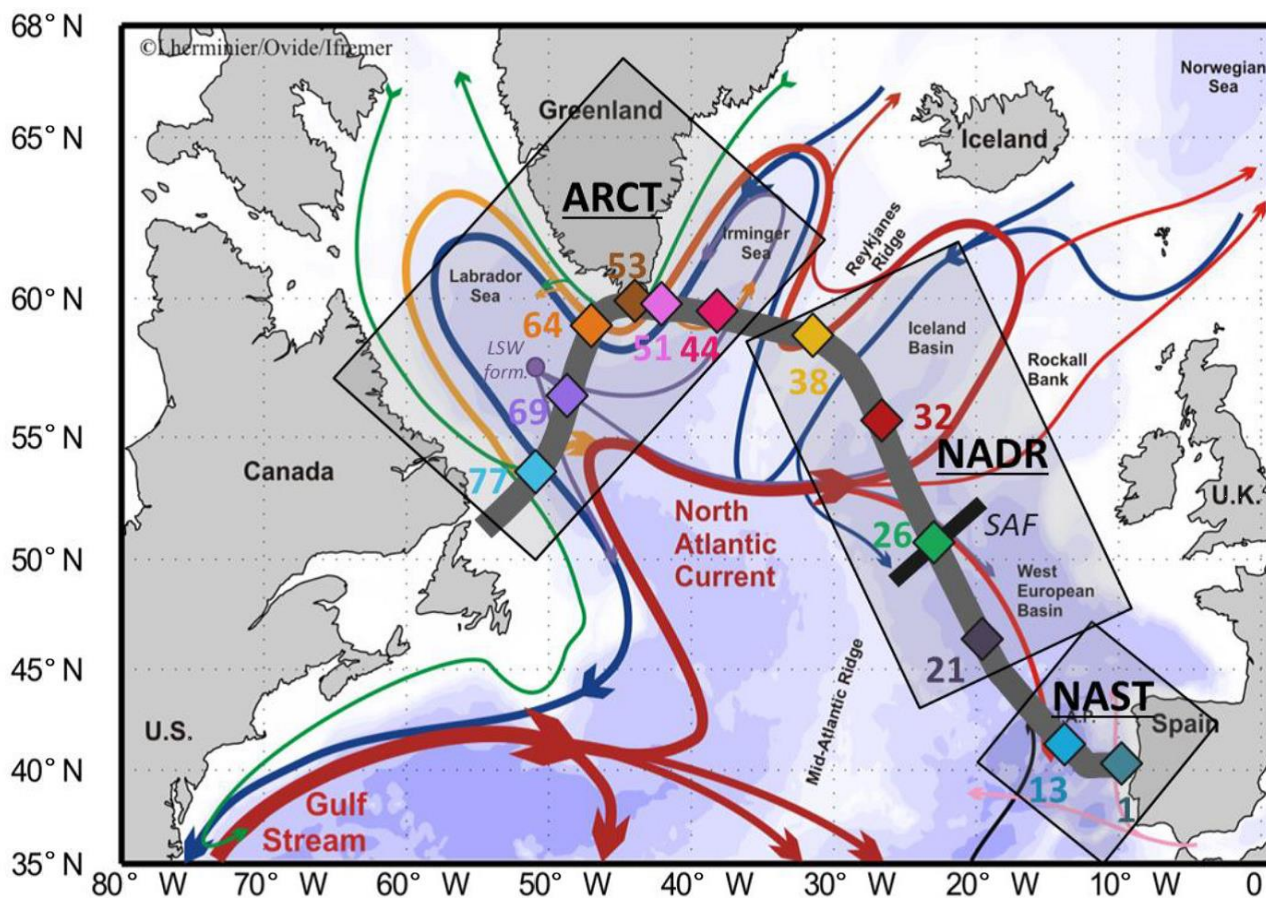








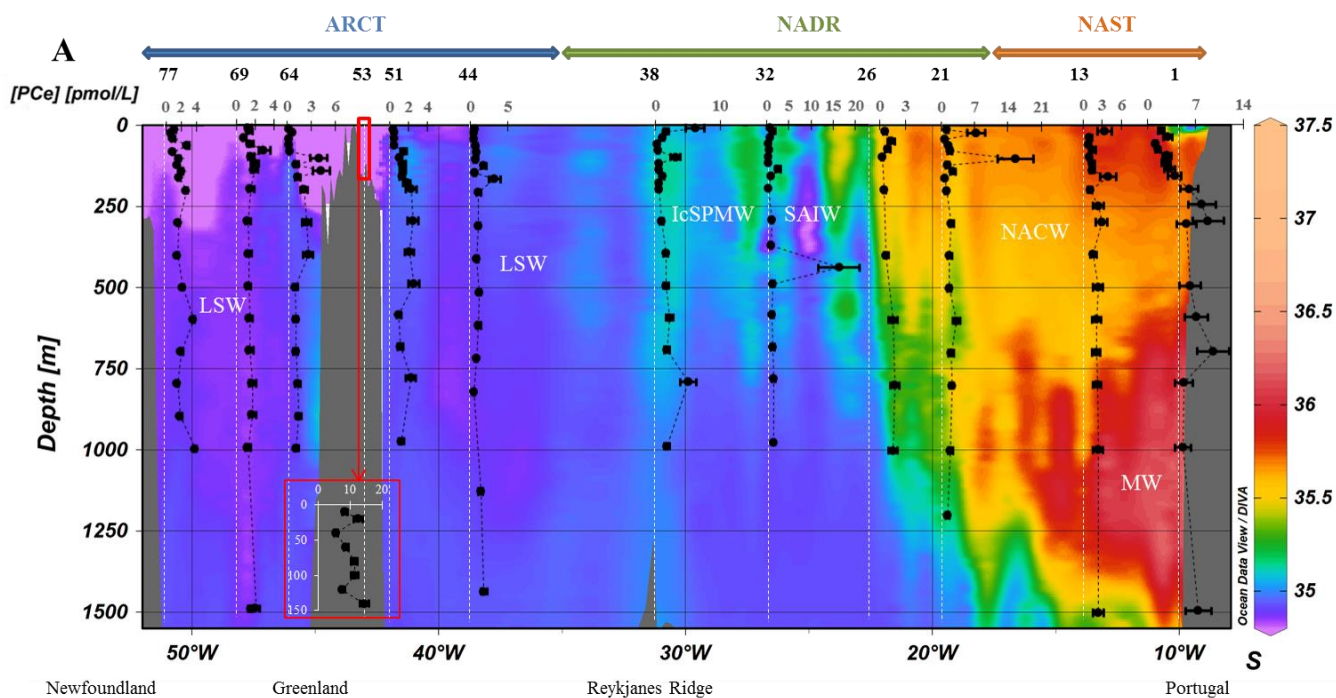
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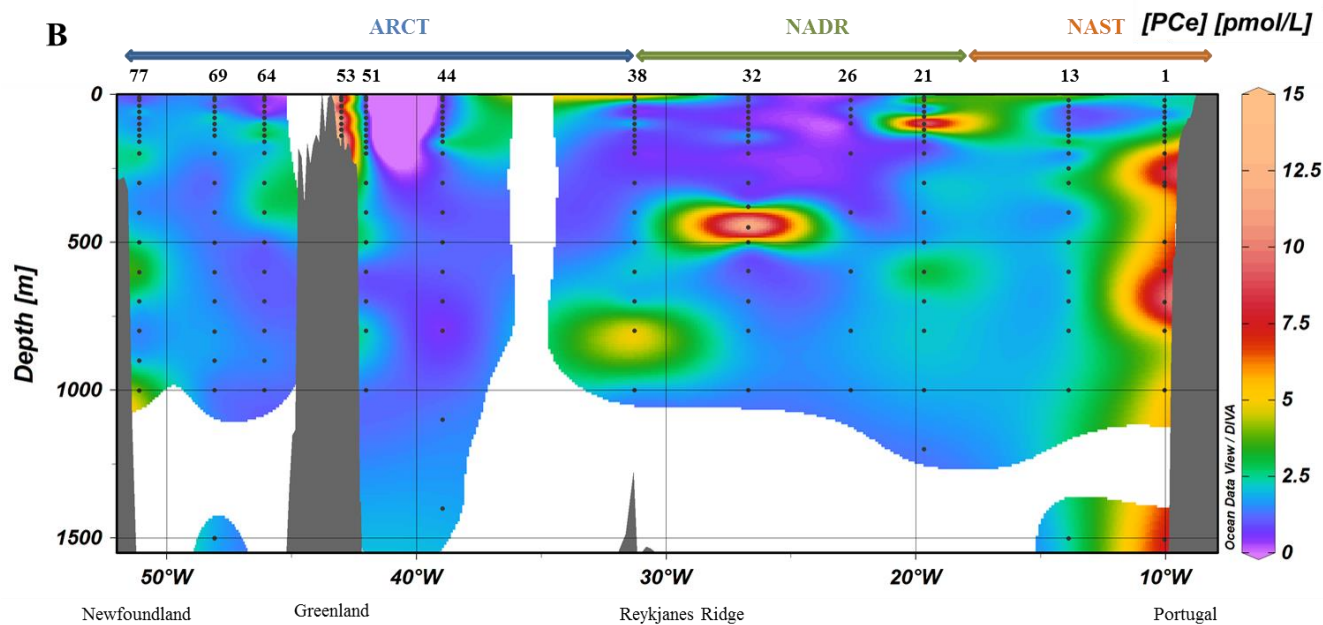
630 Figure 1: Map of the studied area (Subpolar North Atlantic, SPNA), including schematized circulation features, adapted from  
García-Ibáñez et al. (2015). Bathymetry is plotted in color with interval boundaries at 100 m, at 1000 m, and every 1000 m below  
635 1000 m. The red and green arrows represent the main surface currents, the pink and orange arrows represent currents at  
intermediate depths, and the blue and purple arrows represent the deep currents. Diamonds indicate station positions, located in 3  
distinct areas (grey squares): the North Atlantic Subtropical province (NAST), the North Atlantic Drift region (NADR), and the  
Arctic region (ARCT). The approximate locations of the subarctic front (SAF; black bar crossing station #26) and the formation site  
of the Labrador Sea Water (LSW form.) are indicated. The section used in ODV figures is symbolized by the thick grey line. From  
Lemaitre et al. (2018).

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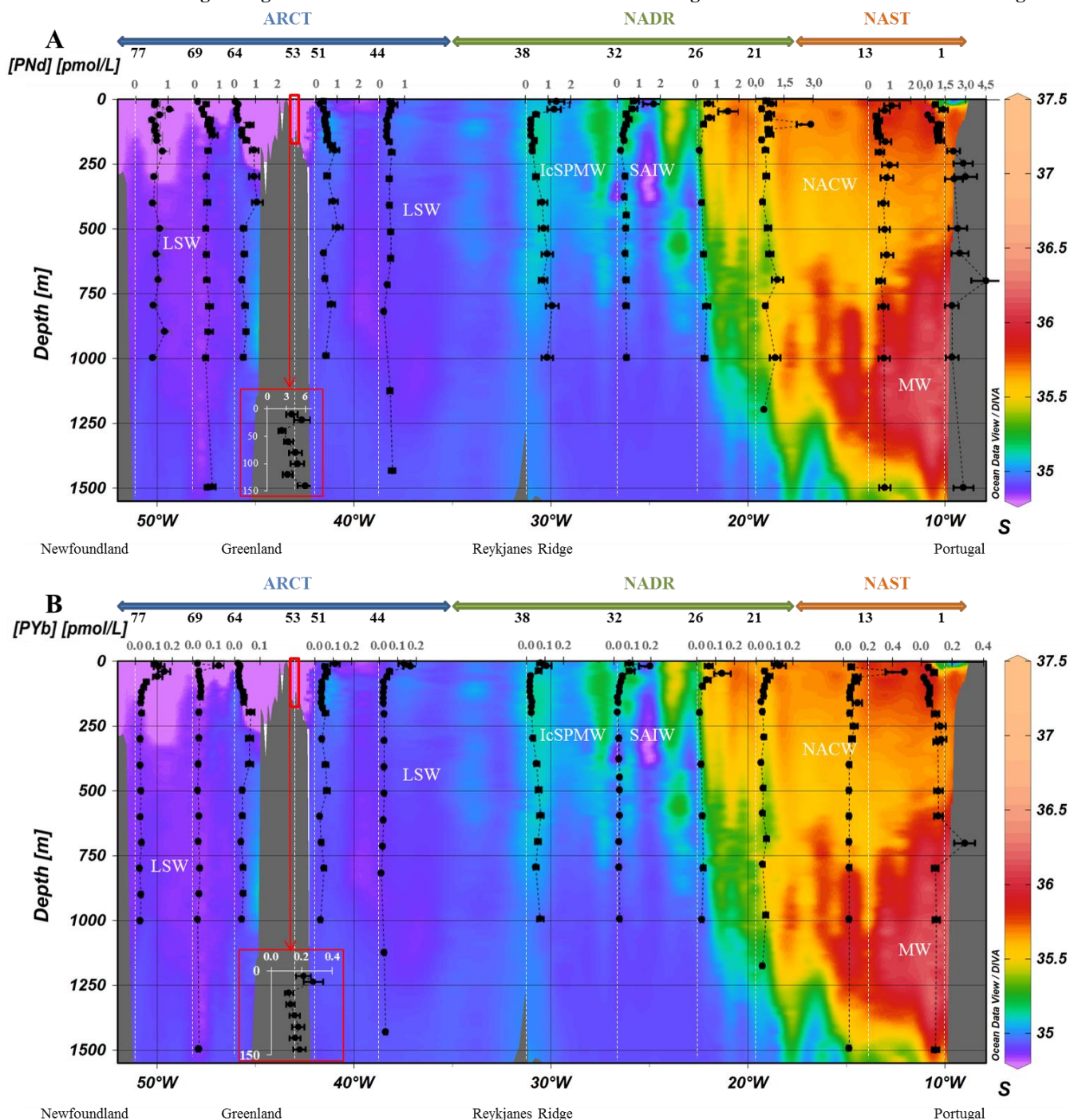
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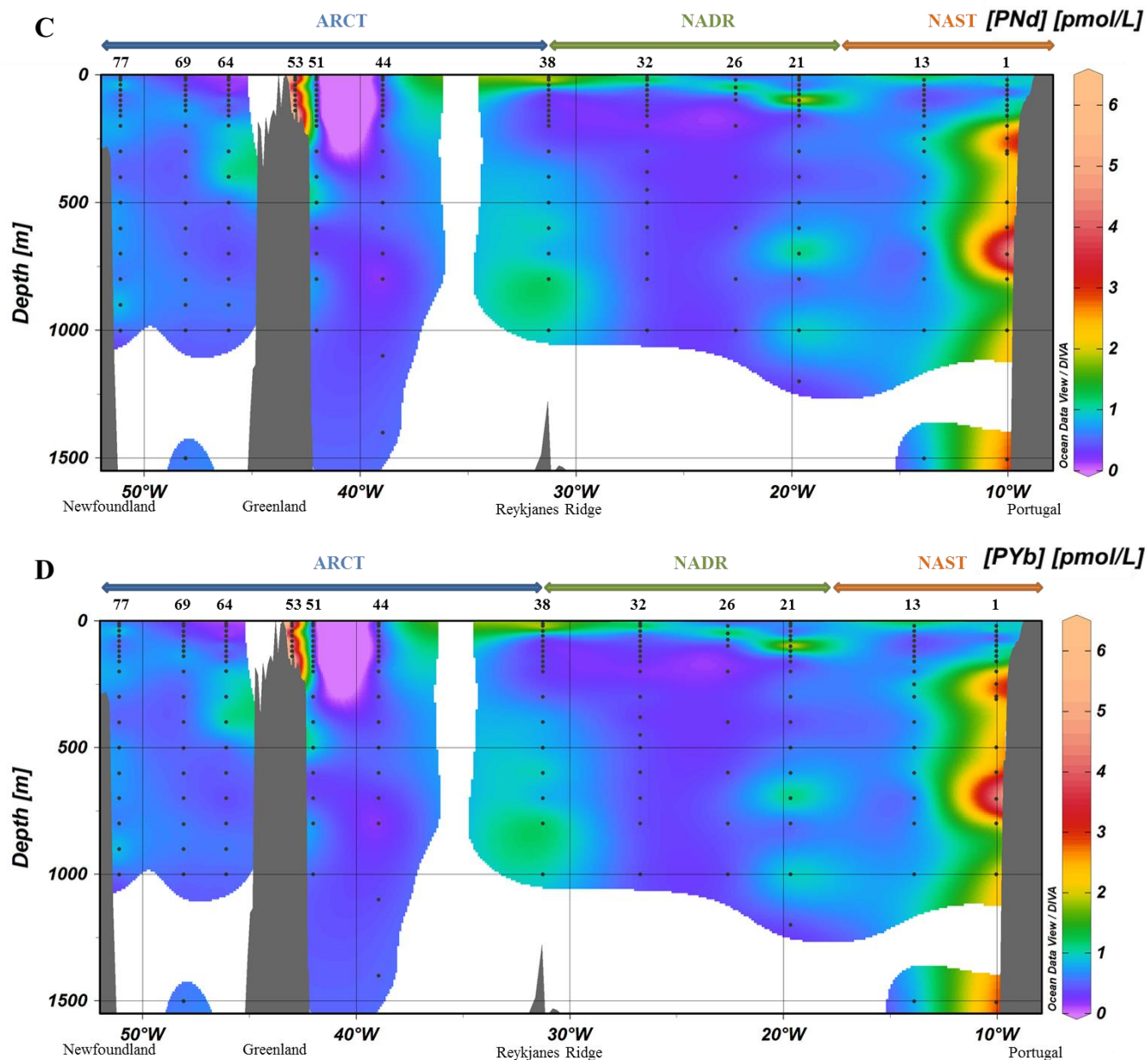




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Figure 2: A. Profiles of particulate [Ce] concentrations superimposed on salinity (S) measured by CTD at every GEOVIDE station (Lherminier and Sarthou, 2017); in white, water masses characterized by a multiparametric (OMP) analysis (García-Ibáñez et al., 2018). For the station #53, profiles are shifted to the bottom at a lower scale because of the shallow depth of the station. This map and the following were created with the software Ocean Data View (Schlitzer, 2016). B. Particulate [Ce] concentrations interpolated with the DIVA gridding function of Ocean Data View along the section defined in Fig. 1.





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Figure 3: A. Profiles of particulate [Nd] and B. [Yb] concentrations superimposed on salinity (S) measured by CTD at every GEOVIDE station (Lherminier and Sarthou, 2017); in white, water masses characterized by OMP analysis (García-Ibáñez et al., 2018). At station #53, profiles are shifted to the bottom at a lower scale because of the shallow depth of the station. C. Particulate [Nd] and D. [Yb] concentrations interpolated with the DIVA gridding function of Ocean Data View along the section defined in Fig. 1.

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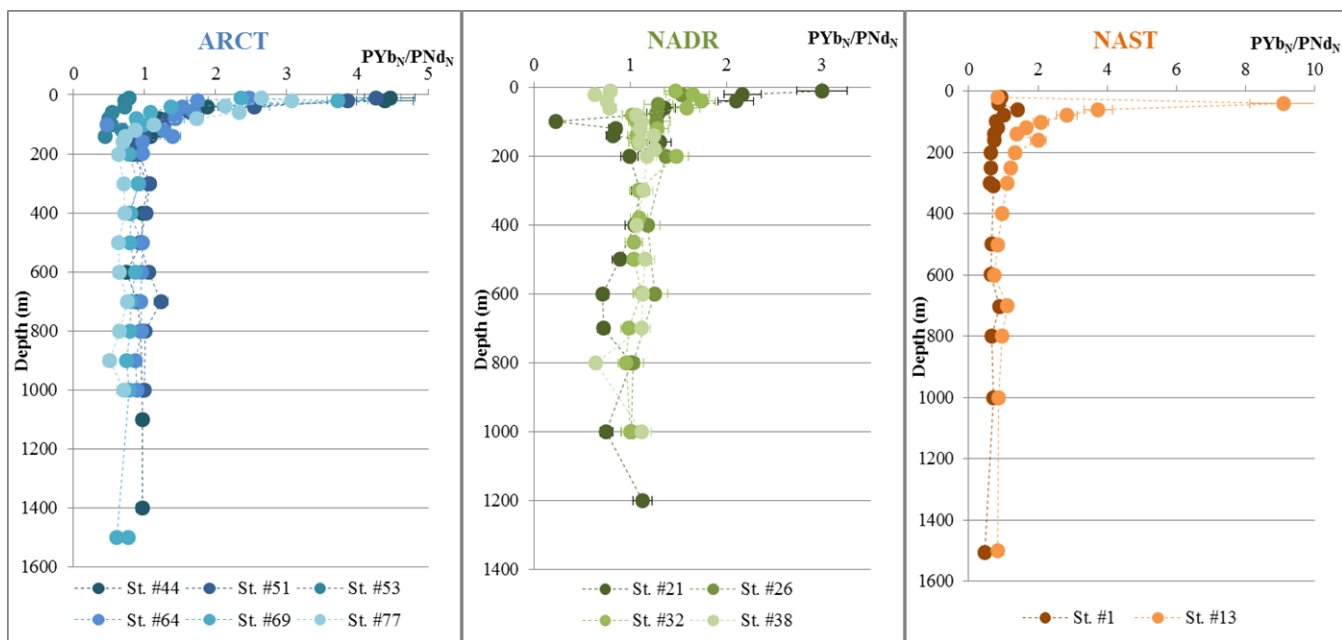
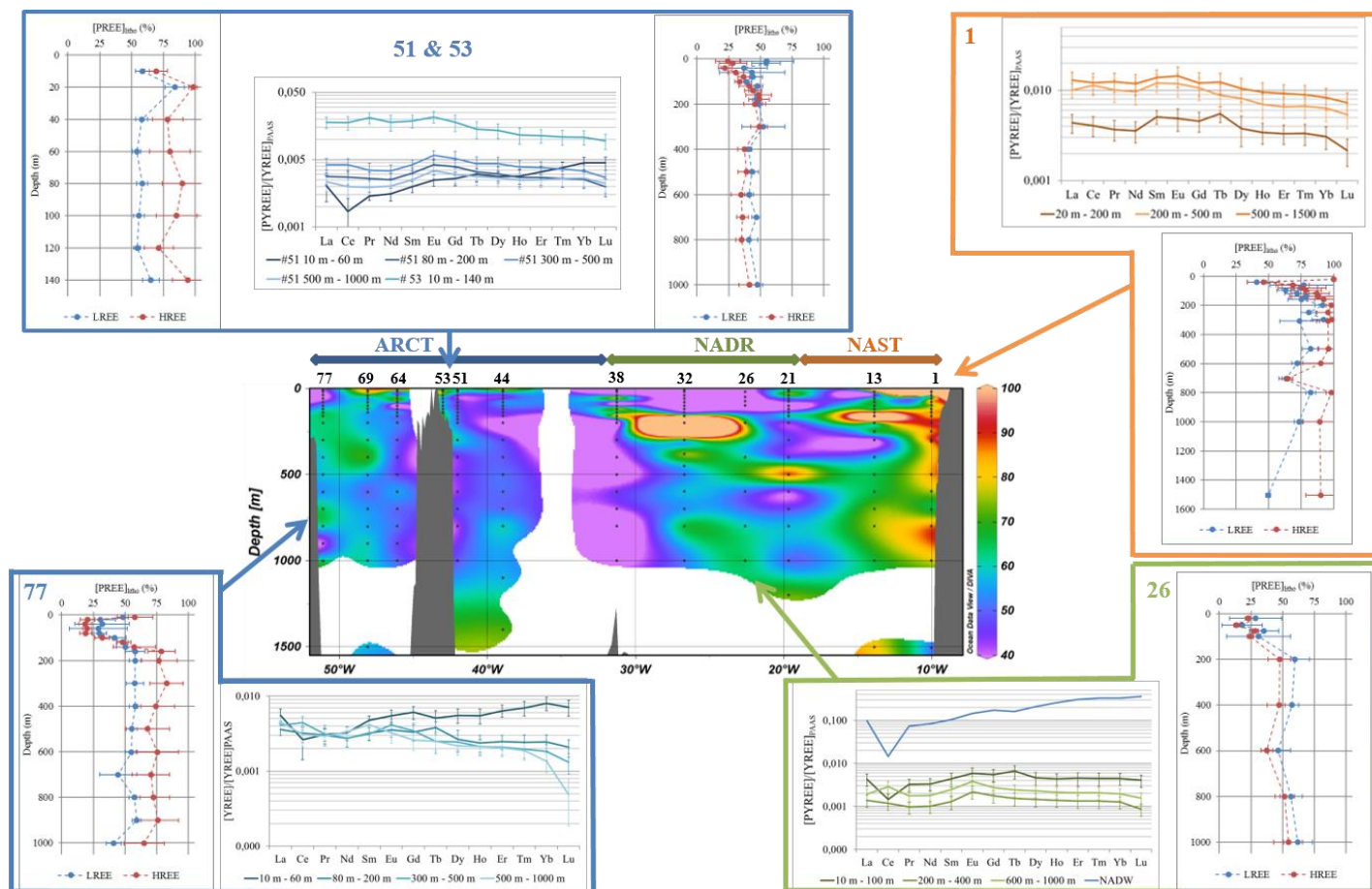
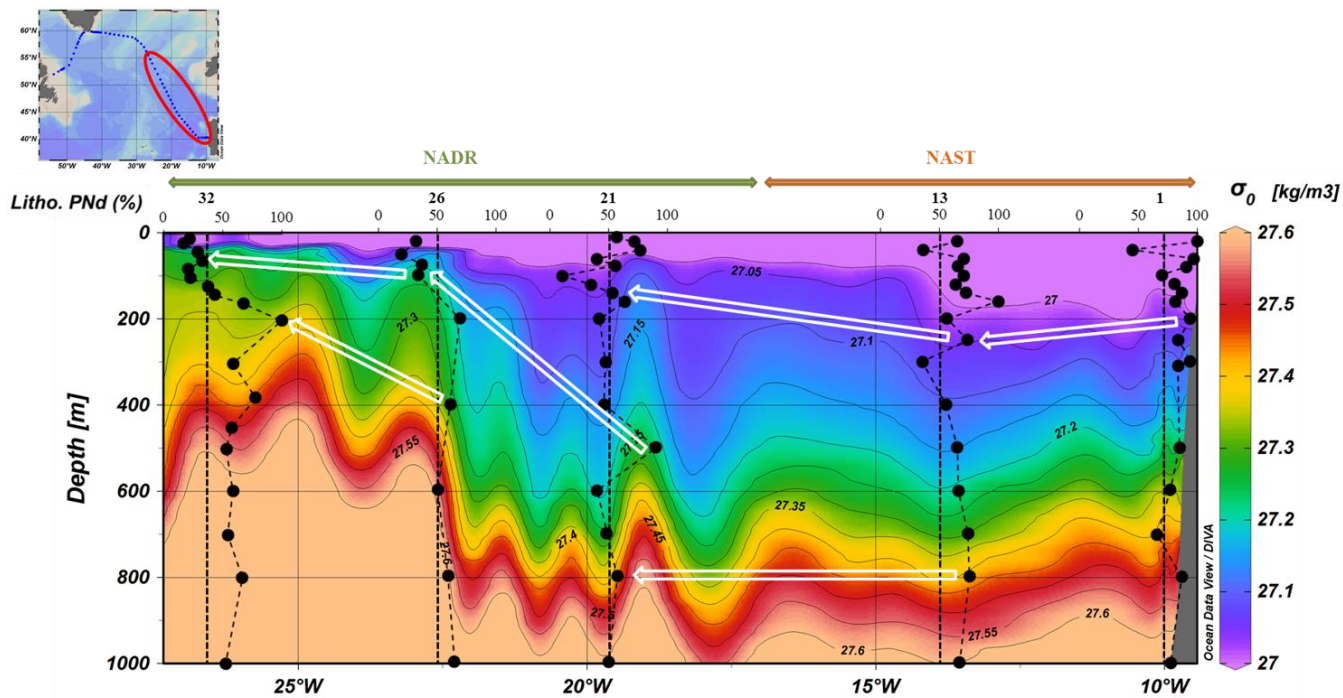


Figure 4: PYb/PNd ratio normalized to PAAS in each biogeochemical province

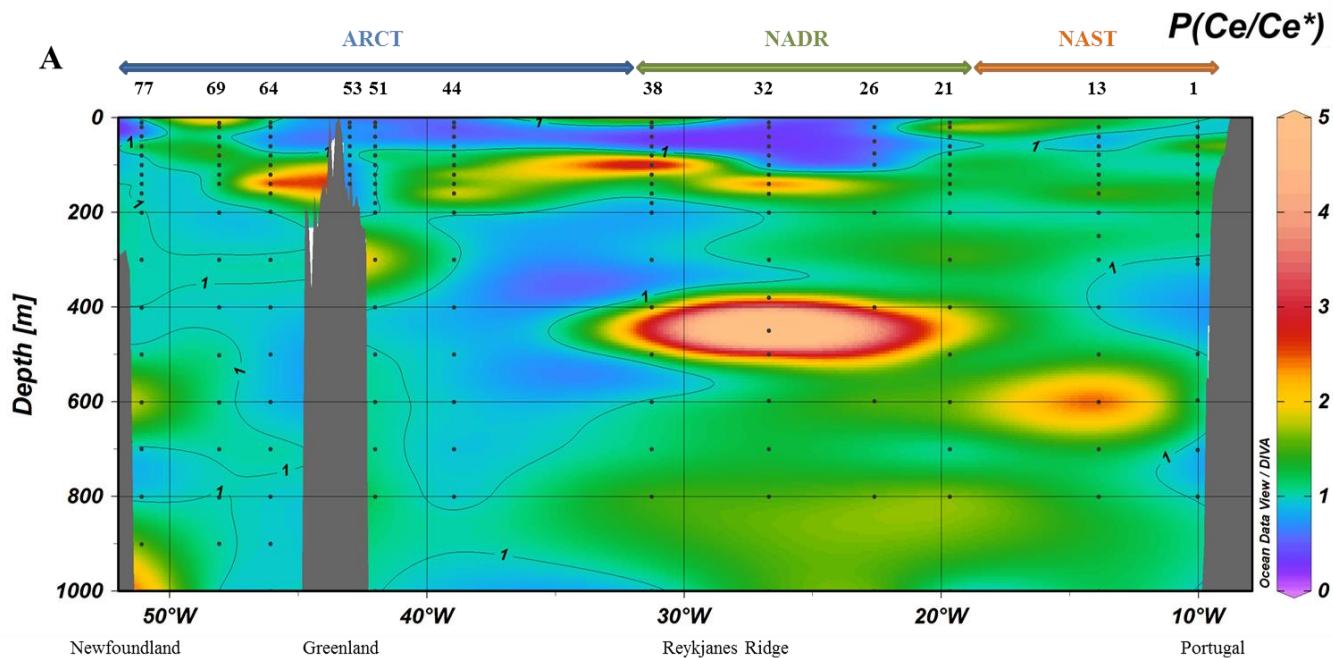


665 **Figure 5:** Center: proportion of lithogenic PNd along the GEOVIDE section (in %); Borders: vertical profiles of the lithogenic fraction of LREEs (except Ce, blue lines) and HREEs (red lines) and PAAS-normalized REE patterns of the total fraction, averaged by depth layers, at stations #1, #26, #51, #53 and #77.



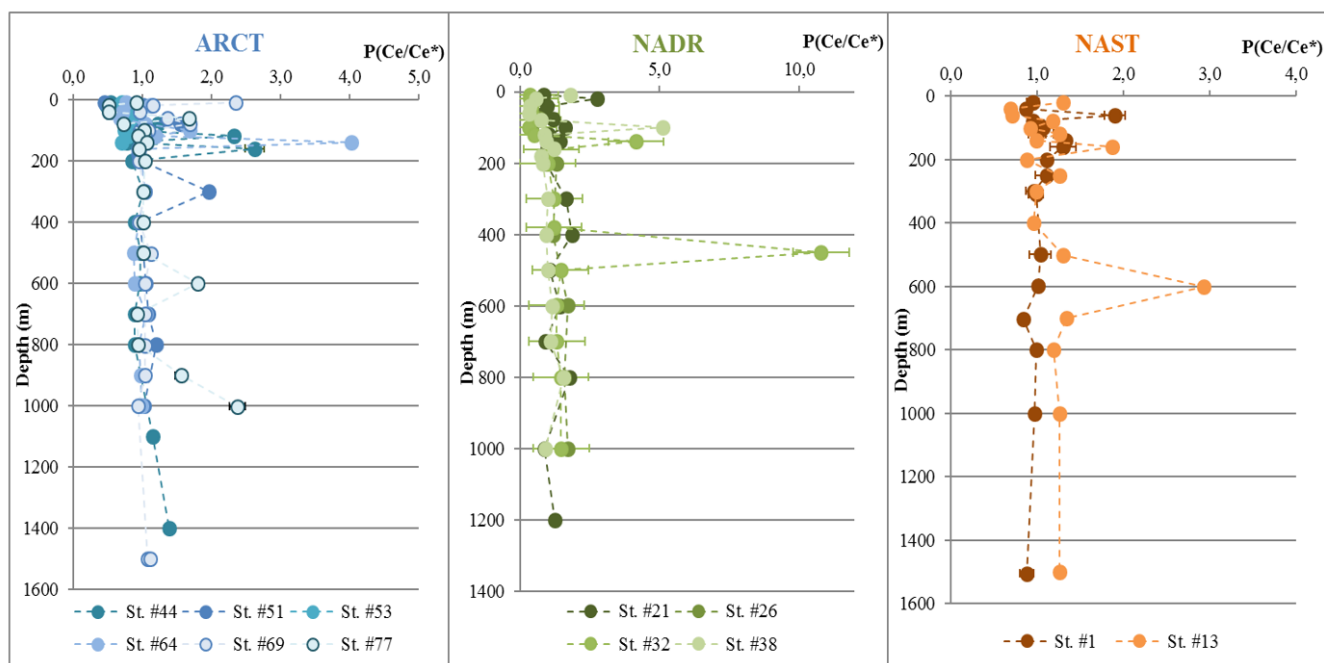
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Figure 6: Proportion of lithogenic PNd profiles superposed to density from station #1 to #32

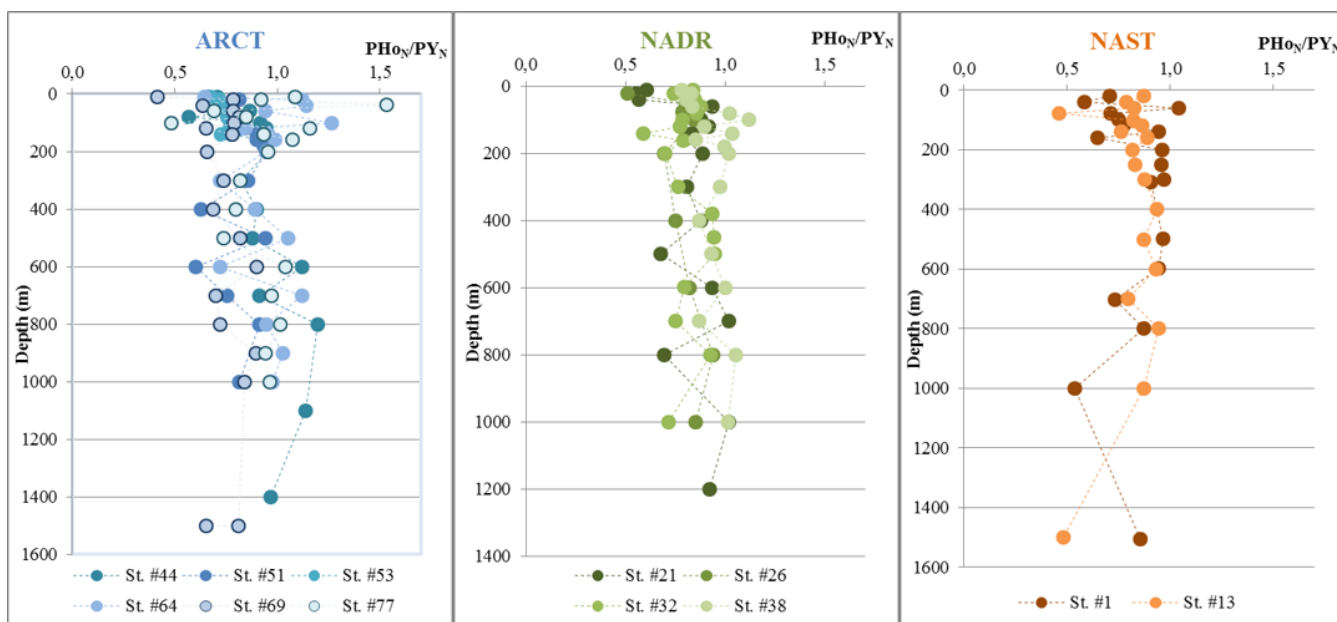




**B**



675 **Figure 7: A. Particulate Ce anomaly ( $Ce/Ce^*$ ) along the GEOVIDE section, interpolated with the DIVA gridding function of Ocean Data View and B.  $Ce/Ce^*$  profiles by biogeochemical provinces.**



680 **Figure 8: PAAS-normalized PHo/PY profiles by biogeochemical provinces.**

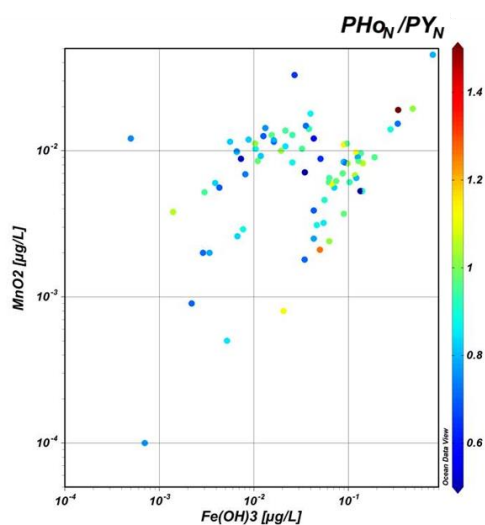


Figure 9: PAAS-normalized PHO/PY ratio as a function of Fe(OH)<sub>3</sub> and MnO<sub>2</sub> concentrations (in μg.L<sup>-1</sup>).

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#### Author contribution

N.L. did the sampling during the cruise, helped by C.J. N.L. did the leaching on the filter and first Ba measurements. C.J., M.B., M.G. and M.L. did REE measurements. ML wrote the manuscript, and C.J., H.P., M.G., N.L. and P.L. did the proofreading.

#### Competing interests

690 The authors declare that they have no conflict of interest.

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