



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⁻¹ to 16 pmol.L⁻¹, particulate neodymium (PNd) ones from 0.09 pmol.L⁻¹ to 6.1 pmol.L⁻¹ and particulate ytterbium (PYb) ones from 0.01 pmol.L⁻¹ to 0.5 pmol.L⁻¹. 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_N/PYb_N 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 away. 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 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⁻¹), but their 30 concentration decrease with depth (5 to 60 µg.L⁻¹ on average in the subsurface and deep ocean, (McCave and Hall, 2002; Stemmann 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 nmol.L^{-1} when dissolved Fe (DFe) does not exceed 2.5 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 clay 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.

50 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.

55 The North Atlantic is a key region of the global ocean, as it is the highest oceanic sink of anthropogenic 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).

60 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⁻².d⁻¹, station #26, Fonseca-Batista et al., 2019) and high carbon export (up to 80 molC.m⁻².d⁻¹, 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 EGCC 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 100 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}Th concentrations were 105 measured at both places, allowing us to compare our procedures. Regarding the samples collected with the clean rosette, Ba, ^{232}Th and Y (with the latter belonging to REEs, named YREEs when Y is included) were also measured. Ba and ^{232}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 110 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 115 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 μm porosity (Nuclepore®, 47 mm or 90 mm of diameter) were mounted. After sample filtration, the container was rinsed with ≤ 5 mL of ultra-pure water (Milli-Q; $18.2\text{ M}\Omega\text{.cm}$) 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 120 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 125 Teflon vial (Savillex®). The filter was then digested with a strong acid solution made of 1.5 mL HCl, 1 mL HNO₃ and 0.5 mL HF, all concentrated (Merck® Suprapur Grades). Vials were subseqently 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}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~~ $20 \cdot 10^{-12} \text{ g.g}^{-1}$ of REE was measured every 5 samples. The certified reference material SLR-¹⁴⁰ (NRC Canada) was systematically analyzed with the samples and their concentrations are within 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.

145 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 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}Th . It was conducted using an inductively coupled plasma quadrupole mass spectrometer (ICP-QMS; X Series 2 Thermo Fischer®). Ba, Y and ^{232}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}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}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 $P^{232}Th$ concentrations is compiled in Table 2. For sake of clarity, we only displayed PCe, 165 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. 170 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⁻¹ (station #64) and 16.3 pmol.L⁻¹ (station #32; Fig. 2). They are higher close to the Iberian margin (station #1: 1 pmol.L⁻¹ < PCe < 9.4 pmol.L⁻¹) and on the Greenland shelf (station 175 #53: 5.7 pmol.L⁻¹ < PCe < 14.6 pmol.L⁻¹). 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⁻¹ 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⁻¹). Maximum concentrations are observed at the 180 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⁻¹ < PCe < 2 pmol.L⁻¹). 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** 185 **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⁻¹ 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⁻¹. Low PNd values were also measured at 190 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 195 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_N/PYb_N ratios

200 To highlight a possible fractionation between LREE and HREE, the PNd_N/PYb_N 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_N/PYb_N is lower at the surface (< 0.7) except at stations #1, #38 and #53, and increases in the subsurface layers (0.7 < PNd_N/PYb_N < 1) in the open ocean. The **strongest** ratio value is observed 205 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_N/PYb_N 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 210 set of concentrations was published by Kuss et al. (2001), who measured PREEs in samples centrifuged from several m³ 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⁻¹ and 4.9 pmol.L⁻¹ 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⁻¹ 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 215 zone of the north-east tropical Atlantic, directly influenced by Saharan dust (6 g.m⁻².yr⁻¹ to 15 g.m⁻².yr⁻¹, Rea, 1994), are higher than those reported here (PNd = 2.6 pmol.L⁻¹ and PYb = 0.94 pmol.L⁻¹ 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⁻².yr⁻¹, Rea, 1994) but higher than that found during the GEOVIDE cruise (2 ng.m⁻³ to 500 ng.m⁻³, 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 CaCO₃) and metal oxides and hydroxides such as MnO₂ and Fe(OH)₃. REEs in the authigenic phase are **scavenged** by organic coatings **at** 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 (CaCO₃, Palmer, 1985 and BSi, Akagi, 2013) or biogenic byprod**ucts** as barite 230 (Ba_{xs}, 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 235 processes by the authigenic phase, while the lithogenic **one enables to picture** continental inputs. The high PREE concentrations 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 232Th. 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 ²³²Th 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 ²³²Th concentration in a given sample by the ratio of the considered REE on ²³²Th in the upper crust (Rudnick and Gao, 2014, Eq. (1)).

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

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

$$\text{REE}_{\text{authi}} = \text{REE}_{\text{total}} - \text{REE}_{\text{litho}} \quad (3)$$

245 These PREE lithogenic concentrations are then divided by the total PREE concentrations to obtain the percentage of particulate 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}Th in the particles, likely authigenic, or a difference between the adsorption kinetics of ^{232}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 270 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 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 ± 1.9 Sv, Daniault 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 (ϵ_{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 ± 0.2 Sv, Daniault 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.

300 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 in the east tropical Atlantic.

305 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 310 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}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}Ac do not permit to further compare data between these tracers except at the surface of station #1, where a maximum of ^{227}Ac is consistent from the lithogenic PREE signal.

315 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 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 m.s^{-1} to 0.1 m.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)₃ and MnO₂ (Bau, 1999; Bau et al., 1996). This PCe enrichment is commonly
330 quantified by the ratio of the PCe concentration ~~on~~ the theoretical PCe concentration calculated using its neighbors PNd and
PPr 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 PCe is depleted compared to other PREEs, 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 PCe to Mn and Fe (hydr)oxides, particulate Fe(OH)₃ and MnO₂ concentrations are calculated with the formula of
Lam et al. (2017, Figure S6) using PMn, PFe and PAI data from Gourain et al. (2019). The observed decoupling between Ce
anomaly and MnO₂ 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). CaCO₃ 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 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 MnO_2 depletion in the surface waters of NADR region would support this hypothesis, although this MnO_2 depletion reaches 500 m (ie below the euphotic layer, Fig S6A in supplementary). In the NAST region, a 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 365 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 370 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 375 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}Th and the assumption that REEs and ^{232}Th 380 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 SiOH4 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 390 50 m in the Irminger Sea and the Labrador Sea, where BSi concentrations are also the highest (Sarthou 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 $R^2=0.06$ for Ho to $R^2=0.4$ for Lu), this correlation coefficient rises with the atomic mass number 395 (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 400 silicate, and not only to a conservative mixing as shown by Zheng et al. (2016) and de Baar et al. (2018). This relationship would depends 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 405 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 PHoN/PYN measured in our particulate samples to the PAAS ratio to reveal any relative loss or enrichment 410 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 FeOH3 and MnO2. 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 FeOH3 415 and MnO2 doesn’t fit to any pattern (Fig. 9). PHoN/PYN is higher when $[Fe(OH)3] > 10-2 \mu g.L^{-1}$, while there is no evidence of a higher HoN/YN ratio when MnO2 content increases. However, while there is a pronounced east-west gradient in the



Fe(OH)3 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 MnO2 and Fe(OH)3 (Fig. S6 in supplementary), leading to a weak adsorption of Ho. All 420 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. 425 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.**

430 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.

435 Thus, our results show that high PHoN/PYN ratio not only reflects sorption processes driven by the occurrence of Fe(OH)3 and to a lesser extent MnO2 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 masses and current abbreviations.

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

620 **Table 2:** Particulate REE, Y, Ba and ^{232}Th concentrations with the corresponding 2σ error.

Station	Longitude	Latitude	Depth [m]	La	2g	Pr	2g	Nd	2g	Eu	2g	Gd	2g	Tb	2g	Ho	2g	Dy	2g	Er	2g	Tm	2g	Yb	2g	Lu	2g	Y	2g	Ba	2g	Th										
1	-10.0359	40.333	20	962	234	1997	476	216	54	757	182	159	41	32	8	124	31	18	5	107	26	20	5	51	14	8	2	49	12	5	1	1321	321	168667	43630	1031	45					
1	-10.0359	40.333	40	1730	377	2904	635	367	85	1377	326	333	77	60	13	238	35	8	192	44	36	8	97	25	13	3	82	18	8	2	2908	631	269439	59703	150	36						
1	-10.0359	40.333	60	596	133	1101	245	15	218	11	34	111	112	3	44	10	7	2	41	9	8	2	23	6	4	1	21	5	2	0	1	948	206	406435	85960	113	24					
1	-10.0359	40.333	70	1014	214	3497	317	155	34	510	111	112	30	3	45	21	31	20	31	24	14	3	39	10	6	1	3	36	8	4	1	3	14	3	1	948	206	406435	85960	113	24	
1	-10.0359	40.333	79	1014	214	3497	317	155	34	510	111	112	30	3	45	21	31	20	5	125	29	13	20	5	68	19	2	1	2	143	331	301392	127194	180	43							
1	-10.0359	40.333	98	1552	365	2348	637	289	77	1061	252	222	63	44	10	153	40	2	17	29	14	3	68	19	2	1	2	143	331	301392	127194	180	43									
1	-10.0359	40.333	119	1248	320	2649	677	273	78	955	267	230	68	37	9	147	37	20	6	116	30	22	5	58	16	8	2	1	2	1321	345	384719	105833	187	49							
1	-10.0359	40.333	139	1303	517	3179	773	261	64	963	254	214	54	36	9	147	35	57	15	111	27	27	27	5	58	15	7	2	1	2	49	12	6	1	2	1644	441	323704	93522	221	58	
1	-10.0359	40.333	160	1466	384	3938	1015	73	46	911	1239	228	228	12	12	48	22	6	126	34	23	6	62	17	8	3	57	15	7	2	1	2	1644	441	323704	93522	221	58				
1	-10.0359	40.333	200	2591	579	6041	1335	578	131	2090	470	362	86	77	17	282	66	38	9	213	48	38	8	104	24	14	3	93	21	12	3	1848	419	401111	90744	475	109					
1	-10.0359	40.333	249	3458	935	2045	769	213	2815	724	535	158	27	392	100	57	156	286	74	51	13	133	37	19	6	124	32	17	4	2	2464	638	618995	173326	573	151						
1	-10.0359	40.333	289	3735	970	8831	2298	904	259	3001	850	443	130	109	28	401	103	53	301	177	53	14	133	35	20	6	130	33	20	4	2	2558	67	428470	130733	684	173					
1	-10.0359	40.333	309	2553	654	692	1421	602	167	2139	644	626	161	77	19	308	76	41	11	234	68	43	11	118	33	20	5	107	27	14	3	2	2218	569	21646	307430	57446	361				
1	-10.0359	40.333	3179	1303	517	3179	773	261	64	963	254	214	54	36	9	147	35	57	15	111	27	27	27	5	58	15	7	2	1	2	1	2	1644	441	323704	93522	221	58				
1	-10.0359	40.333	3499	2821	726	6219	1590	654	196	2426	698	483	145	90	24	338	107	47	13	253	79	46	12	122	36	18	5	111	29	14	4	2	2219	582	397429	1404586	500	129				
1	-10.0359	40.333	3597	3392	817	1103	1706	59	259	639	496	131	97	24	330	88	20	259	63	47	11	17	32	17	5	113	27	32	5	1	2	1	2	1644	441	323704	93522	221	58			
1	-10.0359	40.333	702	5732	1400	9612	2346	1228	301	4505	1113	826	217	184	55	177	103	26	610	148	121	29	333	85	27	14	9	11	280	68	39	9	7731	1893	244048	59668	719	116				
1	-10.0359	40.333	800	2554	610	5303	1264	558	136	1979	477	366	95	70	17	239	63	36	9	200	48	37	9	103	26	14	3	91	22	12	3	1898	478	231312	55034	417	102					
1	-10.0359	40.333	1000	2558	601	1145	222	132	1994	471	378	98	70	21	276	65	41	11	222	54	41	10	112	27	16	4	98	23	12	3	3	3594	80	25706	374	88						
1	-10.0359	40.333	1505	3644	961	7402	1916	844	240	2849	744	497	134	71	18	286	78	41	12	221	57	40	10	108	32	15	4	94	24	12	3	3	321	10	210230	57446	361	91				
13	-13.8877	41.383	120	853	262	1375	423	122	38	460	82	82	28	7	88	27	12	4	79	26	16	8	138	45	26	8	80	29	18	6	65	21	8	3	1380	460	385242	131035	176	57		
13	-13.8877	41.383	140	1219	380	1035	324	187	58	785	246	202	65	57	18	254	80	50	16	403	125	106	33	388	122	69	21	496	153	82	25	113	19	67714	69	21	104	601	455716	142611	345	107
13	-13.8877	41.383	160	1258	395	3917	1226	225	72	823	259	161	52	35	11	166	58	25	8	169	53	36	11	111	35	17	6	115	36	17	5	1904	601	455716	142611	345	107					
13	-13.8877	41.383	60	999	513	893	279	141	40	444	322	284	147	35	21	1029	37	21	14	109	31	23	10	85	30	18	6	80	26	15	4	104	32	1029	362	145918	76	26				
13	-13.8877	41.383	78	918	285	476	1467	456	135	426	133	88	31	20	6	91	31	13	4	81	25	17	5	55	17	8	3	82	17	4	2	2449	67	247745	77277	80	25					
13	-13.8877	41.383	100	612	187	1004	308	117	36	429	137	271	99	52	17	110	35	18	6	113	38	24	10	88	20	11	3	82	17	4	2	2449	67	247745	77277	80	25					
13	-13.8877	41.383	120	853	262	1375	423	122	38	460	82	82	28	7	88	27	12	4	79	26	16	8	102	22	19	6	50	16	7	3	1495	77	575153	191525	77	25						
13	-13.8877	41.383	140	775	237	1356	416	147	416	147	356	295	96	45	14	127	41	14	8	96	31	18	6	46	20	7	3	1495	77	302221	93035	77	25									
13	-13.8877	41.383	160	979	299	1610	494	190	59	731	224	139	48	30	10	128	40	18	6	94	31	18	6	47	17	8	3	1495	77	286891	98	30										
13	-13.8877	41.383	100	964	323	2325	769	202	77	775	239	149	57	32	11	142	51	22	18	6	94	31	18	6	47	17	8	3	1495	77	286891	98	30									
21	-19.6724	46.544	10	978	244	1078	324	112	318	116	312	1312	318	162	41	681	165	125	37	108	32	8	110	26	16	4	83	17	4	1	2	1	2	1	1607	44	545540	158414	34			
21	-19.6724	46.544	20	3837	209	46344	140	1050	256	2426	605	195	49	191	114	32	34	9	123	30	17	5	90	24	17	4	45	12	7	2	2	2	2056	625	10738	312975	48					
21	-19.6724	46.544	40	756	189	819	22	327	80	771	19	28	7	69	16	5	17	3	57	15	11	3	31	9	4	1	40	10	6	2	2	37	9	15	1	2	144	33	423791	147719	78	
21	-19.6724	46.544	60	962	241	1433	358	195	51	764	189	147	43	26	7	148	38	23	6	147	39	29	7	81	20	11	3	1	2	1	2	1	162	345	213842	586486	33					
21	-19.6724	46.544	76	988	257	1824	471	171	46	632	174	122	51	43	14	129	42	18	6	97	24	17	7	3	57	15	11	3	1	2	1	2	1	162	345	213842	586486	33				
21	-19.6724	46.544	100	1025	246	1947	478	260	66	1029	266	215	58	55	17	171	42	14	25	25	1																					



Station	Longitude	Latitude	Depth [m]	La	26	Ce	26	Pr	26	Eu	26	Gd	26	Tb	26	Dy	26	Er	26	Ho	26	Tm	26	Yb	26	Lu	26	Y	26	Ba	26	Th							
32	-26.7030	55.5115	40	1142	271	751	178	200	51	754	186	154	42	35	8	154	36	23	6	141	37	29	7	90	23	13	3	1632	21	14	3	1632	21	14	3				
32	-26.7030	55.5115	60	593	145	398	96	112	29	426	108	89	25	21	5	90	22	13	4	79	21	16	4	48	13	7	2	47	11	6	2	851	21	12	2				
32	-26.7030	55.5115	80	827	213	606	153	144	40	545	141	119	38	27	7	108	20	14	4	84	12	16	4	43	10	4	1	35	10	4	1	32	7	10	4	1			
32	-26.7030	55.5115	100	627	150	362	150	36	119	25	426	101	90	25	21	3	67	18	13	3	35	12	16	4	43	10	4	1	762	180	140814	150	23	6					
32	-26.7030	55.5115	120	558	140	403	100	89	23	337	65	75	20	18	5	71	18	9	2	60	17	12	3	32	9	5	1	30	8	4	1	704	178	311306	78820	31	8		
32	-26.7030	55.5115	140	381	92	2518	602	70	17	273	67	60	17	31	8	35	17	13	3	56	13	17	3	23	6	3	1	20	5	2	1	691	21	72744	71899	29	7		
32	-26.7030	55.5115	161	649	158	896	218	89	22	335	84	161	70	18	31	8	71	17	3	39	18	13	10	3	55	12	7	4	1	25	1	1	1	574	145	418735	106021	53	13
32	-26.7030	55.5115	200	312	72	432	99	50	12	192	45	47	11	13	3	39	10	6	1	35	13	7	2	21	6	3	1	20	5	2	1	460	125	646966	10885	124	31		
32	-26.7030	55.5115	300	589	140	1143	269	101	21	26	7	69	16	13	4	58	15	11	3	31	9	4	1	28	7	3	1	679	157	497786	126347	54	12						
32	-26.7030	55.5115	380	543	131	975	235	90	24	347	87	68	11	20	5	247	90	11	3	57	16	12	3	57	16	11	3	1	26	8	3	1	536	147	463739	116271	65	16	
32	-26.7030	55.5115	450	11425	2812	16272	4695	140	35	428	108	91	22	24	6	99	25	12	3	60	16	12	3	33	9	5	1	31	1	1	1	596	185	590904	142516	60	18		
32	-26.7030	55.5115	500	545	132	1346	328	108	27	418	103	89	24	23	6	81	20	13	3	64	17	12	3	35	9	5	1	30	7	4	1	612	151	357061	91240	54	13		
32	-26.7030	55.5115	598	470	111	1201	287	102	57	104	120	93	72	18	17	5	70	17	10	3	60	16	11	3	32	9	5	1	29	7	3	1	705	193	282115	76794	55	14	
32	-26.7030	55.5115	600	609	145	558	125	125	31	418	110	78	21	18	6	71	18	6	1	63	17	12	3	32	10	4	1	28	7	4	1	590	147	316075	87121	68	17		
32	-26.7030	55.5115	800	578	144	1565	386	115	30	423	104	80	23	27	5	375	97	68	24	11	3	63	17	12	3	32	10	4	1	28	7	4	1	367	88	176360	44333	18	5
32	-26.7030	55.5115	1000	559	138	1469	365	114	29	442	115	72	20	5	82	20	5	82	20	5	82	20	5	82	20	5	2	1	20	5	2	1	336	83	249864	61826	20	5	
38	-31.2660	58.843	100	4901	1132	6127	1419	372	87	1393	338	247	58	57	14	274	72	33	8	188	45	36	9	100	24	12	3	76	18	2166	503	196968	46599	37	9				
38	-31.2660	58.843	200	2725	607	1704	379	504	112	2535	364	355	79	80	18	420	94	48	11	271	61	52	12	138	31	18	4	110	25	14	2	2937	634	109596	2247	40	9		
38	-31.2660	58.843	400	1667	398	1095	259	345	86	1276	303	244	64	54	21	217	55	30	8	169	44	31	17	12	3	67	16	9	2	1826	430	184556	46234	34	13				
38	-31.2660	58.843	600	609	145	558	125	125	31	418	110	78	21	18	6	71	18	6	1	63	17	12	3	31	9	5	1	26	6	3	1	682	167	115360	27528	111	29		
38	-31.2660	58.843	800	607	143	558	125	125	31	418	110	78	21	18	6	71	18	6	1	63	17	12	3	31	9	5	1	26	6	3	1	682	167	31650	145273	27	7		
38	-31.2660	58.843	1000	578	142	558	125	125	31	418	110	78	21	18	6	71	18	6	1	63	17	12	3	31	9	5	1	26	6	3	1	682	167	15023	348	20	5		
38	-31.2660	58.843	1200	540	141	558	125	125	31	418	110	78	21	18	6	71	18	6	1	63	17	12	3	31	9	5	1	26	6	3	1	682	167	15023	348	20	5		
38	-31.2660	58.843	1400	865	214	1615	398	197	50	769	198	146	41	51	13	154	39	23	6	132	34	25	6	68	19	9	2	57	14	1338	340	679261	117376	68	18				
38	-31.2660	58.843	2000	834	500	1652	401	80	1616	205	185	49	52	21	217	55	70	18	203	52	175	33	81	91	24	12	3	65	16	8	2	1420	346	428812	108888	63	17		
38	-31.2660	58.843	2800	1145	274	524	441	61	980	247	224	501	244	211	70	175	55	80	18	175	52	175	33	81	91	24	12	3	65	16	8	2	1540	347	52523	133169	107	26	
38	-31.2660	58.843	3600	931	218	1782	423	196	46	802	192	239	57	10	160	37	25	6	138	32	26	6	74	19	9	2	62	15	8	2	1421	336	732581	178220	80	20			
38	-31.2660	58.843	4000	200	578	142	1022	251	120	31	477	121	102	28	37	10	98	24	15	4	82	22	16	4	44	12	3	2	38	10	4	1	749	194	745923	188937	52	13	
38	-31.2660	58.843	5000	834	120	356	133	133	31	418	110	78	21	18	6	71	18	6	1	63	17	12	3	31	9	5	1	27	6	3	1	510	114	151594	24301	82	20		
44	-38.954	59.62	10	719	169	592	136	121	29	445	105	89	22	25	6	115	26	25	6	129	36	29	7	100	27	17	5	138	21	5	1	1911	455	1911455	20162	82	19		
44	-38.954	59.62	20	823	147	110	131	131	32	564	145	97	23	25	6	171	23	7	127	121	5	153	38	8	1	32	21	6	1	557	14	435227	99893	34	8				
44	-38.954	59.62	40	402	93	608	140	85	20	307	71	67	15	25	6	101	23	25	6	133	38	8	1	32	21	6	1	534	134	1534	1245	44	10						
44	-38.954	59.62	60	160	373	1799	409	176	33	525	234	229	405	73	17	15	4	87	20	20	5	87	12	3	2	44	11	6	2	473	117	657949	149374	41	9				
44	-38.954	59.62	800	505	112	1082	239	112	25	395	87	82	19	21	5	76	17	12	3	64	14	12	3	34	8	4	1	201	5	1	0	2	1157	282	166579	411536	28	7	
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44	-38.954	59.62	500	603	139	1205	276	128	30	452	104	84	20	26	6	81	18	13	3	62	14	12	3	34	8	4	1	201	5	1	0	2	1011	242	42593	49	11		
44	-38.954	59.62	100	726	162	1113	253	131	30	460	105	91	20	22	5	88	21	17	4	72	17	14	3	39	11	6	1	40	9	1	0	2	1157	187	296424	73162	89	21	



Station	Longitude	Latitude	Depth [m]	La	2g	Ce	2g	Pr	2g	Nd	2g	Gd	2g	Tb	2g	Dy	2g	Ho	2g	Er	2g	Tm	2g	Yb	2g	Lu	2g	Y	2g	Ba	2g	Th								
51	-42.013	59.8	600	444	103	1018	235	105	24	385	88	76	25	6	77	17	11	3	65	15	12	3	34	8	5	1	28	7	3	1	926	222	225811	2006	40	9				
51	-42.013	59.8	700	503	120	1172	268	117	27	431	102	81	20	26	6	88	20	12	3	74	17	14	3	40	10	6	1	37	9	5	1	866	217	259060	59188	50	12			
51	-42.013	59.8	800	530	161	314	226	492	46	729	134	31	484	111	161	153	34	8	5	119	22	13	3	79	18	22	4	5	61	14	8	2	11125	11125	171596	39258	73	15		
51	-42.013	59.8	1000	530	123	1280	295	134	31	484	111	161	153	34	8	5	119	22	13	3	79	18	22	4	5	61	14	8	2	1	33	8	4	1	827	197	171596	39258	57	13
53	-43.006	59.9	10	4261	975	8331	1915	1178	272	3883	887	669	152	35	540	122	73	18	426	101	77	18	218	54	30	7	211	48	30	7	5376	1250	334887	77894	557	128				
53	-43.006	59.9	100	4202	938	7634	1795	1763	414	5223	1278	902	180	41	693	158	95	23	6077	125	95	22	272	66	9	9	278	63	39	5	6246	1698	354567	602175	1145	262				
53	-43.006	59.9	120	6231	1442	12378	2392	712	169	3364	500	408	94	94	22	317	74	44	10	246	61	44	10	125	31	17	4	117	27	16	4	2765	660	156732	37092	360	84			
53	-43.006	59.9	40	645	109	14984	3160	1962	523	1315	932	199	208	45	678	147	86	19	459	109	80	17	221	52	28	7	185	40	24	5	5209	1145	198138	43745	963	214				
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64	-46.083	59.07	199	1221	266	2114	463	244	54	948	208	195	46	45	10	170	39	11	7	141	32	27	6	73	18	10	2	64	14	8	2	1341	299	103634	120	26				
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69	-48.093	55.84	400	637	141	1374	291	149	32	516	113	96	22	24	5	86	18	12	3	34	8	5	1	900	191	509737	105738	76	11											
69	-48.093	55.84	502	700	144	137	269	127	26	466	146	125	28	29	6	108	24	15	3	88	20	16	4	45	11	6	1	637	147	642915	13101	67	14							
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69	-																																							



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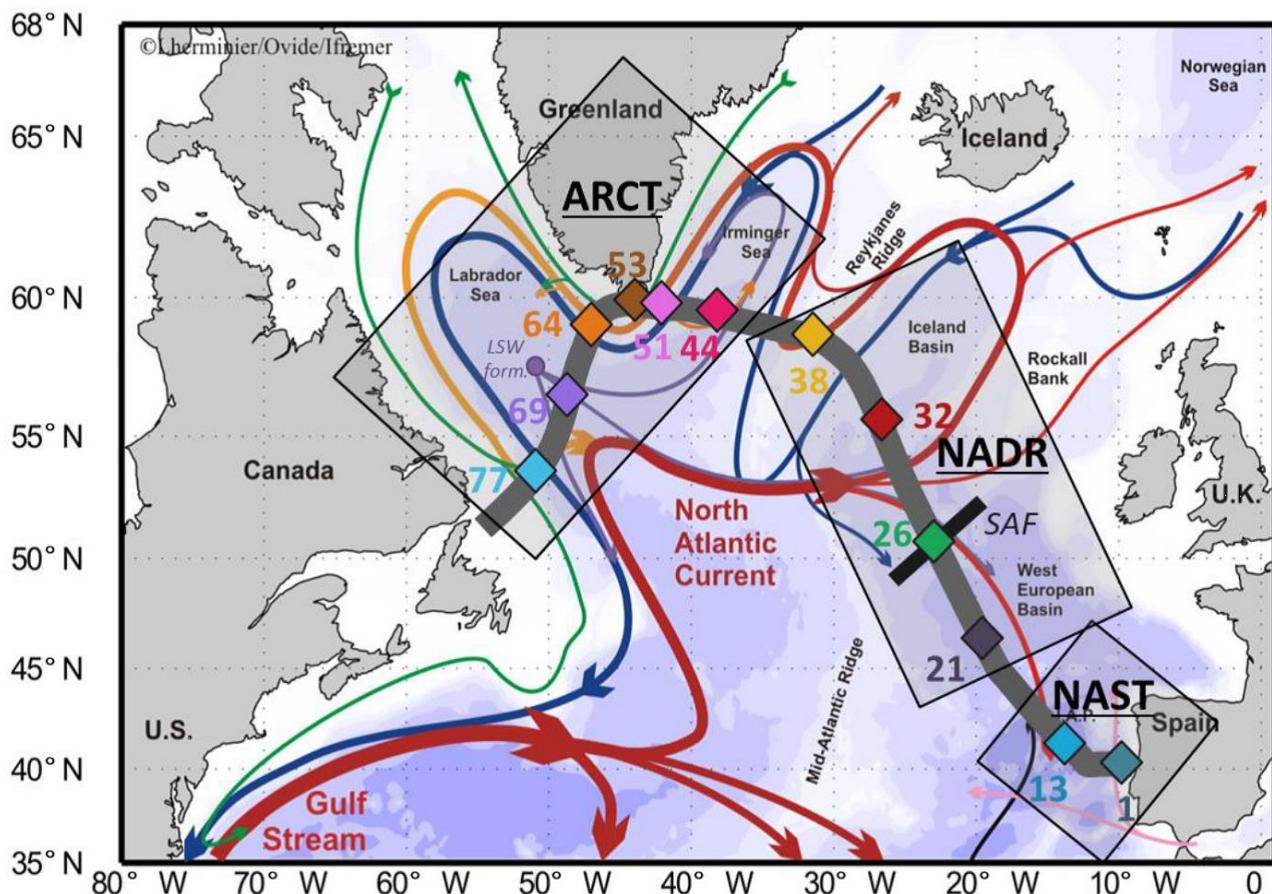
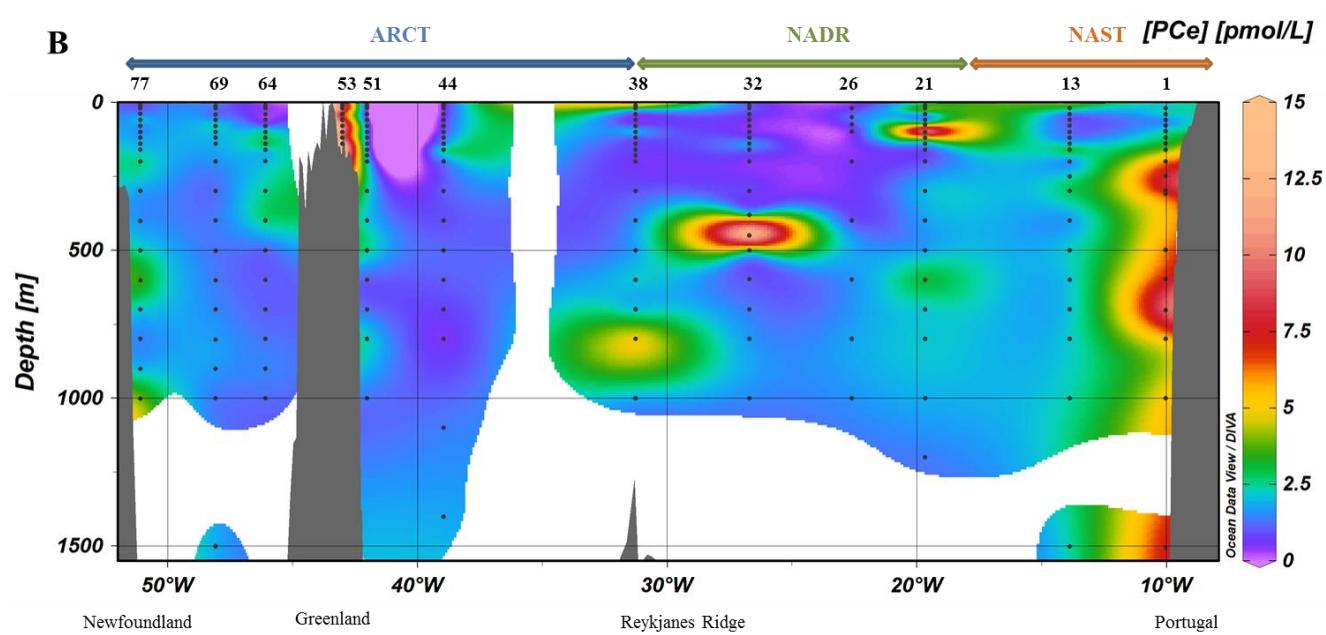
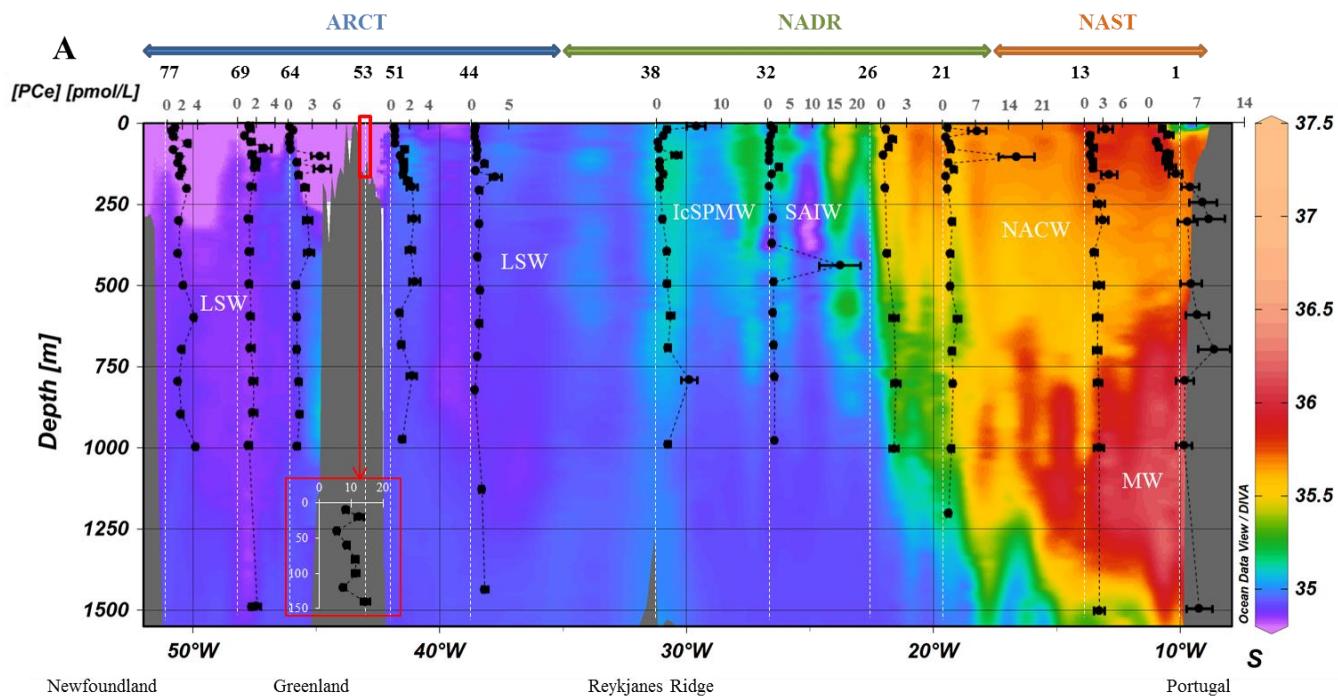


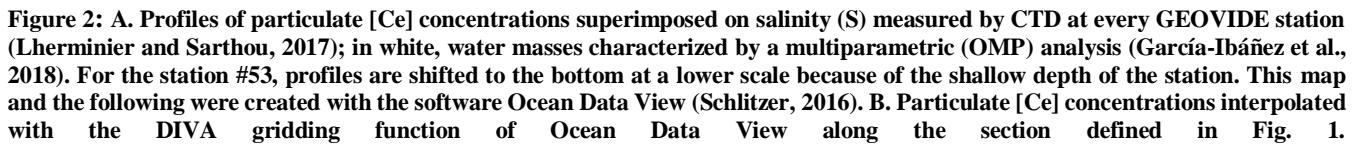
Figure 1: Map of the studied area (Subpolar North Atlantic, SPNA), including schematized circulation features, adapted from García-Ibáñez et al. (2015). Bathymetry is plotted in color with interval boundaries at 100 m, at 1000 m, and every 1000 m below 1000 m. The red and green arrows represent the main 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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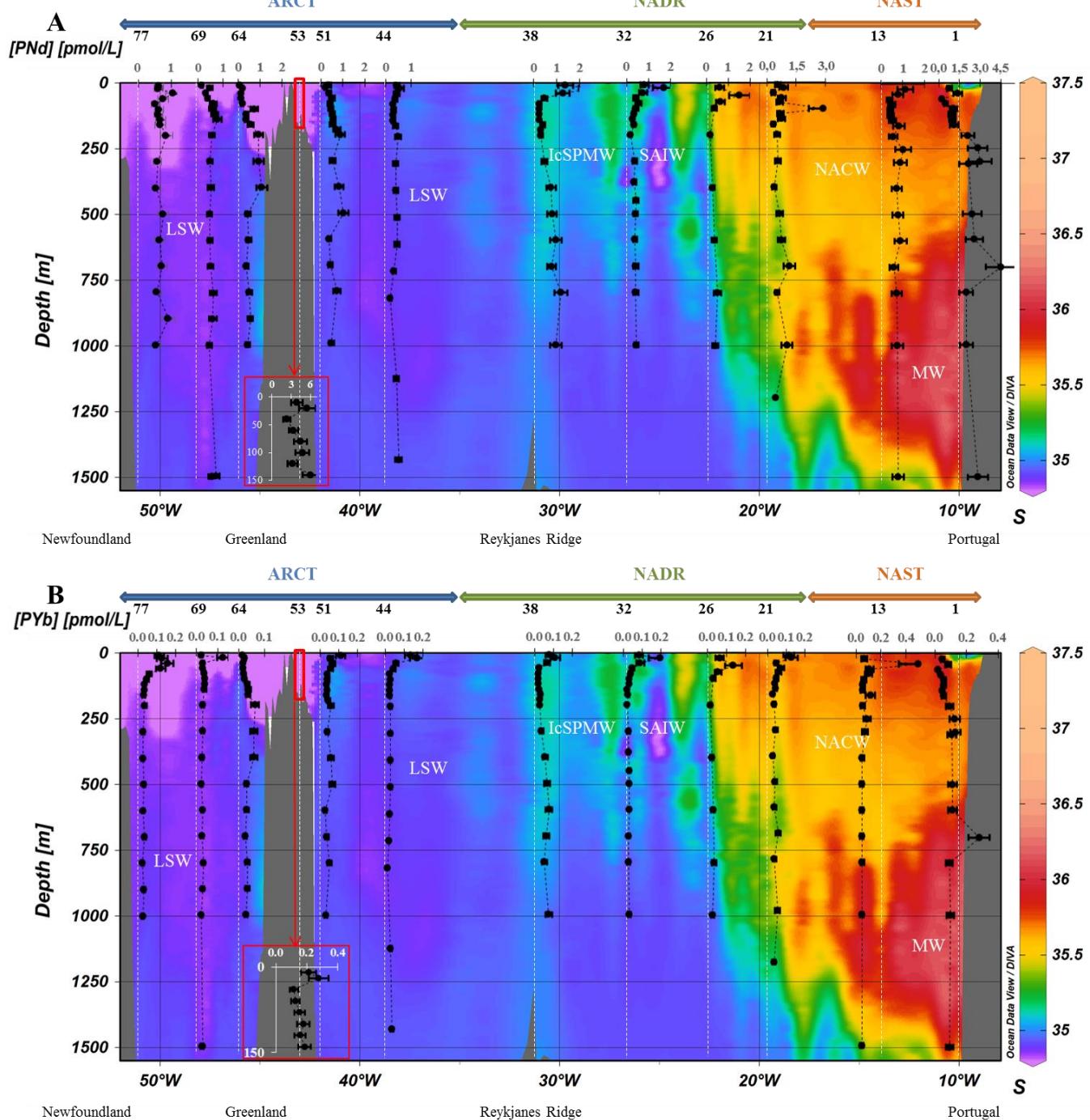
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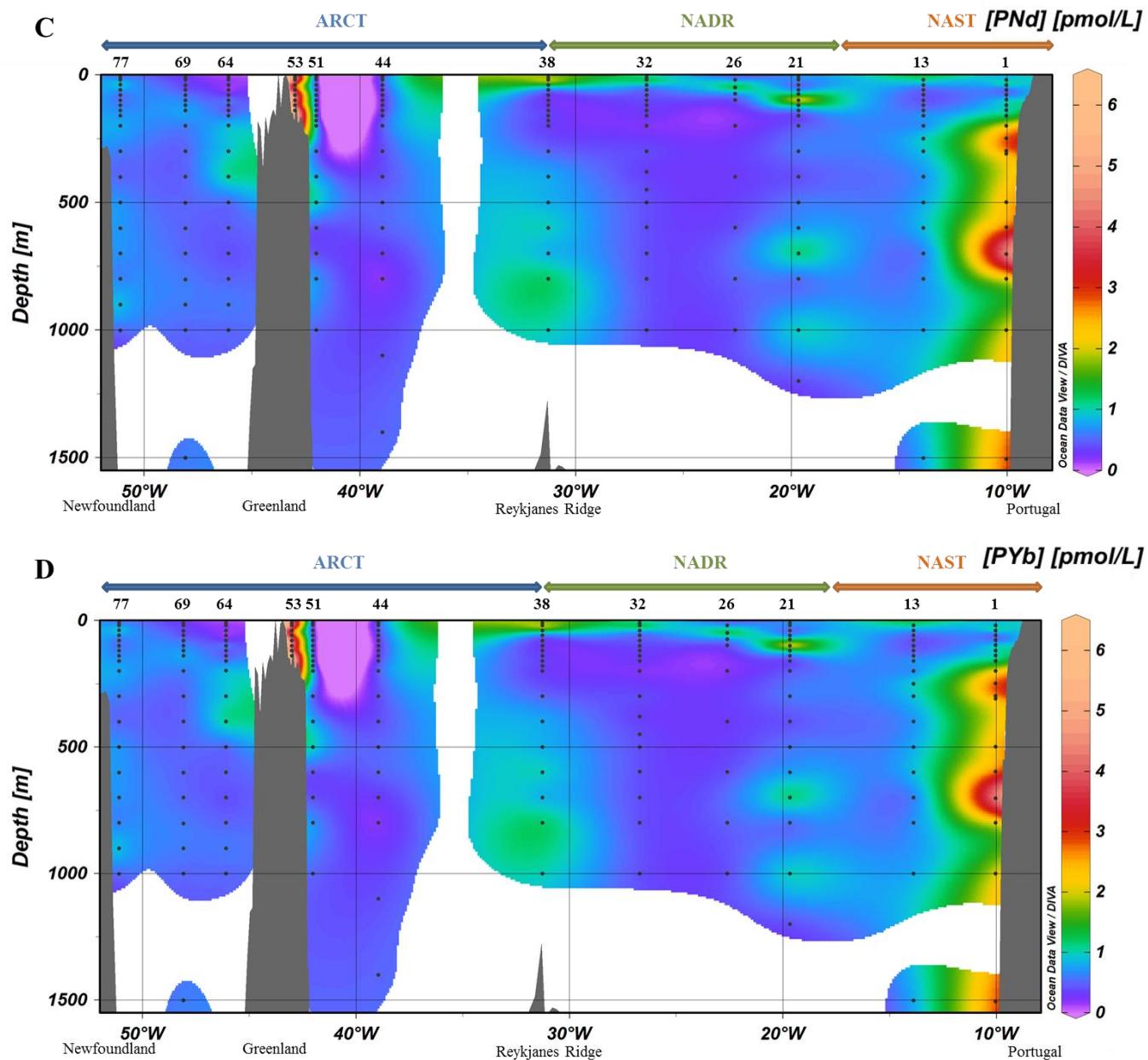
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ARCT NADR NAST





655 **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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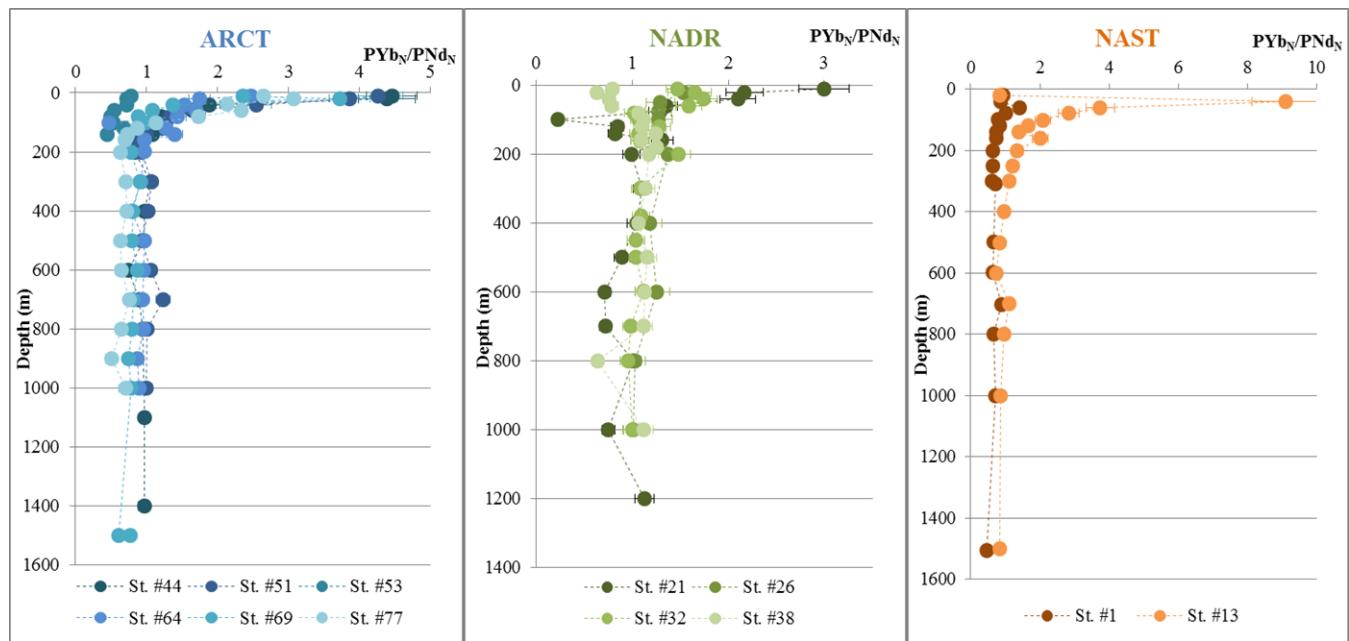
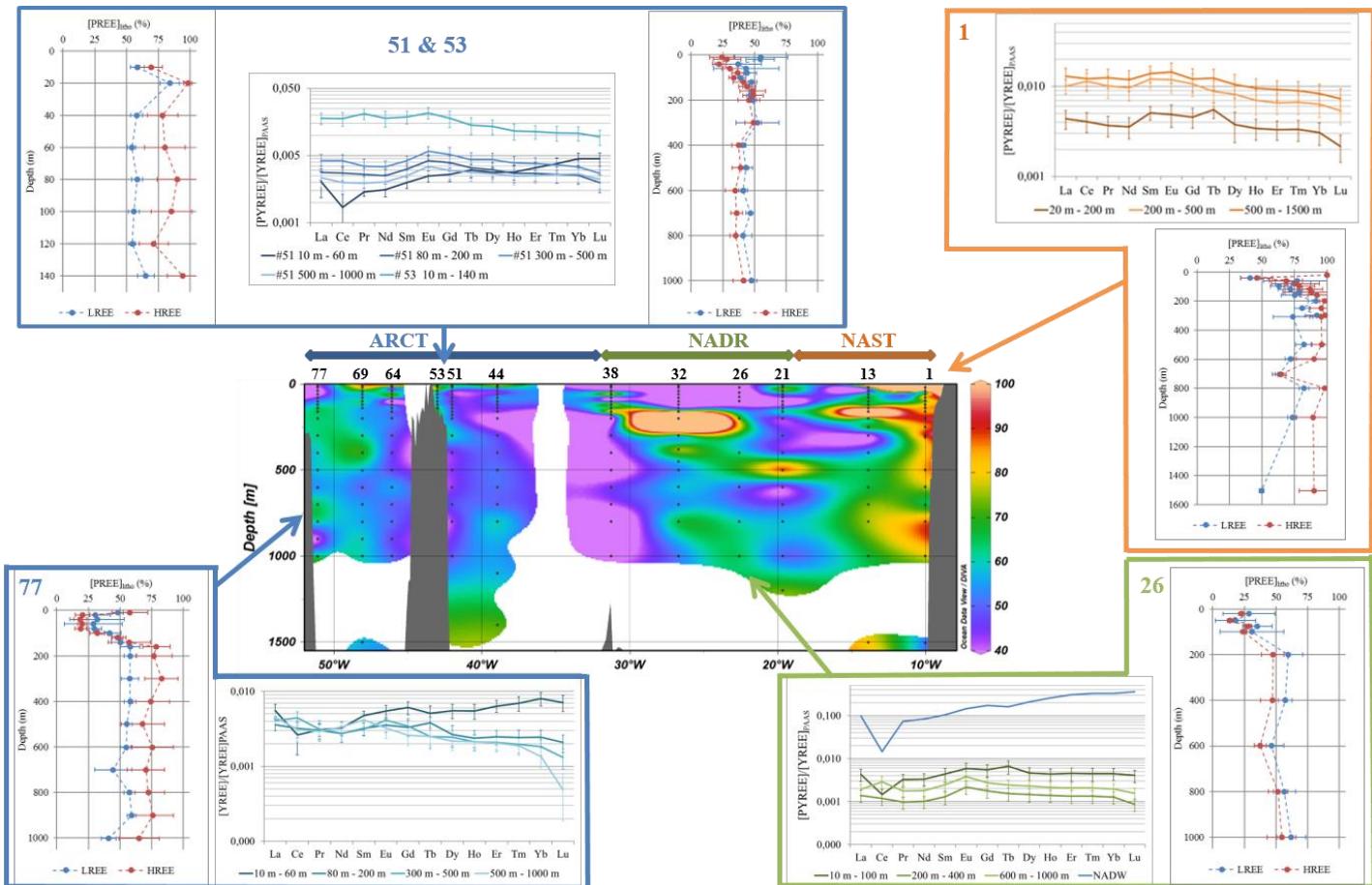
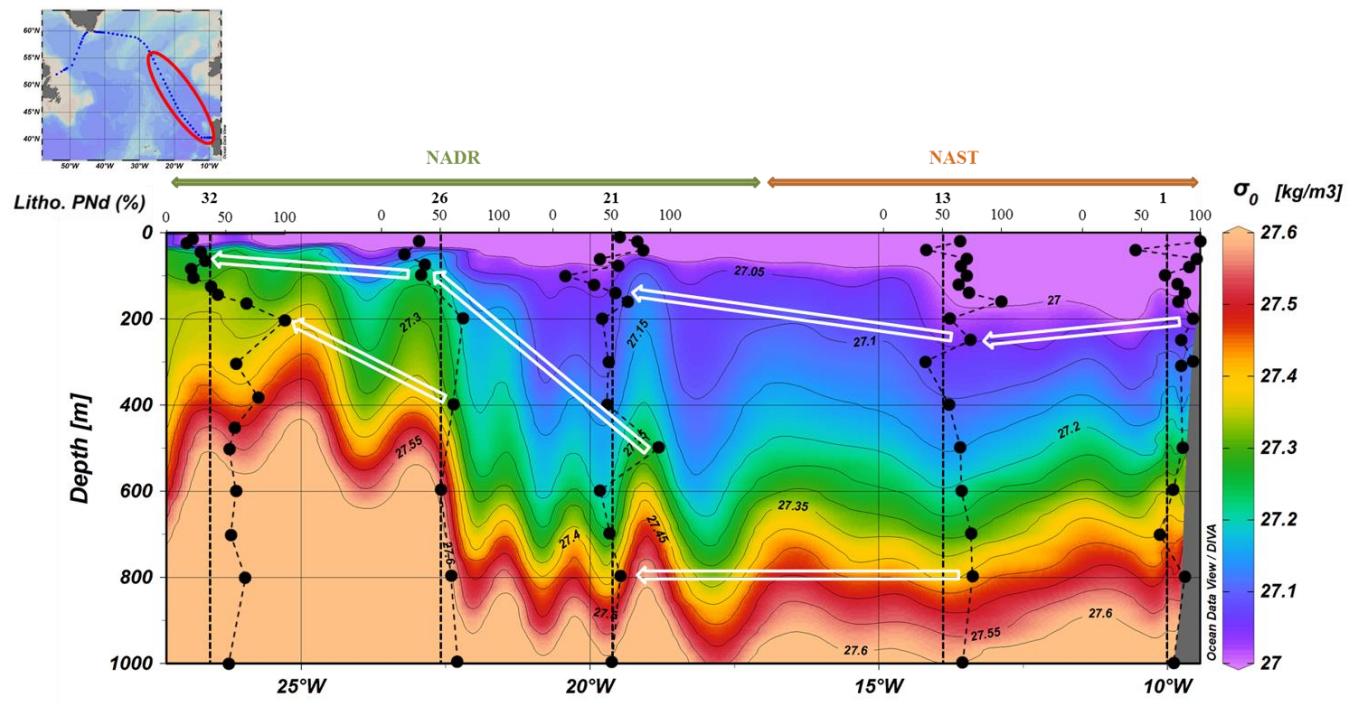


Figure 4: PYb/PNd ratio normalized to PAAS in each biogeochemical province

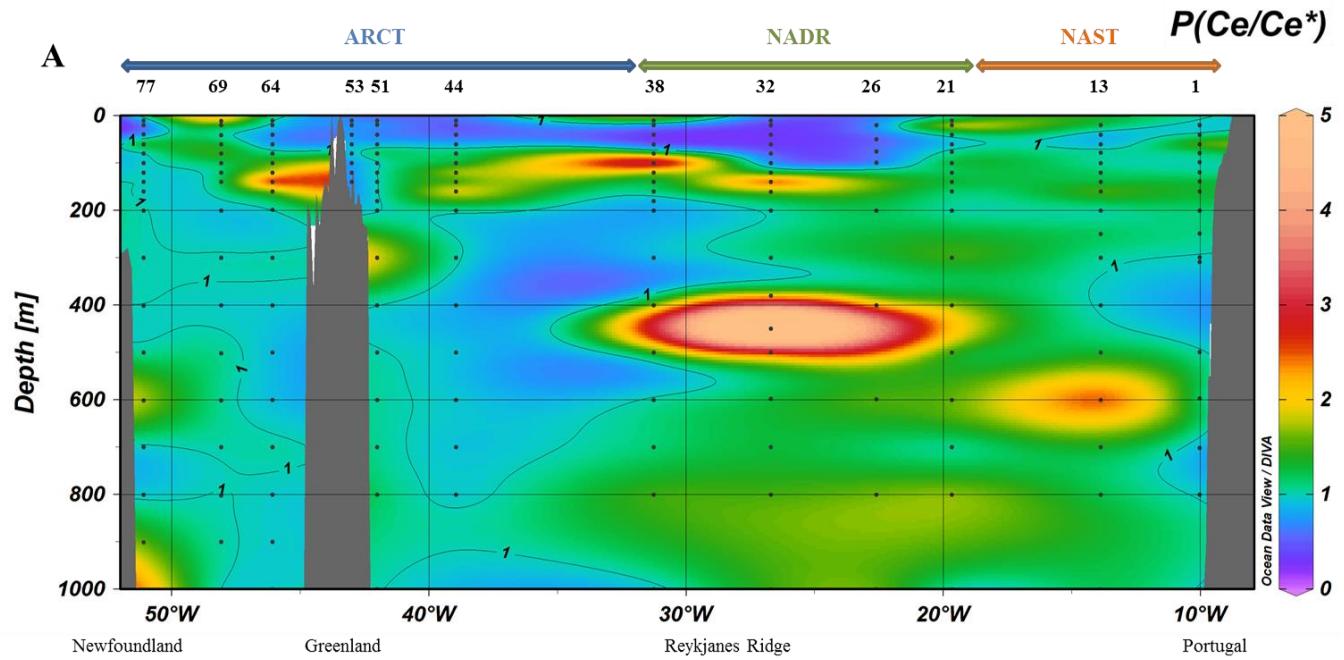


665 **Figure 5:** Center: proportion of lithogenic PNd along the GEOVIDE section (in %); Borders: vertical profiles of the lithogenic fraction of LREEs (except Ce, blue lines) and HREEs (red lines) and PAAS-normalized REE patterns of the total fraction, averaged by depth layers, at stations #1, #26,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



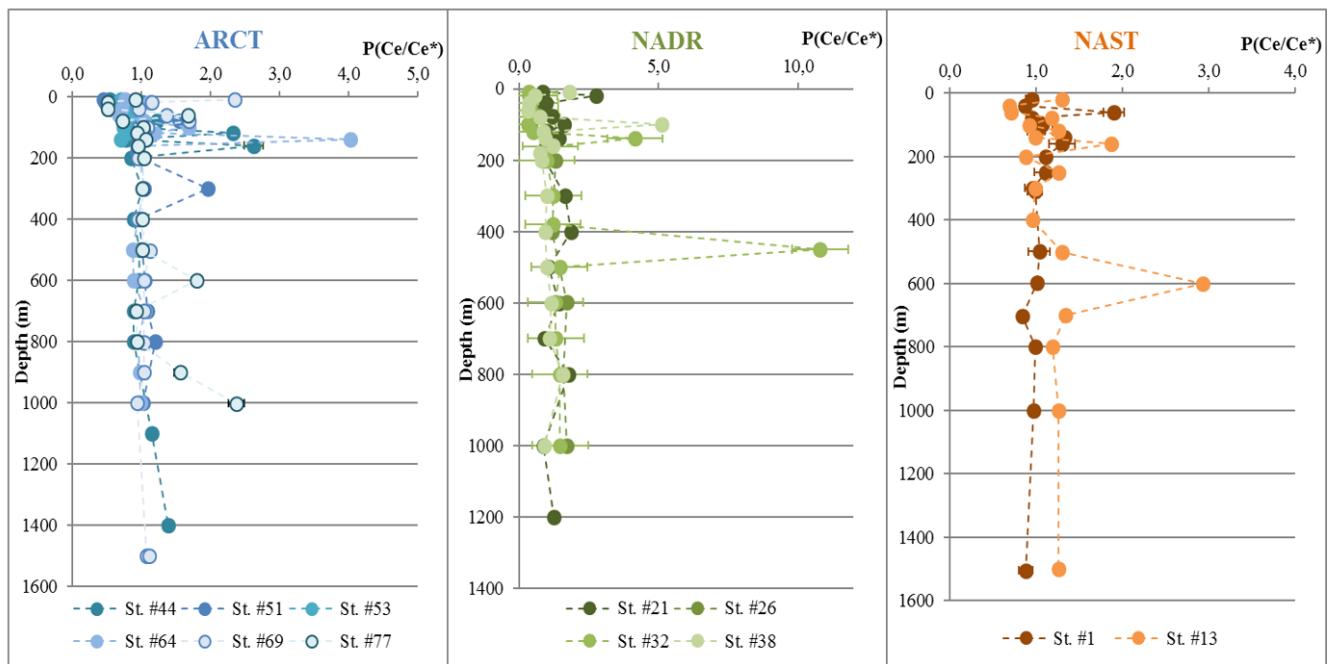
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Figure 6: Proportion of lithogenic PNd profiles superposed to density from station #1 to #32

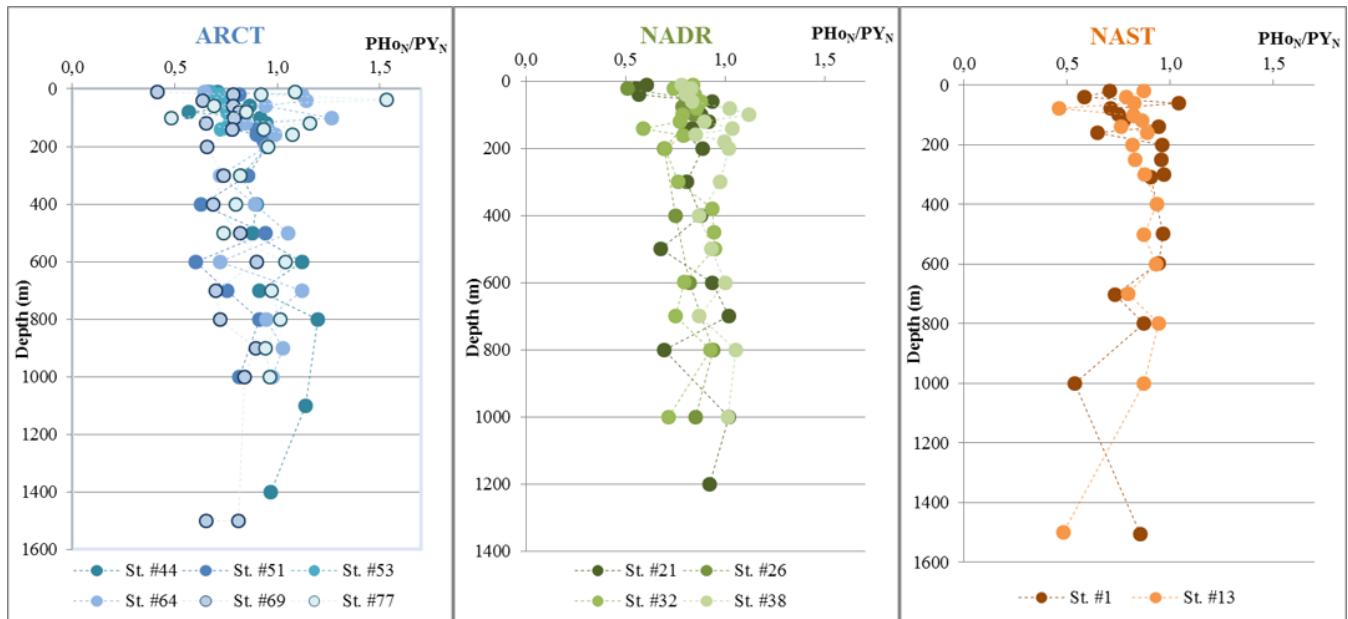




B



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.

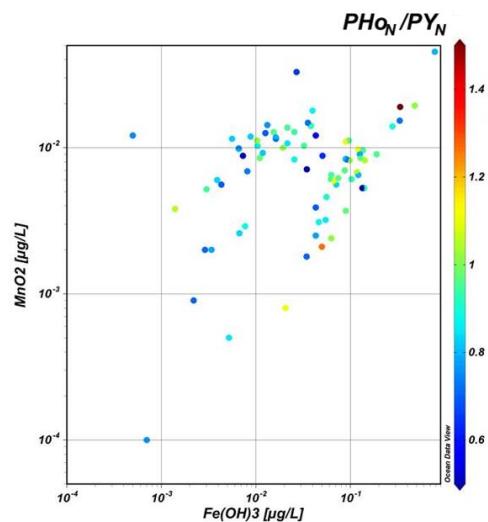


Figure 9: PAAS-normalized PHo/PY ratio as a function of Fe(OH)_3 and MnO_2 concentrations (in $\mu\text{g.L}^{-1}$).

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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. M.L. 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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