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Nolwenn Lemaitre, H el ene Planquette, Frank Dehairs, Fr ed eric Planchon,  
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Maxi Castrillejo

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## Particulate Trace Element Export in the North Atlantic (GEOTRACES GA01 Transect, GEOVIDE Cruise)

Lemaitre Nolwenn <sup>1,2,3,\*</sup>, Planquette Helene <sup>2</sup>, Dehairs Frank <sup>3</sup>, Planchon Frederic <sup>2</sup>,  
Sarhou Geraldine <sup>2</sup>, Gallinari Morgane <sup>2</sup>, Roig Stéphane <sup>2</sup>, Jeandel Catherine <sup>4</sup>, Castrillejo Maxi <sup>5</sup>

<sup>1</sup> Institute of Geochemistry and Petrology, ETH-Zurich, Clausiusstrasse 25, 8092 Zurich, Switzerland

<sup>2</sup> CNRS, Université de Brest, IRD, Ifremer, LEMAR, Technopôle Brest-Iroise, 29280 Plouzané, France

<sup>3</sup> Analytical, Environmental, and Geo-Chemistry, Vrije Universiteit Brussel, Pleinlaan, 1050 Brussels, Belgium

<sup>4</sup> LEGOS, Université de Toulouse (CNRS/CNES/IRD/UPS), Observatoire Midi Pyrénées, 31400 Toulouse, France

<sup>5</sup> Laboratory of Ion Beam Physics, ETH-Zurich, Otto Stern Weg 5, 8093 Zurich, Switzerland

\* Corresponding author : Nolwenn Lemaitre, email address : [nolwenn.lemaitre@erdw.ethz.ch](mailto:nolwenn.lemaitre@erdw.ethz.ch)

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### Abstract :

Vertical export of particulate trace elements (pTEs) is a critically underconstrained aspect of their biogeochemistry. Here, we combine elemental analyses on large (>53  $\mu\text{m}$ ) particles and  $^{234}\text{Th}$  measurements to determine downward export fluxes from the upper layers (40–110 m) of pTEs (Al, Cd, Co, Cu, Fe, Mn, Ni, P, Ti, V, Zn) and mineral phases (lithogenic, Fe- and Mn-oxides, calcium carbonate, and opal) in the North Atlantic along the GEOVIDE transect (Portugal–Greenland–Canada; GEOTRACES GA01 cruise). The role of lithogenic particles in controlling TE fluxes is obvious at proximity of the Iberian margin where the highest pTE export fluxes were estimated (up to 3912  $\mu\text{g}/\text{m}^2/\text{d}$  for pFe). However, high lithogenic and pTE fluxes are also observed up to 1700 km off this margin in the west European and Icelandic basins (up to 931  $\mu\text{g}/\text{m}^2/\text{d}$  for pFe). The lowest pTE export fluxes are determined in the Labrador Sea (as low as 501  $\mu\text{g}/\text{m}^2/\text{d}$  for pFe). High Mn- and Fe-oxide fluxes are estimated at the open ocean stations, suggesting that authigenic particles are an important vector of pTEs. All along the transect, biogenic particles also drive the pTE export fluxes, as shown by the similar pTE/POC ratios between exports and phytoplankton quotas. The shortest residence times (dissolved + particulate) are generally observed where lithogenic particles control the pTE fluxes (as low as 2 days for Fe) whereas pTEs seem to be longer retained when the contribution of biogenic particles become greater (residence times up to 147 days for Fe).

**Keywords :** particulate trace elements, export fluxes, multiple carrier phases, residence times, GEOTRACES

## 40 1. INTRODUCTION

41 Bioactive trace elements (TEs: Cd, Co, Cu, Fe, Mn, Ni, Zn, etc.) are important for the marine  
42 primary productivity<sup>1</sup>, as they are required for numerous metabolic processes<sup>2,3</sup>. Sometimes  
43 in line with other bioactive trace elements, depleted Fe concentrations in the surface waters can  
44 limit the phytoplankton, thus influencing the community structure and, as a result, the overall  
45 marine carbon cycle<sup>4,5</sup>. Therefore, the quantification of biogeochemical processes regulating  
46 the internal cycle of TEs is essential to better understand the carbon cycle and in particular the  
47 biological carbon pump<sup>6,7</sup>.

48 Many TEs reach the ocean through particles, either via atmospheric dusts<sup>8</sup>, rivers<sup>9</sup>, margins  
49<sup>10</sup> or sediments<sup>11</sup>. Marine particles also participate in the removal of TEs, either through  
50 scavenging onto particle surfaces<sup>12</sup>, precipitation of authigenic minerals such as barite<sup>13-15</sup>  
51 and Mn-Fe oxyhydroxides<sup>16</sup>, or sinking to the deep ocean due to lithogenic and biogenic ballast  
52 minerals<sup>17-19</sup>. Small (suspended; 1-53 $\mu$ m diameter) particles mainly trap TEs via scavenging,  
53 though they have been shown to slowly sink after coagulation to other particles<sup>20,21</sup>. Large  
54 (sinking; >53 $\mu$ m diameter) particles export TEs from the biologically active upper water  
55 column down to the interior ocean<sup>22</sup>, with the remineralization length scale controlling the  
56 release of TEs into solution and their subsequent return to the surface. Earlier studies have  
57 revealed that particulate phosphorous (pP), nickel (pNi), zinc (pZn) and organic carbon (POC)  
58 are remineralized faster than particulate iron (pFe) because of a stronger scavenging of  
59 dissolved Fe onto particles<sup>23,24</sup>. Thus, particle-solute interactions determine the residence times  
60 of TEs in the water column. However these residence times are presently not well known  
61 because of scarce estimates of TE inventories and fluxes into or out of the water column<sup>25</sup>.  
62 Despite an increasing number of studies addressing TE export, this process remains still poorly  
63 understood<sup>23,26,35,36,27-34</sup>. Besides the strong temporal and spatial variability, another reason  
64 likely resides in the difficulty in measuring particulate trace element (pTE) fluxes, as TEs are

65 present at very low concentrations in the ocean and are easily prone to contamination. Sediment  
66 traps are used to directly quantify the pTE export fluxes<sup>29,30,37,38</sup> but their deployment tends to  
67 be time- and effort-intensive. They also can be biased because of lateral advection or because  
68 of possible TE contamination from the preservative solution added into the cups to avoid  
69 zooplankton and microbial activities<sup>39</sup>. One alternative for determining particulate export  
70 fluxes is the clean but indirect <sup>234</sup>Th-<sup>238</sup>U method<sup>40-42</sup>. <sup>234</sup>Th is a highly particle-reactive  
71 element with a short half-life ( $t_{1/2} = 24.1$  days) compared to its radioactive parent <sup>238</sup>U ( $t_{1/2} =$   
72 4.47 billion years). While both isotopes are usually at secular equilibrium in subsurface waters,  
73 a deficit of <sup>234</sup>Th relative to <sup>238</sup>U can be observed in the upper ocean, where sinking particles  
74 carry <sup>234</sup>Th downward. This deficit of <sup>234</sup>Th relative to <sup>238</sup>U can be converted into an elemental  
75 export flux when multiplied with the ratio of the element to <sup>234</sup>Th (element:<sup>234</sup>Th hereafter) in  
76 the particulate material at a given depth<sup>34,41</sup>. This method has the benefit to allow flux  
77 determination at multiple stations and for a large suite of elements and mineral phases.

78 The presence of lithogenic and biogenic minerals, as well as oxyhydroxides, are identified as  
79 phases liable to control the settling of particles with depth<sup>19</sup>. In the temperate north Atlantic,  
80 advection of lithogenic material from continental margins and pronounced seasonal  
81 phytoplankton blooms strongly enhance the pTE distributions and downward export fluxes<sup>43-</sup>  
82 <sup>47</sup>. However, occasional lack of nutrients such as dissolved iron (dFe)<sup>48</sup> can limit the primary  
83 productivity, the magnitude of the downward fluxes and thus the strength of the biological  
84 carbon pump<sup>5,49,50</sup>. This is well illustrated in the subtropical north Atlantic, which is  
85 characterized by oligotrophic conditions leading to low primary production<sup>51</sup> and to low export  
86 fluxes of POC<sup>52,53</sup> and pTEs<sup>43</sup>. In this region, exports of POC<sup>54-58</sup> and pTEs<sup>28</sup> show episodic  
87 fluctuations along the season due to nutrient and/or light limitations but also due to lithogenic  
88 inputs mainly originating from margins or associated with atmospheric dust depositions  
89 <sup>28,43,44,59</sup>. The more productive subpolar Atlantic is characterized by lower lithogenic inputs

90 because of the decreasing influence of the Saharan dust plume<sup>43</sup>. Nevertheless, lateral supplies  
91 of lithogenic material from continental shelves have been reported and could enhance the  
92 export fluxes<sup>28,34</sup>.

93 In this study, we aim to better understand the processes controlling the TE distributions in the  
94 upper layers of the North Atlantic Ocean by focusing on particulate TE export. The different  
95 particulate substrates (authigenic, lithogenic and biogenic) liable to carry the pTEs are  
96 investigated and the export efficiencies are evaluated by estimating the residence times of TEs  
97 within the upper ocean.

98

## 99 **2. METHODS**

### 100 2.1. Biogeochemical characteristics of investigated stations

101 Fieldwork was conducted on board the French *R/V Pourquoi Pas?* along the GEOTRACES  
102 GA01 section during the GEOVIDE expedition (Fig. 1). The cruise was carried out in May-  
103 June 2014. We sampled a total of 11 stations located in five different biogeochemical domains  
104 described in details in Lemaitre et al. (2018)<sup>60</sup> and in Table 1. Briefly, the Iberian basin was  
105 sampled after the spring bloom and was characterized by a low primary productivity (PP)<sup>61</sup>.  
106 Station #13 had the highest proportion of cyanobacteria (12% of phytoplankton abundance) of  
107 the all transect<sup>62</sup>. Particulate organic carbon (POC) export was high at Station #1 while low at  
108 Station #13, reflecting the low nutrient availability in subtropical waters<sup>60</sup>. The west European  
109 (Stations #21 and #26) and Icelandic (Stations #32 and #38) basins were sampled during the  
110 bloom development and were the most productive areas with the highest PP observed along  
111 the transect<sup>60</sup>. Diatoms dominated the phytoplankton community (41% of phytoplankton  
112 abundance) but dinoflagellates and haptophytes (including coccolitophorids) also contributed  
113 significantly in the west European basin (~20% of phytoplankton abundance<sup>62</sup>). Conversely,  
114 nano-phytoplankton and mainly haptophytes dominated the community in the Icelandic basin.

115 High POC exports were determined in both basins and particularly at Station #32<sup>60</sup>. The  
116 Irminger basin (Stations #44 and #51) was sampled close to the bloom maximum and PP values  
117 were high, with a clear dominance of diatoms (between 55 and 77% of phytoplankton  
118 abundance<sup>62</sup>). Because of the accumulation of biomass in the surface waters, POC export  
119 fluxes were low, with Station #44 having the lowest one of the entire cruise<sup>60</sup>. The Labrador  
120 basin (Stations #64, #69 and #77) was sampled after the PP peak, at the onset of the bloom  
121 decline<sup>60</sup>. Productivity was relatively low compared to the other studied basins. Diatoms were  
122 also dominating, contributing up to 62% of the phytoplankton abundance<sup>62</sup>. POC export fluxes  
123 were relatively high, likely because of the increasing number of rapidly sinking particles<sup>60</sup>.

124

## 125 2.2. Particle sampling

126 Total <sup>234</sup>Th activities were determined from 4L unfiltered seawater sampled with 12L Niskin  
127 bottles mounted on CTD rosette and were processed following the method of Pike et al. (2005)  
128<sup>63</sup>. Samples were acidified and spiked with a <sup>230</sup>Th yield monitor in order to estimate the <sup>234</sup>Th  
129 recovery during sample processing. After a 12h equilibration, pH was increased and KMnO<sub>4</sub>  
130 and MnCl<sub>2</sub> solutions were added. After a further 12h equilibration, samples were filtered on  
131 quartz-microfiber discs (QMA, Sartorius, nominal porosity=1 μm, diameter=25 mm) and the  
132 <sup>234</sup>Th activities were measured on-board using a low-level beta counter (RISØ®, Denmark).  
133 Residual beta activities were measured ~6 months after the cruise after which samples were  
134 processed for Th recoveries using <sup>229</sup>Th as a second yield tracer. Export fluxes of <sup>234</sup>Th were  
135 then calculated using a 1-D box model<sup>64</sup> under steady state assumptions and neglecting  
136 advection and diffusion<sup>41</sup>. Export fluxes of <sup>234</sup>Th are presented in Lemaitre et al (2018)<sup>60</sup>.

137 Particulate matter for biogenic silica (BSi), calcium carbonate (CaCO<sub>3</sub>) and pTE analyses was  
138 collected on the same *in-situ* pump (Challenger Oceanics® and McLane® pumps, ISP) filter,  
139 whereas particles for POC were collected using a separate filter holder. The later was mounted  
140 either on a second flow path when modified McLane ISP heads were used, or with a separate

141 ISP unit <sup>60</sup> attached 10 to 50 m apart from the ISP dedicated to TEs (see Table S1). Particulate  
142 <sup>234</sup>Th activity in the large size particle fraction (LSF, >53µm) was determined on particles  
143 collected with each ISP system (Fig. S1).

144 Particulate organic carbon (POC) LSF was collected on a 53-µm mesh polyester screen (Petex),  
145 which was cut into quarters. Particles present on one quarter of the Petex screen were rinsed-  
146 off using 0.45 µm filtered seawater obtained during the cruise and subsequently collected on a  
147 silver filter (SterliTech, nominal porosity=0.45 µm, diameter=25 mm) for one quarter, and on  
148 a GF/F filter (Whatman, nominal porosity=0.7 µm, diameter=25 mm) for another quarter,  
149 before being Beta-counted on board. Back in the home laboratory, samples were prepared for  
150 POC analyses: filters were fumed with HCl vapor, dried, packed in pre-combusted silver cups  
151 and analysed with an elemental analyser (EA-IRMS, Delta V Plus, Thermo Scientific). More  
152 details on POC and particulate <sup>234</sup>Th (p<sup>234</sup>Th) analyses can be found in Lemaitre et al. (2018)  
153 <sup>60</sup>.

154 Particulate matter for BSi, CaCO<sub>3</sub> and pTE determinations was filtered on a 142mm-diameter  
155 53-µm mesh polyester screen (Petex) for the LSF upstream of a 142mm-diameter 0.8-µm  
156 polyethersulfone filter (Supor®) for the small size particle fraction (SSF). Before use, filters  
157 were soaked in 1.2M HCl (Suprapur grade, Merck), heated overnight at 60°C and subsequently  
158 rinsed with Milli-Q grade water. On board, filters were processed under a laminar flow unit  
159 within a customized clean “bubble” to prevent contamination. Before and after the ISP  
160 recoveries, pump heads were protected with plastic bags to minimize contamination. After  
161 pump recoveries, filter heads were dismantled and carried inside the clean bubble.

162 Using a clean ceramic scalpel, one quarter of the Petex screen, dedicated to p<sup>234</sup>Th and BSi  
163 analyses, was cut out. Particles were washed off the Petex screen using 0.45-µm filtered  
164 seawater obtained during the cruise. Particles were then collected on polycarbonate filters (PC;  
165 Nuclepore®, porosity=0.4µm, diameter=25mm) mounted on a polysulfone filtration unit.

166 Filters were left to dry at room temperature inside the laminar flow unit and subsequently  
167 prepared for Beta counting. Activities of  $p^{234}\text{Th}$  were also determined on a second quarter of  
168 the Petex screen: particles were washed off, using the 0.45- $\mu\text{m}$  filtered seawater, and collected  
169 on a polyethersulfone filter (Supor®, porosity=0.45  $\mu\text{m}$ , diameter=25 mm) mounted on a  
170 Nalgene filtration unit (Fig. S1). Because Beta counting of samples is probably incompatible  
171 with trace metal clean stringent conditions, the two last quarters of the Petex screen, dedicated  
172 to pTEs, particulate calcium (pCa) and sodium (pNa), were stored in a clean petrislide (Pall  
173 Gelman) and kept at  $-20^{\circ}\text{C}$  until sample processing and analysis in the home laboratory. Since  
174 Supor filters with the SSF were not Beta counted, there are no data for the SSF  $p^{234}\text{Th}$  activity.

175

### 176 2.3. Particulate matter analyses

177 The methods used here have been approved during a GEOTRACES intercalibration exercise  
178 and our elemental concentrations have been submitted to the GEOTRACES Intermediate Data  
179 Product (IDP) 2021. The concentrations obtained from ISP sampling (this study) have been  
180 compared to those obtained by GO-FLO sampling at the same locations (from Gourain et al.,  
181 2019<sup>65</sup> and from Planquette et al., personal communication, 2019). Both datasets were obtained  
182 after using exactly the same digestion and analytical methods. Although similar element  
183 profiles were obtained from both datasets, highlighting data consistency, we note that pTE  
184 concentrations obtained from ISP sampling were generally lower than those obtained from GO-  
185 FLO bottles. This discrepancy could possibly result from particle washout during ISP recovery,  
186 since our ISPs were not systematically equipped with anti-washout systems, or due to some  
187 loss when transferring particles from the Petex screens to other filters (see above). To limit  
188 these effects, our study focuses on elemental ratios and on element: $^{234}\text{Th}$  ratios, rather than on  
189 concentrations or activities.



190 2.3.1. Trace and major elements

191 In the home laboratory the two remaining quarters of Petex screen saved for pTEs, pCa and  
192 pNa analyses were washed off with 0.45- $\mu\text{m}$  filtered, low TE surface seawater collected during  
193 the GEOVIDE cruise (Station #77, 40m, filtered through a Supor filter, 0.45 $\mu\text{m}$ ) and  
194 subsequently collected on acid cleaned 47-mm diameter mixed cellulose esters filters (MF-  
195 Millipore® filters, 0.8 $\mu\text{m}$ ), using Nalgene® filtration units (Fig. S1). Then, filters were  
196 processed following the protocol of Planquette and Sherrell (2012)<sup>66</sup>. Briefly, one half of the  
197 MF filter was kept in a clean petrislide while the other half was placed along the wall of an  
198 acid cleaned Teflon vial (Savillex®) and digested with a HNO<sub>3</sub> 8 M - HF 2.3 M mix solution  
199 (Ultrapur and Suprapur grades, respectively, Merck®), refluxing at 130°C during 4h. After  
200 gentle evaporation close to near dryness, 200  $\mu\text{L}$  of concentrated HNO<sub>3</sub> (Ultrapur grade,  
201 Merck) was added in order to drive off the fluorides. The residue was brought back into solution  
202 with 0.32M HNO<sub>3</sub> spiked with 1  $\mu\text{g/L}$  of indium and stored in acid cleaned centrifuge tubes  
203 (Corning®). Measurements of pTEs were performed using a sector field inductively coupled  
204 mass spectrometer (SF-ICP-MS, Element 2, Thermo). External calibration curves were run at  
205 the start, middle and end of the sequence. The precision and accuracy of our measurements  
206 were assessed by analysing the certified reference material (CRM) BCR-414. Recoveries were  
207 typically within 10% of the certified values and the precision, given by the relative standard  
208 deviation of the five CRM analyses, was between 0.2 and 24% depending on the element (Table  
209 2). Gourain et al. (2019) analysed two other CRM (PACS-3 and MESS-4) by using the exact  
210 same analytical method and found similar accuracy and precision results<sup>65</sup>. The reproducibility  
211 of our analyses was assessed by analytical replicates of 17 samples and differences between  
212 replicates were less than 6% from the mean value.

213 Aluminium (Al) is usually used as a tracer of lithogenic particles because of its high crustal  
214 abundance (Upper Continental Crust or UCC Al = 8.04% by weight<sup>67</sup>) and its stable

215 concentrations among lithogenic sources. However, Al has been shown to be removed from  
216 the surface waters via scavenging onto particles, especially diatom cells <sup>68</sup>. During GEOVIDE,  
217 scavenging onto sinking opal-containing particles was defined as a sink for Al, especially in  
218 the Irminger and Labrador basins where diatoms dominate the phytoplankton community <sup>69</sup>.  
219 Removal of aluminium via other types of particles (i.e. carbonates, lithogenics, organics, fecal  
220 pellets) was not observed in this study, although it cannot be excluded <sup>69</sup>. Using Al as a  
221 lithogenic tracer can thus be questioned, especially for the Irminger and Labrador basins.  
222 Another lithogenic tracer that can be used is titanium (Ti) but it is less abundant in the UCC  
223 (UCC Ti=0.3% <sup>67</sup>) and its concentrations strongly vary between geological materials. We thus  
224 calculated the lithogenic mass (litho) using both tracers:

$$225 \quad \text{Litho } (\mu\text{g/L}) = (p\text{Al} \times 27 \times 10^{-6}) / 0.0804 \quad (1)$$

$$226 \quad \text{or Litho } (\mu\text{g/L}) = (p\text{Ti} \times 47.9 \times 10^{-6}) / 0.003 \quad (2)$$

227 where *pAl* and *pTi* are the particulate Al and Ti concentrations in pmol/L; *0.0804* and *0.003* are  
228 the mass fractions of Al and Ti in the UCC; and *27* and *47.9* are the molar masses of Al and Ti  
229 in g/mol, respectively.

230 The GEOVIDE transect, and the north Atlantic in general, is characterized by multiple  
231 lithogenic sources (atmospheric, sediment or continental inputs) with different geological  
232 characteristics. For example, basaltic rocks present close to Iceland and Greenland have a  
233 different Ti concentration than gabbro from the Iberian margin, potentially leading to wrong  
234 lithogenic estimations. The flux estimates of MnO<sub>2</sub>, Fe(OH)<sub>3</sub> and CaCO<sub>3</sub> are lower, if not  
235 negative, when Ti is used to correct the lithogenic fraction (Fig. S2). We believe that Ti  
236 significantly overestimates the lithogenic fraction when its contribution is low (i.e. at all  
237 stations except close to the Iberian margin). In the following, we therefore use Al-calculated  
238 fluxes, yet keeping in mind that our mineral fluxes might be overestimated, especially in  
239 diatom-rich areas like the Irminger and Labrador basins.

240 Oxyhydroxides of Fe and Mn were calculated by subtracting Fe and Mn associated with  
 241 lithogenic and biogenic materials from total Fe and Mn. Assuming that Fe oxyhydroxides are  
 242 ferrihydrite (Fe(OH)<sub>3</sub> or Fe-oxides hereafter) and Mn oxyhydroxides are birnessite (MnO<sub>2</sub> or  
 243 Mn-oxides hereafter), with formula weights 106.9 g Fe(OH)<sub>3</sub>/mol Fe and 86.9 g MnO<sub>2</sub>/mol Mn  
 244 <sup>70</sup>, it is possible to calculate:

$$245 \quad \text{Fe(OH)}_3 \text{ (}\mu\text{g/L)} = [\text{pFe} - (\text{pAl} \times 0.21) - (\text{POC} \times 0.042)] \times 106.9 \times 10^{-3} \quad (3)$$

$$246 \quad \text{MnO}_2 \text{ (}\mu\text{g/L)} = [\text{pMn} - (\text{pAl} \times 0.00367) - (\text{POC} \times 0.003)] \times 86.9 \times 10^{-3} \quad (4)$$

247 where *pFe*, *pAl* and *pMn* are the total particulate concentrations in nmol/L; POC is the  
 248 particulate organic carbon concentration in  $\mu\text{mol/L}$ ; 0.21 and 0.00367 are respectively the UCC  
 249 *pFe:pAl* and *pMn:pAl* ratios in mol/mol <sup>67</sup>; 0.042 and 0.003 are respectively the average Fe:C  
 250 and Mn:C quota of bulk phytoplankton in nmol/ $\mu\text{mol}$  in the North Atlantic (Table 5 in Twining  
 251 et al., 2015 <sup>71</sup>).

252 Analyses of *pCa* and *pNa* were made using an inductively coupled plasma atomic emission  
 253 spectrometer (ICP-AES, ULTIMA 2, Horiba Jobin Yvon). As for *pTEs*, the accuracy and  
 254 precision were assessed by analysing the CRM BCR-414 (Table 2). Recovery for *pCa* reached  
 255 80%, keeping in mind that only an indicative value for the CRM reference is available.  
 256 Replicate analyses were made for 6 samples and differences from the mean value averaged 1.3  
 257 and 1.2% for *pCa* and *pNa*, respectively. As a mineral forming the shells of coccolithophorids,  
 258 pteropods or foraminifers, we estimate the calcium carbonate (CaCO<sub>3</sub>) concentrations by  
 259 correcting for sea-salt and lithogenic Ca:

$$260 \quad [\text{Ca}]_{\text{CaCO}_3} \text{ (}\mu\text{g/L)} = [\text{pCa} - (\text{Ca:Na})_{\text{sw}} \times \text{pNa} - (\text{Ca:Al})_{\text{UCC}} \times \text{pAl}] \times 100.1 \quad (5)$$

261 where *pCa*, *pNa* and *pAl* are respectively the total particulate calcium, sodium, and aluminium  
 262 concentrations in  $\mu\text{mol/L}$ ; (*Ca:Na*)<sub>sw</sub> is equal to 0.022 mol/mol and represents the mean

263 seawater ratio <sup>72</sup>;  $(Ca:Al)_{UCC}$  is equal to 0.251 mol/mol and represents the mean UCC ratio <sup>67</sup>;  
264  $100.1$  is the molar mass of  $CaCO_3$  in g/mol.

265

### 266 2.3.2. Biogenic silica and opal

267 Following the method of Ragueneau et al. (2005), BSi concentrations were estimated using an  
268 alkaline digestion with correction of the lithogenic silica (LSi) <sup>73</sup>. A 25mm diameter Nuclepore  
269 filter (carrying the LSF) previously counted for Beta activity was inserted in a  
270 polymethylpentene centrifuge tube and digested with a 0.2 M NaOH solution (Merck) at 95°C  
271 for 1h. After cooling, the pH was neutralized by adding 1 M HCl (Analar Normapur, Merck)  
272 and the supernatant was separated from the remaining suspended material by centrifugation.  
273 Silicic acid concentrations were determined following an automated acid/molybdate  
274 colorimetric method <sup>74</sup>, using an AutoAnalyzer3 Bran&Luebbe®. Dissolved aluminium  
275 released during the digestion process was determined by fluorimetric analysis of an Aluminium-  
276 Lumogallion complex (fluorimeter MITHRAS LB 940) <sup>75</sup>. At the end of the digestion, all the  
277 BSi is converted into silicic acid, but some lithogenic Si may have dissolved as well, inducing  
278 a bias in the BSi concentration. This bias was resolved by applying a second digestion, similar  
279 to the first one, allowing the determination of a Si:Al ratio exclusively related to the lithogenic  
280 material present in the samples. As a mineral forming the shells of diatoms, sponges or  
281 radiolarians, we estimate the mass of opal assuming a hydrated form of silica:  $SiO_2 \cdot (0.4 H_2O)$   
282 <sup>76</sup>, or 67.2 g opal/mol BSi:

$$283 \quad \text{Opal } (\mu\text{g/L}) = ([Si_1] - [Al_1] \times (Si:Al)_2) \times 67.2 \quad (6)$$

284 where  $[Si_1]$  and  $[Al_1]$  are the concentrations of silicic acid and aluminium determined during  
285 the first digestion in  $\mu\text{mol/L}$ ;  $(Si:Al)_2$  is the ratio of the concentrations of silicic acid and  
286 aluminium determined during the second digestion; and 67.2 is the molar mass of opal in g/mol.

287

#### 288 2.4. Component:<sup>234</sup>Th ratios and export fluxes

289 Trace element and mineral (lithogenics, Fe- and Mn-oxides, CaCO<sub>3</sub>, opal) export fluxes were  
290 determined using the <sup>234</sup>Th-based approach by multiplying the TE:<sup>234</sup>Th or mineral:<sup>234</sup>Th ratio  
291 of sinking particles with the total <sup>234</sup>Th export flux<sup>60</sup>, both determined at the same depth:

$$292 \quad \text{Component export flux} = (\text{component}:\text{}^{234}\text{Th})_{\text{particulate}} \times \text{}^{234}\text{Th flux} \quad (7)$$

293 with *component* being either a TE or a mineral phase.

294 As we do not have p<sup>234</sup>Th activities available for the SSF, we only consider the  
295 component:<sup>234</sup>Th ratios from the LSF in this study. Large particles (>53μm) are generally  
296 assumed to represent the sinking particulate matter and are thus responsible for the particulate  
297 export flux<sup>77-79</sup>. Using the component:<sup>234</sup>Th ratios from the LSF to calculate export fluxes is  
298 the most common approach<sup>36,80-83</sup>. However, recent studies have shown that the SSF could  
299 also contribute to the export flux of particulate carbon or nitrogen in oligotrophic regions<sup>20,21,84</sup>.  
300 Black et al. (2019) reported no significant differences in SSF and LSF pP:<sup>234</sup>Th, pCo:<sup>234</sup>Th and  
301 pCd:<sup>234</sup>Th ratios contrasting with the higher pMn:<sup>234</sup>Th ratios in the LSF compared to the SSF,  
302 leading to a greater contribution of the LSF to the total pMn flux<sup>36</sup>.

303 Vertical export fluxes were determined at the depth where total <sup>234</sup>Th is back to secular  
304 equilibrium with <sup>238</sup>U (equilibrium depth or Eq hereafter; Table 3). The <sup>234</sup>Th export at Eq  
305 represents the fully-integrated depletion of total <sup>234</sup>Th in the upper waters<sup>60</sup>. To collect  
306 particles, three to four depths were sampled per ISP in the upper 150m while in that same depth  
307 range, Niskin casts sampled nine depths. Because of this difference of depth resolution we use  
308 an interpolation method to estimate the component:<sup>234</sup>Th ratios for the layer between surface  
309 and Eq. The depth-weighted average (DWA) was chosen as this method yields similar TE:<sup>234</sup>Th  
310 or mineral:<sup>234</sup>Th ratios than those obtained from sediment traps<sup>31</sup> (DWA;  
311  $\text{element}:\text{}^{234}\text{Th} = [\sum(\text{element}_i \times Z_i) / \sum(Z_i)] / [\sum(\text{}^{234}\text{Th}_i \times Z_i) / \sum(Z_i)]$  where  $Z_i$  are the depth intervals

312 sampled above Eq). Uncertainties of ratios and fluxes were obtained using error propagation  
313 law.

314

## 315 2.5. Residence times

316 We also investigated the total residence time ( $\tau$ ) of TEs, which was obtained by dividing the  
317 TE inventory within a specific reservoir by the TE flux into or out of this reservoir, thereby  
318 assuming steady state with removal rates equalling supply rates (Equation 8). We focused on  
319 total (dissolved+particulate) residence time ( $\tau_{\text{total}}$ ) within the surface-Eq layer depth (Table 5)  
320 and we considered the particulate export flux as the main output flux of TE from the upper  
321 ocean. Advective and diffusive circulation fluxes are generally slow processes compared to the  
322 vertical export processes and were neglected here <sup>25,35</sup>. However these processes have been  
323 shown to have impact, though limited, on measured <sup>234</sup>Th export fluxes along the GEOVIDE  
324 transect <sup>60</sup>, and therefore  $\tau_{\text{total}}$  of TE might represent a higher end estimation in the present  
325 study.

$$326 \quad \tau = \frac{\text{total TE inventory}}{\text{particulate TE export flux}} \quad (8)$$

327 with the particulate TE export flux in  $\mu\text{g}/\text{m}^2/\text{d}$  at Eq (from this study), and the total TE  
328 inventory in  $\mu\text{g}/\text{m}^2$  obtained by summing the particulate ( $>0.45 \mu\text{m}$ ) and dissolved ( $<0.45 \mu\text{m}$ )  
329 TE phases, both being collected using GO-FLO bottles (Planquette et al., personal  
330 communication, 2019 and <sup>65,69,85</sup>). Inventories were calculated using a depth-weighted  
331 integration in the surface-Eq layer. Uncertainties in Table 5 represent the highest deviation  
332 between the residence time obtained at Eq and those obtained at Eq+20m or Eq-20m (20m  
333 being the average error on the determination of the Eq depth).

334

### 335 3. RESULTS

336 3.1. Activities of  $p^{234}\text{Th}$  and concentrations of TEs, lithogenic, authigenic and biogenic  
337 phases in the large size fraction ( $>53\mu\text{m}$ )

338 Distributions of  $p^{234}\text{Th}$  vary along the transect (Fig. S3, Table S1) with the lowest activities  
339 being determined in the Iberian basin (as low as 0.006 dpm/L in subsurface of Station #1) and  
340 the highest in surface waters of the Irminger basin (up to 0.2 dpm/L in surface of Station #51).  
341 In general, activities are high in surface and decrease with depth but some subsurface maxima  
342 also occur, such as at 100m of Station #64 where activities reach 0.16 dpm/L.

343 As shown in Figure S3 and Table S1,  $>53\mu\text{m}$  concentrations vary between elements, with  
344 values ranging from  $10^{-6}$  to  $10^1$  nmol/L in the suite of Cd, Co < Cu, Mn, Ni, Ti, Zn < Fe < Al,  
345 P. Similarly to  $p^{234}\text{Th}$  activities, concentrations and distributions also vary significantly for  
346 each pTE along the transect, like those of the lithogenic, authigenic and biogenic phases.

347 Concentrations of pAl or lithogenic material, like that of pFe and pTi, which are known to be  
348 associated with lithogenic material, generally increase with depth and are highest at proximity  
349 of the Iberian margin (Station #1) reaching up to 15 nmol/L, 5.2  $\mu\text{g/L}$ , 3.2 nmol/L and 0.2  
350 nmol/L at 550m respectively. Similarly, pMn and pZn show maximal concentrations over the  
351 transect at 550m at Station #1 (0.05 and 0.9 nmol/L, respectively) though high concentrations  
352 are also observed at 100m at Station #64 (0.03 and 0.07 nmol/L, respectively) like pCd, pCu,  
353 pNi and pV (7.1 pmol/L, 0.04, 0.02 and 0.05 nmol/L, respectively; Table S1). Lithogenic  
354 material is also strongly enriched at 100m at Station #64 and 200m at Station #77 ( $> 0.8 \mu\text{g/L}$ ).  
355 Except for these stations located closer to margins, concentrations of lithogenic material are  
356 low, averaging 0.2  $\mu\text{g/L}$ .

357 Particulate Cd, Co and P are characterized by biogenic distributions, with higher concentrations  
358 in surface waters, especially in the productive west European basin (Stations #21 and #26).

359 Other pTEs are characterized by high surface concentrations such as pV and pZn in the

360 Irminger and Labrador basins or pCd, pCu, pFe pNi and pZn in the west European and Icelandic  
361 basins. These coincide with elevated concentrations of both opal and CaCO<sub>3</sub> in the upper 100m,  
362 where they are produced: highest CaCO<sub>3</sub> concentrations mainly occur within the west European  
363 and Icelandic basins (up to 14 µg/L) whereas highest opal concentrations occur within the west  
364 European, Irminger and Labrador basins (up to 95 µg/L). In general, both biogenic phases  
365 display nutrient-like profiles with highest concentrations in surface waters, but deeper CaCO<sub>3</sub>  
366 maxima occur at Station #32 at 100m, Station #38 at 60m and Station #64 at 100m while deeper  
367 opal maxima occur at Stations #38 and #64 at 100m.

368 Slight increase of pFe, pMn, pCd, pCo, pCu, pNi and pZn concentrations are observed in  
369 subsurface, such as at 60m and 100m at Station #64, in the upper 200m at Stations #32 and #38  
370 and below 100m at Station #26. Iron and manganese oxide contents follow similar trends. Both  
371 authigenic minerals are obtained after correction of the contribution of lithogenic and biogenic  
372 fractions, and therefore show low concentrations along the section, with exceptions at the  
373 depths cited just above. At 60m at Station #64, Fe(OH)<sub>3</sub> and MnO<sub>2</sub> concentrations reach 0.16  
374 and 0.003 µg/L respectively, but are also relatively high at 100m, coinciding with elevated  
375 lithogenic contents (0.05 and 0.002 µg/L respectively). High Fe(OH)<sub>3</sub> concentrations are also  
376 observed in the upper 200m of the Icelandic basin (from 0.01 to 0.03 µg/L at Stations #32 and  
377 #38) while high MnO<sub>2</sub> concentrations are seen below 100m of Station #26 (up to 0.002 µg/L).

378 Overall, our >53µm pTE concentrations are comparable with those of the world ocean literature  
379 <sup>31,36,86</sup>. If we compare more closely to data from the GA03 cruise, which also took place in the  
380 North Atlantic (GEOTRACES IDP2017 <sup>87</sup>), our concentrations of pP are slightly higher,  
381 reaching 24 nmol/L during GEOVIDE (4.7 nmol/L during GA03), likely because of the higher  
382 productivity observed in the subpolar compared to the subtropical North Atlantic. On the other  
383 hand, both cruises have similar order of magnitudes in the whole water column for pCd (up to  
384 7.1 and 1.5 pmol/L for GEOVIDE and GA03, respectively), pCo (up to 1.5 and 8.3 pmol/L for



385 GEOVIDE and GA03, respectively), pCu (up to 36 and 28 pmol/L for GEOVIDE and GA03,  
386 respectively), pNi (up to 70 and 158 pmol/L for GEOVIDE and GA03, respectively) pV (up to  
387 92 and 87 pmol/L for GEOVIDE and GA03, respectively) and pZn (up to 0.9 and 0.3 nmol/L  
388 for GEOVIDE and GA03, respectively). However, concentrations during GEOVIDE of pAl  
389 (0.1-15 nmol/L), pFe (0.02-3.2 nmol/L) and pTi (0.004-0.2 nmol/L) are lower than those  
390 observed during GA03 (0.1-98, 0.04-25 and 0.004-3.6 nmol/L, respectively<sup>44</sup>). This might be  
391 due to the fact that both cruises took place at different latitudes, with the GA03 transect located  
392 in the dust rich region of the Atlantic.

393

### 394 3.2. Particulate TE:<sup>234</sup>Th and mineral:<sup>234</sup>Th ratios in the large size fraction (>53µm)

395 Magnitudes of ratios differ among elements (pCd:<sup>234</sup>Th, pCo:<sup>234</sup>Th < pCu:<sup>234</sup>Th, pNi:<sup>234</sup>Th,  
396 pV:<sup>234</sup>Th < pMn:<sup>234</sup>Th, pTi:<sup>234</sup>Th, pZn:<sup>234</sup>Th < pFe:<sup>234</sup>Th < pAl:<sup>234</sup>Th, pP:<sup>234</sup>Th) and vary  
397 between basins as described below. Profiles of pTE:<sup>234</sup>Th and mineral:<sup>234</sup>Th ratios in the >53  
398 µm fraction generally follow those observed for the concentrations (Fig. S4).

399 Ratios of pAl:<sup>234</sup>Th (1204 nmol/dpm) or lithogenic:<sup>234</sup>Th (404 µg/dpm) reach highest values at  
400 250m at Station #1. Similarly, highest pCo:<sup>234</sup>Th (0.08 nmol/dpm), pCu:<sup>234</sup>Th (0.4 nmol/dpm),  
401 pFe:<sup>234</sup>Th (245 nmol/dpm), pMn:<sup>234</sup>Th (4 nmol/dpm) and pTi:<sup>234</sup>Th (18 nmol/dpm) occur at  
402 250m at Station #1. Lithogenic:<sup>234</sup>Th ratios generally increase with depth but also show  
403 elevated values at the surface (15-30m) of Stations #1, #21 and #32.

404 High pP:<sup>234</sup>Th and pV:<sup>234</sup>Th ratios are observed in the upper 100m of the Irminger and Labrador  
405 basins (reaching 121 and 0.9 nmol/dpm, respectively), like high opal:<sup>234</sup>Th ratios (750 µg/dpm  
406 at 30m of Station #69). In the west European and Icelandic basins, ratios of pCd:<sup>234</sup>Th,  
407 pCo:<sup>234</sup>Th, pCu:<sup>234</sup>Th, pFe:<sup>234</sup>Th, pNi:<sup>234</sup>Th, pP:<sup>234</sup>Th and pZn:<sup>234</sup>Th increase towards the  
408 surface, similarly to CaCO<sub>3</sub>:<sup>234</sup>Th (reaching 271 µg/dpm at 109m at Station #38).

409 Some exceptions are observed at 60m at Station #64 and in the Icelandic basin, especially at  
410 200m at Station #32, where we determined high ratios of pCo:<sup>234</sup>Th (0.01 and 0.04 nmol/dpm  
411 at Stations #64 and #32, respectively), pCu:<sup>234</sup>Th (0.17 nmol/dpm at Station #32), pNi:<sup>234</sup>Th  
412 (0.14 and 1.04 nmol/dpm at Stations #64 and #32, respectively) and pZn:<sup>234</sup>Th (from 1.5 to 5.2  
413 nmol/dpm in the upper 60m of the Icelandic basin). These high values correspond to the highest  
414 Fe(OH)<sub>3</sub>:<sup>234</sup>Th ratios (6.5 µg/dpm at 60m at Station #64, and 1.04-2.25 µg/dpm in the upper  
415 200m at Station #32). The highest MnO<sub>2</sub>:<sup>234</sup>Th ratios are also observed at 60m at Station #64,  
416 and at 153m at Station #26, coinciding with a slight increase of the pZn:<sup>234</sup>Th ratio (1.2  
417 nmol/dpm).

418

### 419 3.3. Export fluxes

420 Export fluxes at Eq (between 40 and 110m) significantly vary between elements and between  
421 basins (Table 3, Fig. 2). The most striking results are the maximal flux of pAl or lithogenic  
422 material (9207 µg/m<sup>2</sup>/d and 115 mg/m<sup>2</sup>/d, respectively) and of some pTEs in vicinity of the  
423 Iberian margin (Station #1), with extreme values for pCo, pFe, pMn, pP and pTi (3.6, 3912,  
424 55, 8141 and 340 µg/m<sup>2</sup>/d, respectively). Such high fluxes evidence particulate inputs from the  
425 Iberian margin, leading to the export of pTE out of the surface layer.

426 The highest CaCO<sub>3</sub> export fluxes occur within the west European and Icelandic basins, where  
427 blooms of coccolithophorids were observed during GEOVIDE <sup>62</sup>. There, we also observe high  
428 fluxes of pCd, pCu, pNi or pP, which at Station #21 reach values of 11, 18, 84 and 4648  
429 µg/m<sup>2</sup>/d, respectively. Opal fluxes are the highest in the Irminger and Labrador basins, where  
430 diatom blooms were declining during GEOVIDE <sup>60</sup> (568 mg/m<sup>2</sup>/d at Station #64). Surprisingly,  
431 the settling of diatoms in these basins is characterized by low pTE export fluxes.

432 High Fe(OH)<sub>3</sub> export flux is observed in the Icelandic basin (Station 32) and in the western  
433 Labrador basin (Station #64). At Station #32, the high Fe(OH)<sub>3</sub> flux (1.3 mg/m<sup>2</sup>/d) goes with

434 high fluxes of pAl, pCd, pCo, pCu, pFe, pMn, pNi, pP, pV and pZn (469, 5.1, 2.7, 10, 931, 13,  
435 33, 4145, 1.7 and 396  $\mu\text{g}/\text{m}^2/\text{d}$ , respectively). Export fluxes of  $\text{MnO}_2$  are small compared to  
436 other mineral fluxes (0.007  $\text{mg}/\text{m}^2/\text{d}$  compared to 0.36  $\text{mg}/\text{m}^2/\text{d}$  for  $\text{Fe}(\text{OH})_3$  on average). In  
437 general, high fluxes of  $\text{MnO}_2$  and  $\text{Fe}(\text{OH})_3$  coincide but  $\text{MnO}_2$  fluxes are particularly high in  
438 the west European (Station #26) and Irminger (Station #44) basins where we can observe a  
439 slight increase of pCo, pMn and pV fluxes (reaching 0.4, 9.3 and 0.4  $\mu\text{g}/\text{m}^2/\text{d}$ , respectively, at  
440 Station #26).

441 Particulate TE export fluxes determined using the  $^{234}\text{Th}$  approach are still scarce in the  
442 literature. Comparing different biogeochemical areas is difficult because of differences in  
443 sampling periods (and different productivities), export depths (surface versus deep or Eq depth  
444 versus fixed depth) or locations (shelf versus open-ocean). However, the overall ranges of pTE  
445 export fluxes between GEOVIDE and the literature are comparable. The pFe export flux at  
446 proximity of the Iberian margin (3912  $\mu\text{g}/\text{m}^2/\text{d}$ ) is by far the highest observed along the  
447 GEOVIDE transect but is still lower than fluxes determined on the Scotian shelf (7874  $\mu\text{g}/\text{m}^2/\text{d}$   
448 <sup>88</sup>), or close to the Crozet island (8098  $\mu\text{g}/\text{m}^2/\text{d}$  <sup>32</sup>), where lithogenic inputs are even higher.  
449 Conversely, the lower pAl export fluxes in the Labrador Sea (67-281  $\mu\text{g}/\text{m}^2/\text{d}$  at GEOVIDE  
450 Stations #64, #69 and #77 and 432-594  $\mu\text{g}/\text{m}^2/\text{d}$  in 2005 <sup>34</sup>) indicate lower lithogenic inputs,  
451 which seem to drive lower pFe export fluxes (41-501  $\mu\text{g}/\text{m}^2/\text{d}$  at GEOVIDE Stations #64, #69  
452 and #77 and 480-614  $\mu\text{g}/\text{m}^2/\text{d}$  in 2005 <sup>34</sup>). Even though GEOVIDE took place during the spring  
453 bloom, export of pP (266-8141  $\mu\text{g}/\text{m}^2/\text{d}$ ) is lower than observed along the GP16 transect, from  
454 the Peruvian shelf to the subtropical Pacific gyre (254-27876  $\mu\text{g}/\text{m}^2/\text{d}$  <sup>36</sup>) likely due to high  
455 productivities and high biogenic exports induced by the coastal upwelling there. Similarly,  
456 particulate organic carbon (POC) export reaches 960  $\text{mg}/\text{m}^2/\text{d}$  during GP16 compared to 139  
457  $\text{mg}/\text{m}^2/\text{d}$  during GEOVIDE <sup>83</sup>. For that same Pacific ocean area, Black et al. (2019)<sup>36</sup> reports  
458 similar pCo fluxes (0.1-4  $\mu\text{g}/\text{m}^2/\text{d}$ ) but much higher pCd (0.2-112  $\mu\text{g}/\text{m}^2/\text{d}$ ) and pMn export

459 fluxes ( $6\text{-}549 \mu\text{g}/\text{m}^2/\text{d}$ ) compared to fluxes in the North Atlantic reaching up to  $4 \mu\text{g pCo}/\text{m}^2/\text{d}$ ,  
460  $11 \mu\text{g pCd}/\text{m}^2/\text{d}$ ,  $55 \mu\text{g pMn}/\text{m}^2/\text{d}$  for the present GEOVIDE section and  $3 \mu\text{g pCd}/\text{m}^2/\text{d}$  for the  
461 Scotian shelf area <sup>88</sup>. Finally, Smith et al. (2014) <sup>88</sup> reports similar pCu export fluxes for the  
462 Scotian shelf ( $1\text{-}22 \mu\text{g}/\text{m}^2/\text{d}$ ) compared to those observed for the GEOVIDE transect ( $1\text{-}16$   
463  $\mu\text{g}/\text{m}^2/\text{d}$ ).

464

#### 465 3.4. Residence times

466 Along the GEOVIDE transect, TE inventories and exports, and consequently residence times,  
467 vary considerably (Table 5). Trace element residence times in the surface-Eq depth layer range  
468 from 2 to 13297 days: Al ( $4\pm 0.2 - 106\pm 3$  days), Fe ( $2\pm 0.1 - 147\pm 5$  days) < Mn ( $89\pm 25 -$   
469  $626\pm 80$  days), Zn ( $4\pm 0.4 - 582\pm 18$  days) < Co ( $64\pm 3 - 3427\pm 209$  days), Cu ( $236\pm 11 - 3646\pm 698$   
470 days) < Ni ( $339\pm 15 - 13297\pm 407$  days).

471 High particulate and dissolved inventories, high export fluxes and short  $\tau_{\text{total}}$  are observed at  
472 Station #1, close to the Iberian margin, for all TEs. There, we observe the shortest residence  
473 times for Al ( $\tau_{\text{total}}=4$  days), Co ( $\tau_{\text{total}}=64$  days), Cu ( $\tau_{\text{total}}=236$  days) and Fe ( $\tau_{\text{total}}=2$  days).  
474 However,  $\tau_{\text{total}}$  values for Mn, Zn and Ni at Station #1 are not the shortest ones along the  
475 transect.

476 The Icelandic and western European basins are also characterized by short element residence  
477 times. For example, the residence time for Fe is only 3 days (at Stations #32 and #38) and Ni  
478 and Zn residence times are shorter there (Ni:  $\tau_{\text{total}}=339$  days at Station #21; Zn:  $\tau_{\text{total}}=4$  days at  
479 Station #32) than near the Iberian margin. A major difference with the Iberian margin is the  
480 generally lower surface water particulate and dissolved inventories for most TEs in the  
481 Icelandic and west European basins (Table 5).

482 Finally,  $\tau_{\text{total}}$  for all TEs are much longer, generally of the order of years (5, 9, 7, 36 and 2 years  
483 for Co, Cu, Mn, Ni and Zn respectively) within the Labrador and Irminger basins, while they

484 are less than a year or even only a few days, within the west European/Icelandic and Iberian  
485 basins. For example, Fe residence times average 47 days within the Labrador and Irminger  
486 basins compared to an average of 10 days for the west European/Icelandic basins and 2 days  
487 for Station #1 at the Iberian margin. For all TEs, except Co,  $\tau_{\text{total}}$  is maximal at Station #77 in  
488 the Labrador Sea. For Co, the maximum  $\tau_{\text{total}}$  is reached at Station #64, also in the Labrador  
489 Sea.

490

#### 491 **4. DISCUSSION**

492 Since particulate  $^{234}\text{Th}$  was not analysed on filters dedicated to trace metal analyses in the SSF,  
493 element: $^{234}\text{Th}$  ratios could only be determined for the LSF, which is assumed to be  
494 representative of sinking particles<sup>89</sup>. To our knowledge, this assumption has been used in all  
495 studies dedicated to TE export fluxes and using ISP<sup>31,32,34-36</sup>. We are aware though, that small  
496 particles may contribute to the TE export.

497

##### 498 4.1. Statistical analyses

499 In order to gain more insight about the vector phases carrying each elemental flux, we examined  
500 the Spearman rank correlation coefficients between TE and mineral exports (XLStat software;  
501 Table 4). The analysis was conducted on log-transformed export fluxes to ensure that input  
502 variables are more normally distributed and to reduce the influence of extreme values. The  
503 influence of lithogenic materials on the pTE export fluxes is highlighted by the significant  
504 correlations, especially for pCu, pFe and pZn (p-value < 0.05 and  $R \geq 0.9$ ; Table 4). At a lesser  
505 extent but still significantly, pCd, pCo, pNi and pTi export fluxes are also correlated to  
506 lithogenic fluxes (p-value < 0.05 and  $R \geq 0.6$ ; Table 4). Biogenic (opal and  $\text{CaCO}_3$ ) and oxide  
507 ( $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_2$ ) phases do not show any significant correlations with the pTEs, likely due  
508 to the significance of lithogenic particles in controlling TE fluxes in the North Atlantic (Table

509 4). In order to disentangle the roles of the biogenic and oxide phases on pTE fluxes, we used a  
510 principal component analysis (PCA; XLStat software) considering excess pTE exports (ie. pTE  
511 export fluxes corrected from the lithogenic fraction; Fig. 3). Recent studies have applied a PCA  
512 approach for large datasets of element concentrations, including small and large particle size  
513 fractions<sup>19,44,65,90</sup>, but we only consider here export fluxes at the Eq depth based on the large  
514 particle size fraction (with GEOVIDE particulate concentrations being reported and discussed  
515 elsewhere; Planquette et al., personal communication, 2019 and Gourain et al., 2019<sup>65</sup>). To  
516 only comment on the distribution of the pTEs, neither mineral exports nor chemical variables  
517 are included in the PCA. The PCA has been conducted after a Varimax rotation which appeared  
518 to clarify the relationship among variables by better capturing known dynamics of the water  
519 column<sup>19,91</sup>. This analysis is also conducted on log-transformed export fluxes to limit the  
520 influence of extreme values and to ensure a more normal distribution of the variables<sup>19,92</sup>. We  
521 identified four principal components that together explain 95% of the total dataset variance  
522 (Fig. 3).

523 The first principal component (33 % of the total variance) likely describes the biological  
524 influence as it explains 84 and 81% of the excess pCd and pP flux variances, respectively. This  
525 component also explains 55% of the excess pCu flux and between 9 and 17% of the excess  
526 pCo, pNi and pZn fluxes. In Table 4, pP appears to be correlated with most pTEs (p-value <  
527 0.05 and  $R > 0.65$  for pCd, pCo, pCu and pMn fluxes and  $R > 0.45$  for pAl, pNi and pZn). To  
528 investigate the biological influence on pTE fluxes, we also examined their correlations with  
529 POC, CaCO<sub>3</sub> and opal. No significant correlation was observed.

530 The second component (30% of the total variance) explains 74% of both excess pCo and pZn  
531 fluxes variances and also explains, at a lesser extent, the export fluxes of other pTEs (12-41%  
532 of excess pCd, pCu, pNi variances and 6% of excess pP variance). Interestingly, Ohnemus et  
533 al. (2019) also found a factor strongly driven by pCo abundances, with additional - smaller -

534 contributions for other pTEs. They related this factor to a secondary (heterotrophic) biomass  
535 phase<sup>19</sup>.

536 The third principal component (19% of the total variance) is strongly indicative of authigenic  
537 Fe oxides, as it explains 89% of the variability of excess pFe fluxes. In addition, this third  
538 component also explains 21% of the variance of excess pNi flux and between 4 and 9% of the  
539 variances of excess pCo, pCu, pMn, pP and pZn fluxes, reflecting the scavenging of these TEs  
540 onto this authigenic phase<sup>93</sup>. Furthermore, the correlation analysis highlights links between  
541 authigenic Fe oxide and Mn oxide fluxes ( $R=0.77$ ),  $\text{CaCO}_3$  fluxes ( $R=0.63$ ) and pTEs,  
542 especially pNi, pCu and pZn fluxes ( $R = 0.30 - 0.46$ ; Table 4).

543 Finally, the fourth component (14% of the total variance) probably describes the influence of  
544 authigenic Mn oxides as it explains 90% of the variance of excess pMn fluxes. It is associated  
545 at 6-8% with excess pFe and pNi fluxes, and at 1-3% with pCd, pCo, pCu and pP fluxes.

546

#### 547 4.2. Lithogenic contribution to fluxes

548 Lithogenic particles play a central role in the North Atlantic (Table 4). They can originate from  
549 different sources such as atmospheric deposition, glacial meltwater, advection of sediment-  
550 enriched water masses or lateral mixing with shallow coastal waters under continental  
551 influence. The importance of lithogenic sources is particularly clear for Station #1, suggesting  
552 an input from the Iberian margin (Fig. 2) in agreement with the literature<sup>44,59</sup>. There, we  
553 determined the highest fluxes for lithogenic material and some pTEs, which were accompanied  
554 by pTE:pAl ratios close to UCC<sup>67</sup> (Fig. 4; Fig. S5). This is especially the case for pFe and pMn  
555 for which the respective ratios show only 2 and 20% offset relative to UCC ratios (Fig. 4). For  
556 other pTEs, these ratios are slightly greater than for UCC, pointing to the presence of another  
557 driver of export fluxes. Such TE enrichments relative to the UCC have also been reported in  
558 the estuary of the Tagus river<sup>94</sup> for which the plume has been shown to reach Station #1<sup>69,85</sup>.

559 This river is known to receive effluents from agricultural, industrial and urban sources and thus  
560 represents an important discharge of dissolved and particulate TE concentrations to the estuary  
561 <sup>95-98</sup>. The slightly higher pTE:pAl ratios compared to UCC may indicate that fluxes at Station  
562 #1 are under anthropogenic influence via the discharge from the Tagus estuary.

563 Stations at proximity of the Greenland and Newfoundland margins are also characterized by  
564 some higher pTE:pAl ratios (i.e., pCd:pAl or pCu:pAl; Fig. 4), implying additional processes  
565 in the export of these pTEs. Although lithogenic particles settle quickly through the water  
566 column, they can also adsorb elements onto their surfaces <sup>44,99,100</sup>. Such scavenging processes  
567 could explain the higher pTE:pAl ratios. Interestingly, the Greenland and Newfoundland  
568 margin stations are characterized by much lower lithogenic and pTE flux intensities compared  
569 to the Iberian margin (Fig. 2), suggesting that lithogenic material is not similarly released at all  
570 margins. Such differences can depend on the morphology of the margin and on the  
571 hydrodynamical forcing, providing (or not) significant amounts of lithogenic particles and  
572 leading (or not) to the formation of nepheloid layers <sup>101</sup>. Indeed, relatively high lithogenic  
573 export fluxes are also observed at open-ocean stations beyond the Iberian margin (up to Station  
574 #32). The Iberian margin is known to be an efficient exporter of particulate matter to the open  
575 and deep sea <sup>102,103</sup> and during GEOVIDE, high proportions of lithogenic particulate rare earth  
576 elements <sup>101</sup> and pFe <sup>65</sup> were observed up to 1700 km far from the Iberian margin. These  
577 enrichments were attributed to the presence of intermediate nepheloid layers transported along  
578 the isopycnals, which then likely drive pTEs fluxes to the deep ocean. To a lesser extent,  
579 lithogenic particles were also transported to the west of the Greenland margin <sup>65</sup>, in line with  
580 the moderate lithogenic export fluxes observed at Station #64, in the eastern Labrador basin.  
581 Conversely, lithogenic particles do not seem to spread off the Newfoundland margin, thereby  
582 explaining the lower lithogenic export fluxes at Station #77.

583



584 4.3. Authigenic contribution to fluxes

585 High fluxes of Mn- and Fe-oxides were determined at some stations close to margins, also  
586 under lithogenic influence (i.e. Station #64), and at open-ocean stations, which are not  
587 necessarily characterized by high particulate lithogenic exports. For example, Station #26  
588 presents one of the lowest lithogenic and Fe(OH)<sub>3</sub> fluxes, while MnO<sub>2</sub> fluxes are among the  
589 highest at this station. This decoupling between high pMn and low pAl fluxes has already been  
590 observed and was attributed to a distant shelf source of lithogenic particles<sup>30</sup>. Indeed, nepheloid  
591 layers sourced at the shelves lose particles by gravitational settling during lateral advection,  
592 but in the case of Mn, it has been shown that dissolved Mn, remobilized from the shelf, oxidizes  
593 very slowly, enriching the particulate phase during transport<sup>104</sup>. Long distance transport  
594 inducing a subsurface pMn maximum was observed off the Kuril/Kamchatka margin, in the  
595 western subarctic Pacific<sup>18</sup>. High pMn concentrations and fluxes at Station #26 could thus have  
596 originated from authigenically precipitated Mn during its transport from the American coasts,  
597 via the North Atlantic Current (NAC, Fig. 1). The distance between Station #26 and North  
598 Carolina coasts (USA) is around 4500km, which roughly corresponds to the distance of  
599 4220km calculated by multiplying a NAC velocity of 0.4 m/s<sup>105</sup> by the inverse of the oxidation  
600 rate constant of Mn ( $k_{ox}=0.341 \times 10^{-3} \text{ h}^{-1}$ <sup>106</sup>). Interestingly, the high Mn-oxide fluxes determined  
601 at Stations #26, #32, #44 and #64 and to a lesser extent at Stations #13 and #38 drive other pTE  
602 fluxes. Indeed, Figure 3 shows that Mn oxides could be responsible for 3-8% of the excess  
603 export fluxes of pCu, pFe and pNi.

604 Similarly, Fe-oxide fluxes are high at Stations #32, #38 and #64. As seen in Figures 2 and 3,  
605 Fe-oxides could represent an important carrier phase for pCo, pCu, pMn, pNi and pZn (from 4  
606 to 21% of the variance explained in the PCA on excess - i.e., non-lithogenic - fluxes, as already  
607 discussed in other studies<sup>46, 107, 19</sup>.

608

#### 609 4.4. Biogenic contribution to fluxes

610 In addition to Figure 3 and Table 4, the comparison of pTE:POC ratios at each station with  
611 those of phytoplankton cells suggests that biogenic particles partly influence pTE exports (Fig.  
612 5). Despite large uncertainties associated with this approach, some pTE:POC ratios are  
613 comparable to ratios reported for functional phytoplankton groups (diatoms, autotrophic  
614 flagellates and autotrophic picoplankton) collected in the upper 150m of the North Atlantic <sup>71</sup>  
615 (Fig. 5; Fig. S5). This suggests that pTE exports, and especially those of pCd, pCo, pCu, pMn,  
616 and pZn, can also be driven by biogenic particles. However, higher pTE:POC ratios than cell  
617 ratios are also observed. Trace elements are known to be scavenged onto particles with depth  
618 <sup>12,108</sup> (see previous sections) and it is usual to observe an increase of the bulk ratios compared  
619 to cellular ratios <sup>24,109,110</sup>. This can be caused by the presence of detrital, authigenic and  
620 lithogenic particles on the filters leading to an increase of the pTE:POC, as observed in Figure  
621 5. Moreover, the intracellular TE:C considerably changes between taxa and regions depending  
622 on the environmental conditions (e.g. nutrients, sunlight limitations <sup>3</sup>): Fe:C quota usually  
623 range between 10-1700  $\mu\text{g/g}$  for diatoms and coccolithophorids in natural and culture  
624 experiments <sup>3,111,112</sup> but Sunda and Huntsman (1995) have measured a Fe:C ratio equalling  
625 8230  $\mu\text{g/g}$  <sup>113</sup>, highlighting the high variability of the ratio and the difficulty to generalize the  
626 intracellular phytoplankton TE:C ratios. Therefore, we searched for indicators of the  
627 phytoplankton community structure, such as  $\text{CaCO}_3$ , opal and pigment analyses using  
628 CHEMTAX <sup>62</sup>. The highest  $\text{CaCO}_3$  fluxes have been determined within the west European and  
629 Icelandic basins (Fig. 2) where coccolithophorids were present <sup>62</sup>. The contribution of  
630 coccolithophorids to export pZn, pCu, pNi and pMn is indicated by relatively high correlation  
631 coefficients ( $0.3 < R < 0.5$ ) between these pTEs and  $\text{CaCO}_3$  exports (Table 4). Opal fluxes are  
632 high at Stations #51, #64 and #69 (Irminger and Labrador basins; Fig. 2) where diatoms  
633 dominate the phytoplankton community <sup>62</sup>. In the Labrador Sea, high POC and opal fluxes are

634 associated with surprisingly low pTE export fluxes (Fig. 2). This basin was sampled during the  
635 decline of the bloom (Station #69: 7 weeks after the bloom peak) and was also characterized  
636 by an important remineralization event in the mesopelagic layer, evidenced from the excess  
637 barium ( $Ba_{xs}$ ) proxy<sup>114</sup>. Both results suggest either a pTE accumulation in surface waters while  
638 POC would be preferentially exported, or a limitation of dissolved TEs that would impede a  
639 pTE export due to enhanced recycling in surface waters<sup>115</sup>.

640

#### 641 4.5. Residence time of TEs and efficiency of export

642 Although only few TE residence times within the upper ocean are available in the literature,  
643 the  $\tau_{total}$  values estimated from the present dataset are comparable with those of other studies.  
644 In the surface global ocean, the majority of  $\tau_{total}$  for Fe fall between 10 and 100 days<sup>35</sup>, which  
645 corresponds to the 2-147 days range estimated in this study. Hayes et al. (2018) examined the  
646 dissolved TE residence times in the upper 1000m of the North Atlantic (note the wider depth  
647 layer) and found that Fe had the shortest residence time relative to other TEs, of about 30-60  
648 days<sup>25</sup>. The authors estimated dissolved residence times of less than 6 years for Zn, Co and  
649 Mn (0.01 to 6 years in our study, except at Station #64 where  $\tau_{total}$  for Co reaches 14 years) and  
650 of 80-90 years for Cu (0.65-15 years in this study; Table 5). The good consistency between  
651 these different studies allows us to rank the turnover rate of TEs in the upper ocean as follows:  
652  $Fe < Zn < Mn < Co < Cu$ .

653 In the following, our attention is mainly devoted to Fe (Fig. 6). The shortest  $\tau_{total}$  (2 days) is  
654 observed close to the Iberian margin, indicating an efficient Fe export. Similar short  $\tau_{total}$  within  
655 the upper ocean (<5 days) have been observed in coastal areas where lithogenic particles  
656 probably play an important role in transporting TEs out of the upper ocean<sup>32,35,88</sup>. These  
657 lithogenic particles advected from margins may represent a continuous Fe input in surface  
658 waters explaining the high inventories and export observed during GEOVIDE at Station #1,

659 even in post-bloom conditions. For example, they contribute for 98% of the total Fe export at  
660 Station #1 (Fig. 6). As it consists of dense particles, the sinking rate of lithogenic material is  
661 known to be high. Here the particle sinking rate is estimated by dividing the particulate  
662 residence time by the surface-Eq depth layer. At Station 1, the sinking rate reaches 63 m/d for  
663 pFe, which is in the same order of magnitude as estimated using Stokes law (88 m/d for a  
664 particle of 53 $\mu$ m diameter and of density of 1860 kg/m<sup>3</sup>, representing an average density for a  
665 mixed aggregate composed of lithogenic, transparent exopolymer particles (TEP), detritus,  
666 opal and CaCO<sub>3</sub>; <sup>116</sup>). Similarly, high particulate and dissolved inventories, high export fluxes  
667 and short  $\tau_{\text{total}}$  are observed at Station #1 for other TEs, suggesting a fast supply to and removal  
668 from the upper ocean by lithogenic particles (Table 5). However,  $\tau_{\text{total}}$  values for Mn, Zn and  
669 Ni at Station #1 are not the shortest observed along the transect, indicating that lithogenic  
670 particles are not the only drivers of TE export, even at this coastal station.

671 The Icelandic and western European basins were sampled during the bloom development and  
672 were thus characterized by an important productivity event <sup>60,61</sup>. In these basins, we observe a  
673  $\tau_{\text{total}}$  averaging 3 days for Fe, suggesting an efficient transport to the deep ocean. As seen  
674 previously, Stations #21, #32 and #38 are characterized by high export fluxes of Fe- and Mn-  
675 oxides, carrying other TEs to the deep ocean. At these stations, pFe sinks faster compared to  
676 the Iberian margin (up to 135 m/d at Station #32), likely because of the presence of Fe-oxides  
677 (contributing to 62% of total Fe export in these basins; Fig. 6). These mineral phases are  
678 presumably denser than lithogenic particles (the density of ferrihydrite is about 3.8 g/cm<sup>3</sup>  
679 compared to a typical clay density of 2.7 g/cm<sup>3</sup>) but the sinking speed is also controlled by the  
680 size of the particle, which might be an important factor in the west European and Icelandic  
681 basins. Other TEs also have short  $\tau_{\text{total}}$  and high sinking rates in these basins, confirming the  
682 important contribution of oxides to export pTEs.

683 Finally, the Labrador and Irminger basins were sampled during the bloom decline and the  
684 average pFe export flux is the lowest of the whole transect (182  $\mu\text{g}/\text{m}^2/\text{d}$  compared to 441 and  
685 3912  $\mu\text{g}/\text{m}^2/\text{d}$  for respectively the west European/Icelandic basins and Iberian margin). Longer  
686 residence times are also determined within the Labrador and Irminger basins, suggesting that  
687 most of pFe is not exported as efficiently as in the eastern basins. This may be due to the more  
688 important fraction of Fe carried by biogenic matter (12% compared to 1 and 3% in the Iberian  
689 and west European/Icelandic basins, respectively), leading to a slower export of Fe and/or  
690 active recycling processes. The median sinking rate of 3 m/d (Table 5) is similar to the rate  
691 estimated by using Stokes law (3.5 m/d) for an organic particle of 53 $\mu\text{m}$  diameter and a density  
692 of 1060  $\text{kg}/\text{m}^3$ . Indeed, Fe removal rate from the upper ocean via biological processes has been  
693 shown to be much smaller than via lithogenic and authigenic processes<sup>35</sup>. A greater  $\tau_{\text{total}}$  is also  
694 estimated for other TEs. The slower removal of biogenic TEs can also be reflected by the longer  
695 residence times of less detrital TEs, such as Ni, Co or Cu (from 65 days to >35 years) compared  
696 to more detrital TEs (Al, Fe with  $\tau_{\text{total}} < 150$  days).

697

## 698 CONCLUSION

699 Using the <sup>234</sup>Th approach and the elemental composition of large, sinking particles, this study  
700 investigated the pTE export fluxes, sinking rates and residence times in the North Atlantic.

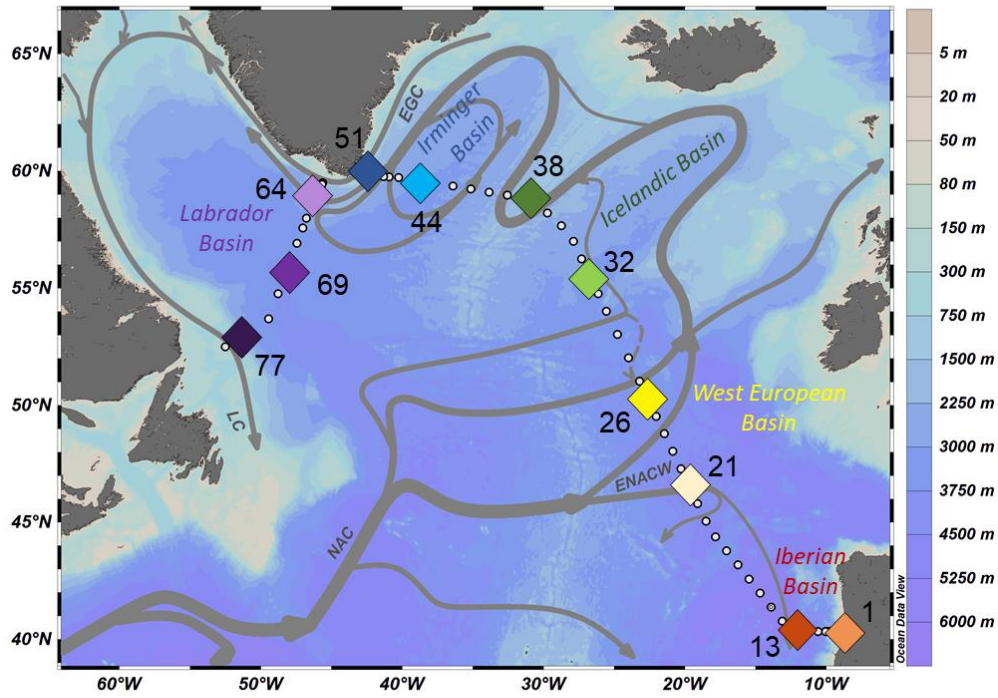
701 Lithogenic material is present everywhere along the section, but mainly controls the fluxes near  
702 the Iberian margin, where the highest pTE fluxes are observed. As a result, TE residence time  
703 in the upper ocean is short in vicinity of the Iberian Margin. In the open ocean, and especially  
704 within the Icelandic basin, Mn- and Fe-oxides are likely the main TE carriers to the deep ocean.  
705 Zinc and Ni, for example, have shorter residence times there compared to the Iberian basin  
706 which is under lithogenic influence. Biogenic particles also contribute to export pTEs, as  
707 reflected by the similarity of pTE:POC export ratios and TE:C cell ratios. Particulate TE export

708 fluxes especially those of pZn, pCu, pNi and pMn might be enhanced by sinking  
709 coccolithophorid cells within the west European and Icelandic basins, where CaCO<sub>3</sub> exports  
710 are the highest. Diatoms are dominating the phytoplankton community within the Irminger and  
711 Labrador basins, in agreement with the highest opal fluxes. However there, pTE fluxes are low,  
712 possibly suggesting TE recycling due to dissolved TE limitations in surface waters, in line with  
713 the decline of the bloom. The inefficient pTE export in this area is also illustrated by the longer  
714 residence times, which may be due to greater biogenic contribution.

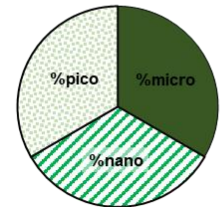
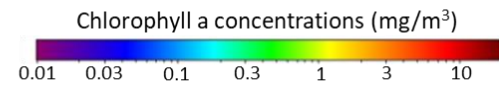
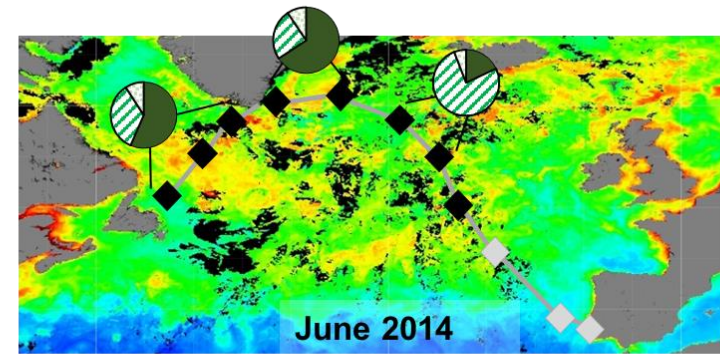
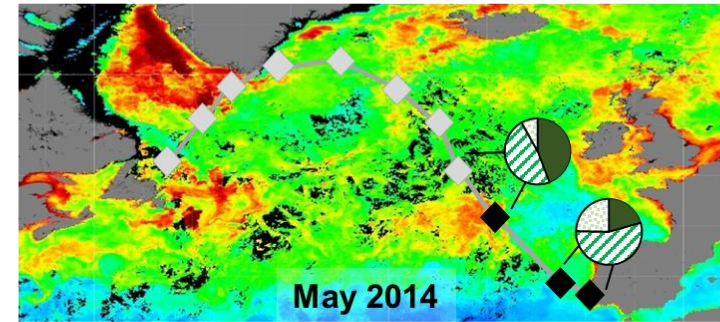
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FIGURE 1

a)



b)



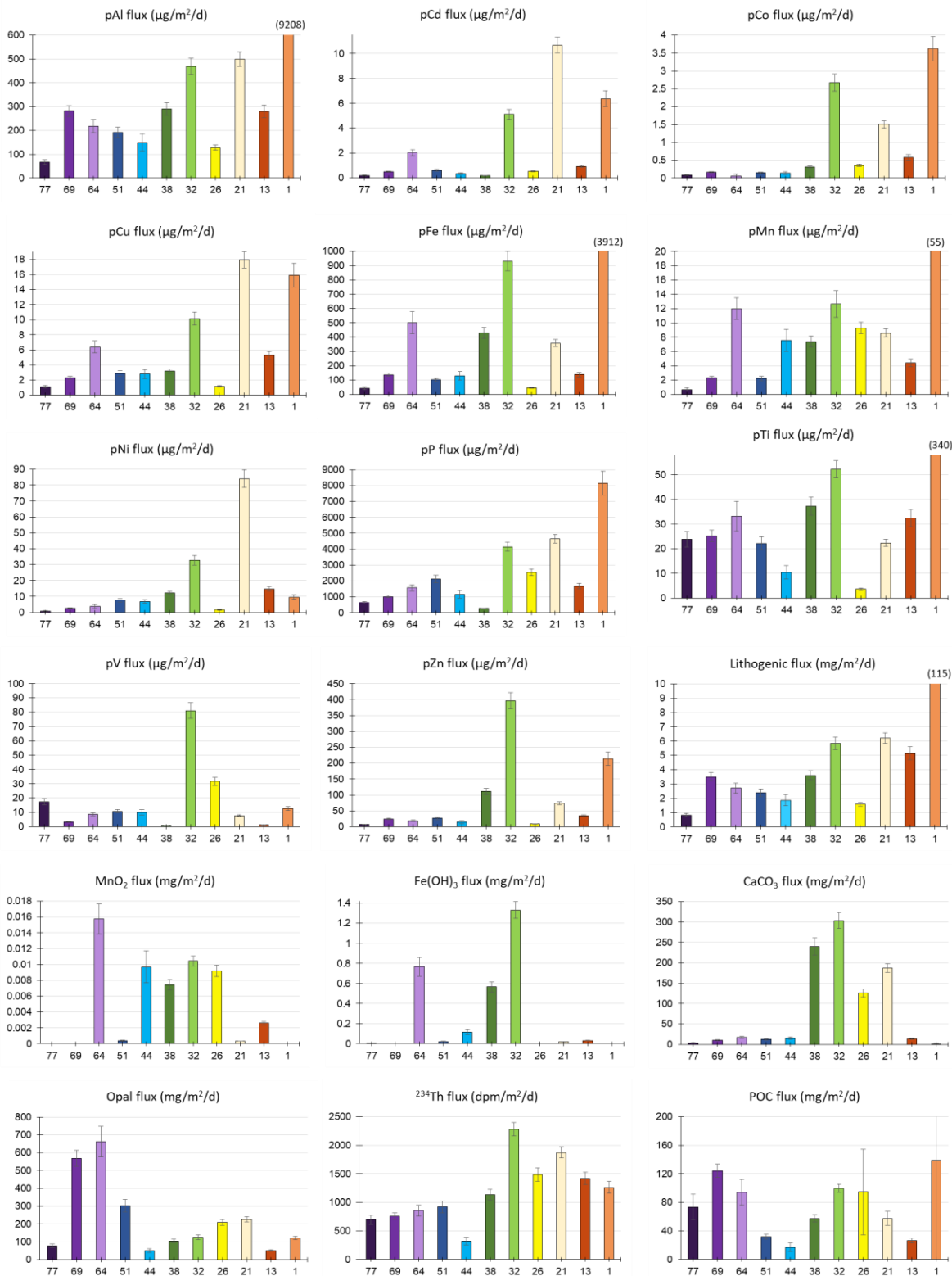
716

717 **Figure 1:** a) Schematic diagram of the surface circulation superimposed on the bathymetric map of the North Atlantic <sup>117</sup>. Coloured symbols  
718 represent the stations discussed in this study (red: Iberian basin; yellow: West European basin; green: Icelandic basin; blue: Irminger basin; purple:  
719 Labrador basin). Abbreviations for the main surface hydrographic features in the upper 500m indicate the East North Atlantic Central Water  
720 (ENACW), Labrador Current (LC), East Greenland Current (EGC) and the North Atlantic Current (NAC). b) Satellite-derived chlorophyll-*a*  
721 concentrations (MODIS Aqua from [oceancolor.gsfc.nasa.gov](http://oceancolor.gsfc.nasa.gov)) averaged over May (top panel) and June (bottom panel) 2014. The GEOVIDE  
722 transect is indicated by the grey line and black symbols indicate stations sampled during the corresponding month. The pie charts indicate the  
723 proportion of micro-phytoplankton (dark green), nano-phytoplankton (hatched green) and pico-phytoplankton (dotted light green) encountered in  
724 each basin during GEOVIDE <sup>62</sup>.



725

**FIGURE 2**



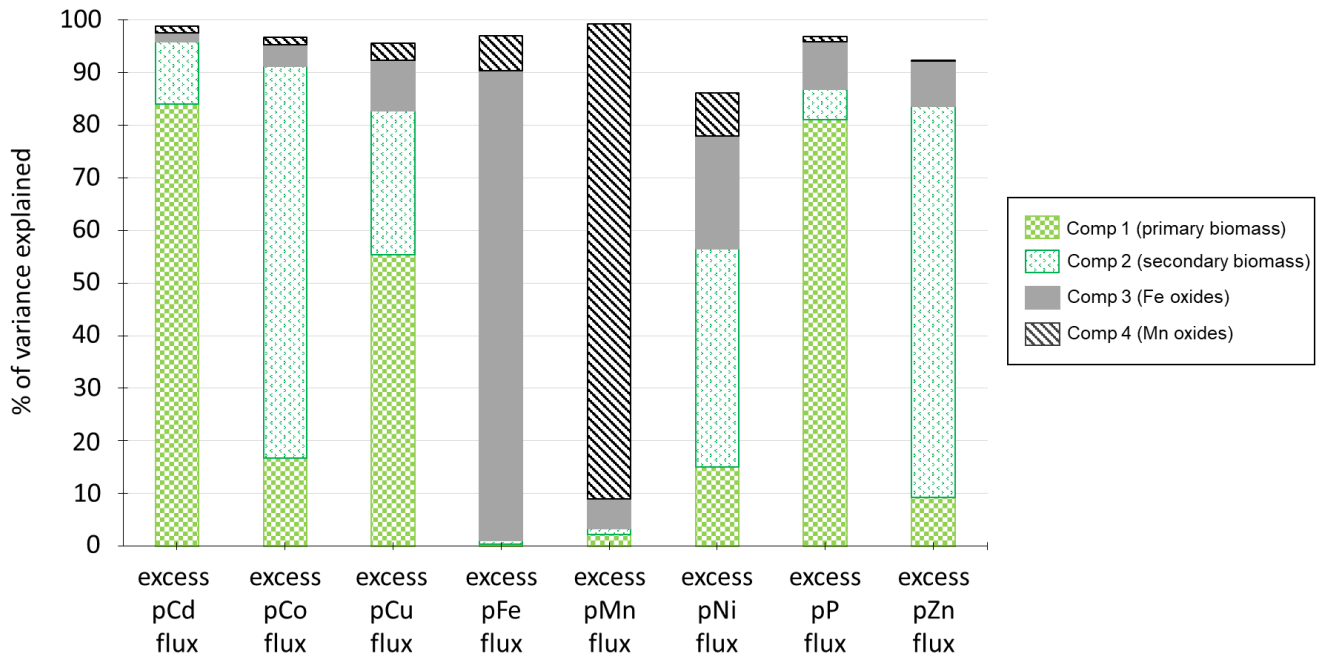
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727

728 **Figure 2:** Particulate trace element and mineral export fluxes in  $\mu\text{g}/\text{m}^2/\text{d}$  or  $\text{mg}/\text{m}^2/\text{d}$  estimated  
 729 in the large size fraction at the Eq depth. <sup>234</sup>Th (in  $\text{dpm}/\text{m}^2/\text{d}$ ) and POC (in  $\text{mg}/\text{m}^2/\text{d}$ ) export  
 730 fluxes in the large size fraction and at the Eq depth are also presented for comparison <sup>60</sup>.

731

FIGURE 3

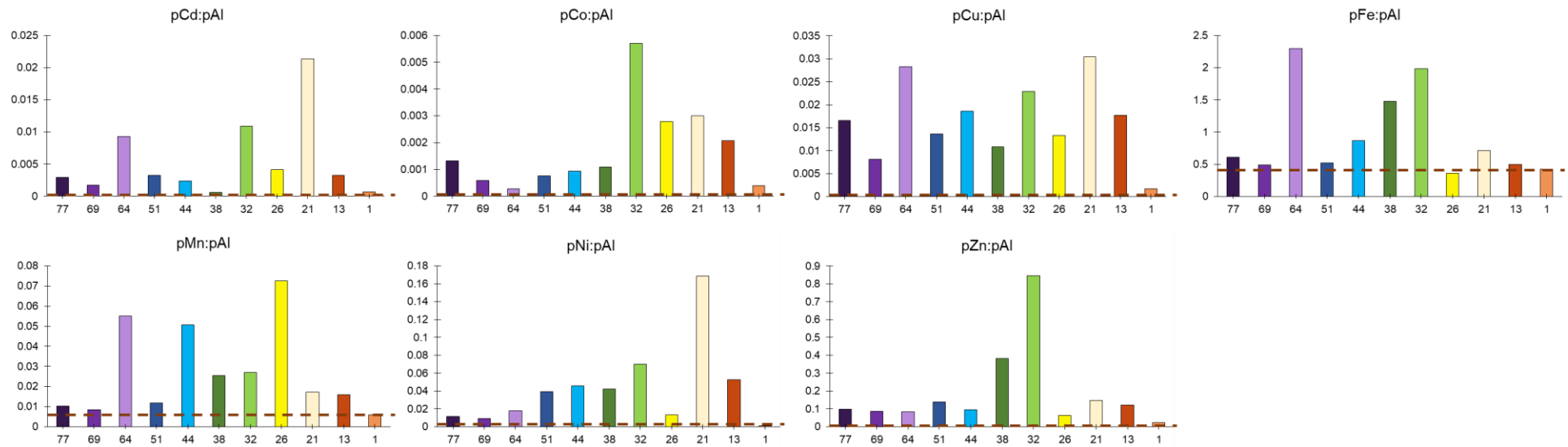


732

733 **Figure 3:** Variance explained for eight excess pTE export fluxes at Eq, captured by the first  
734 four principal components in principal component analysis (XLStat software). The description  
735 of the components is provided in the text. Excess pTE export fluxes are calculated by removing the  
736 lithogenic fraction of the flux (excess pTE flux = pTE flux - [pAl flux × ( $\frac{pTE}{pAl}$ )<sub>UCC</sub>]; with the UCC ratio  
737 from <sup>67</sup>).

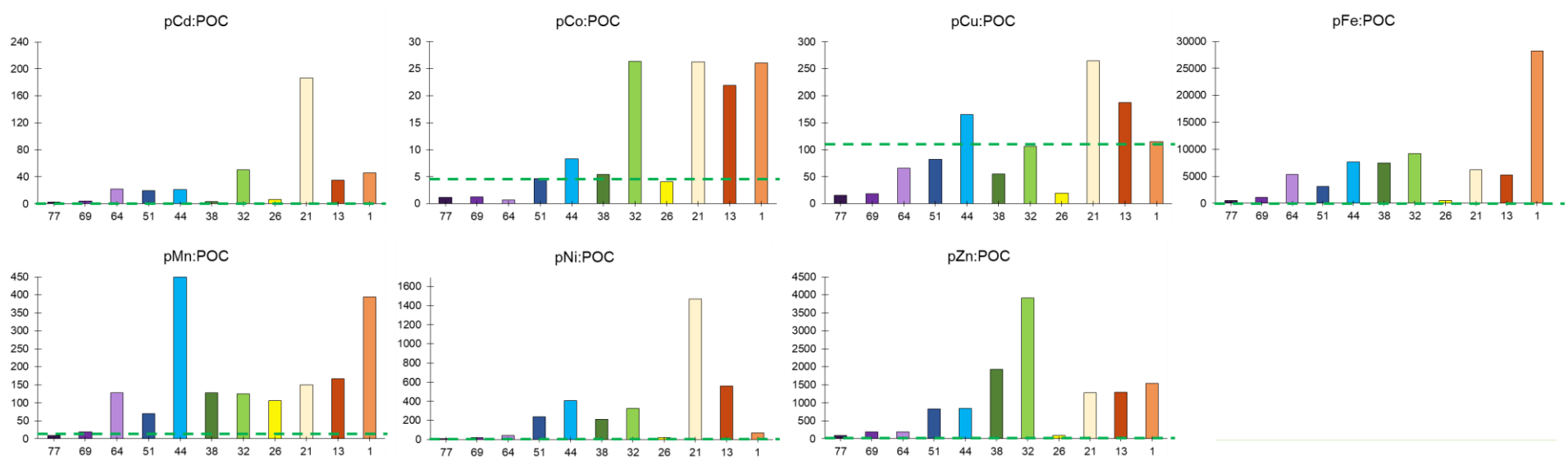
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**FIGURE 4**



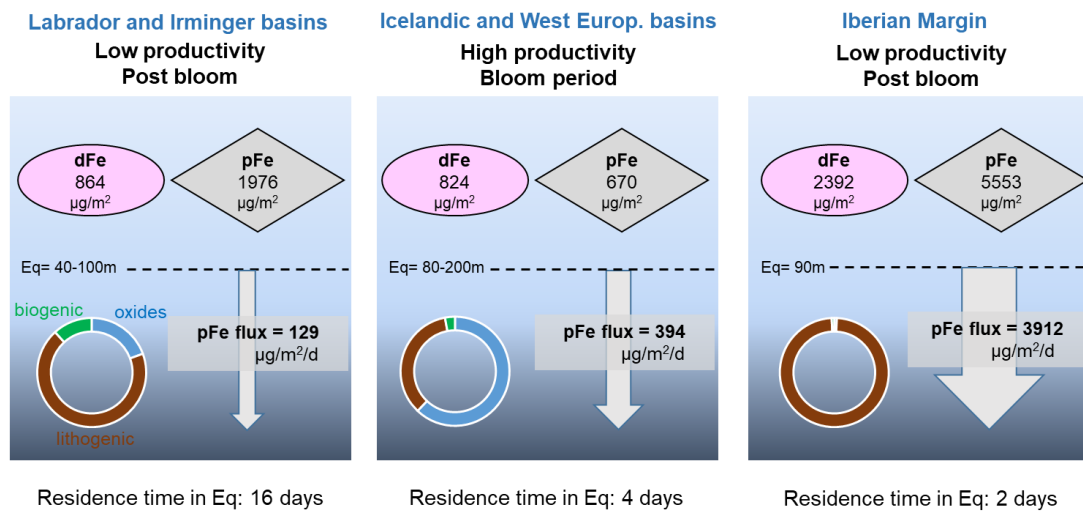
**Figure 4:** Ratios of the pTEs over pAl fluxes (in g/g, on y-axis) determined at Eq along the GEOVIDE transect (station numbers on x-axis). The brown horizontal dashed lines represent the ratios for the upper continental crust (UCC) <sup>67</sup>.

FIGURE 5



**Figure 5:** Ratios of the pTEs over particulate organic carbon (POC) fluxes (in  $\mu\text{g/g}$ , on y-axis) determined at Eq along the GEOVIDE transect (station numbers on x-axis). The green horizontal dashed lines indicate the average intracellular metal stoichiometries <sup>71</sup>.

**FIGURE 6**



**Figure 6:** Biogeochemical iron budget in the upper ocean for the Labrador and Irminger basins (left box), for the Icelandic and west European basins (middle box) and for the Iberian margin (right box). For each area, we show the median inventories of dissolved iron (dFe<sup>85</sup>; pink circles) and particulate iron (pFe<sup>65</sup>; grey diamonds) in  $\mu\text{g}/\text{m}^2$ , the median particulate iron fluxes (pFe flux; grey rectangles) in  $\mu\text{g}/\text{m}^2/\text{d}$  and the median total residence times ( $\tau_{\text{tot}}$ ) in days. The total residence time is calculated for the depth interval 0-Eq. The size of the arrows is roughly proportional to the magnitude of the pFe fluxes. The fractions of the pFe flux driven by lithogenic, authigenic or biogenic particles are represented by the brown, blue and green colours, respectively. Lithogenic pFe flux was estimated by multiplying the pAl flux by the pFe:pAl ratio in the upper continental crust (UCC, i.e., 0.44 g/g)<sup>67</sup>. Authigenic pFe flux is equal to the Fe(OH)<sub>3</sub> flux (see details in section 2.3) and the biogenic pFe flux is obtained by multiplying the POC flux<sup>60</sup> by an average Fe:C ratio determined in phytoplankton cells of the North Atlantic (193.7  $\mu\text{g}/\text{g}$ )<sup>71</sup>.

**TABLE 1**

	Station	Number of weeks since beginning of spring bloom	In-situ primary production (mmol/m <sup>2</sup> /d)	Phytoplankton class	POC export (mmol/m <sup>2</sup> /d)
Iberian basin	1	10	33	diatoms & coccolith.	12
	13	11	79	pelagophytes & cyano.	2.2
west Europ. Basin	21	9	135	diatoms	4.8
	26	8	174	diatoms	7.9
Icelandic basin	32	5	105	coccolith.	8.3
	38	4	68	coccolith.	4.8
Irminger basin	44	5	137	diatoms	1.4
	51	4	166	diatoms	2.7
Labrador basin	64	5	54	diatoms	7.8
	69	4	27	diatoms	10
	77	5	80	diatoms	6.1

**Table 1:** Station characteristics with the number of weeks between the sampling time and beginning of the spring bloom (obtained from satellite data products <sup>60</sup>), primary production (obtained from incubations <sup>61</sup>), POC export fluxes (obtained with the <sup>234</sup>Th approach <sup>60</sup>), and phytoplankton classes (from HPLC pigment analysis and CHEMTAX analysis <sup>62</sup>).

**TABLE 2**

	Al <sup>+</sup>	Ca <sup>+</sup>	Cd	Co*	Cu	Fe*	Mn	Na <sup>^</sup>	Ni	P <sup>+</sup>	Ti <sup>+</sup>	V	Zn
Blank (ppm)	1.6E-03	1.4	1.2E-06	3.2E-06	1.3E-05	1.5E-03	1.4E-04	936	3.4E-04	2.5E-03	1.0E-04	7.3E-06	2.6E-04
BCR-414 (n=5; ppm)	3112	51133	0.385	1.44	29.7	1860	301	6601	17.8	15541	95	9	112.4
RSD (%)	15	2.1	5.2	15	13	12	14	0.2	16	24	8	1	17
Recovery CRM (%)	118	80	101	101	101	101	101	/	95	113	75	111	101

**Table 2:** Blanks, average concentrations of the certified reference material (CRM; BCR-414), relative standard deviation (RSD) of the 5 analyses of the CRM and recoveries. Elements without any superscript sign have certified concentrations (Cd, Cu, Mn, Ni, V and Zn); elements marked with (\*) have indicative concentrations reported on the official certificate (Co and Fe); elements marked with (+) have indicative concentrations reported on the GEOREM website (Al, Ca, P, and Ti) and Na has no reported concentration. The official certificate can be found at <https://crm.jrc.ec.europa.eu/p/40455/40461/By-material-matrix/Animal-materials/BCR-414-PLANKTON-trace-elements/BCR-414> .

**TABLE 3**

Basin	Station	Eq m	Al flux		Cd flux		Co flux		Cu flux		Fe flux		Mn flux		Ni flux		P flux		Ti flux		V flux		Zn flux	
			$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd	$\mu\text{g}/\text{m}^2/\text{d}$	sd
Iberian	1	90	9208	883	6.4	0.6	3.6	0.3	16	2	3912	364	55	6	9.7	1.4	8141	758	340	34	13	1	214	21
	13	110	280	26	0.9	0.1	0.58	0.08	5.0	0.5	138	15	4.4	0.5	15	1	1673	160	32	4	1.2	0.1	34	3
west Europ.	21	110	500	30	10.7	0.6	1.5	0.1	15	1	358	25	8.6	0.6	84	6	4648	278	22	1	7.8	0.5	74	5
	26	100	128	11	0.53	0.05	0.36	0.03	1.7	0.1	46	4	9.3	0.8	1.7	0.2	2537	212	3.5	0.4	32	3	8	1
Icelandic	32	130	469	35	5.1	0.4	2.7	0.2	11	1	931	69	13	2	33	3	4145	285	52	4	81	5	396	25
	38	80	290	26	0.18	0.02	0.31	0.03	3.1	0.3	429	40	7.4	0.8	12	1	266	24	37	4	1.0	0.1	111	10
Irminger	44	40	150	36	0.36	0.07	0.14	0.04	2.8	0.6	129	30	7.6	1.6	6.9	1.1	1158	237	10	3	10	2	14	6
	51	100	192	22	0.63	0.07	0.15	0.02	2.6	0.3	101	12	2.2	0.3	7.6	1.0	2105	242	22	3	11	1	26	3
Labrador	64	80	218	29	2.0	0.2	0.06	0.05	6.2	0.8	501	77	12	2	3.8	1.2	1562	185	33	6	8.6	1.0	18	2
	69	40	281	23	0.49	0.04	0.16	0.01	2.3	0.2	137	11	2.4	0.2	2.6	0.3	1017	82	25	2	3.2	0.3	24	2
	77	60	67	10	0.19	0.02	0.09	0.01	1.1	0.1	41	10	0.7	0.2	0.8	0.3	627	73	24	3	17	2	7	1

Basin	Station	Eq m	Lithogenic flux		Fe(OH) <sub>3</sub> flux		MnO <sub>2</sub> flux		CaCO <sub>3</sub> flux		Opal flux		<sup>234</sup> Th flux	
			$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{mg}/\text{m}^2/\text{d}$	sd	$\text{dpm}/\text{m}^2/\text{d}$	sd
Iberian	1	90	115	11	nd	nd	nd	nd	nd	nd	122	10	1264	104
	13	110	3.5	0.3	0.032	0.003	0.0026	0.0002	14	1	52	4	1418	111
west Europ.	21	110	6.2	0.4	0.020	0.001	0.00032	0.00002	187	10	226	14	1873	97
	26	100	1.6	0.1	nd	nd	0.009	0.001	126	10	209	17	1486	117
Icelandic	32	130	5.8	0.4	1.3	0.1	0.010	0.001	303	19	127	13	2282	119
	38	80	3.6	0.3	0.57	0.05	0.007	0.001	240	21	105	9	1134	95
Irminger	44	40	1.9	0.4	0.11	0.02	0.010	0.002	15	3	51	11	321	66
	51	100	2.4	0.3	0.024	0.003	0.00038	0.00004	12	1	303	34	922	103
Labrador	64	80	2.7	0.4	0.8	0.1	0.016	0.002	17	2	661	86	855	95
	69	40	3.5	0.3	nd	nd	nd	nd	10	1	568	46	758	57
	77	60	0.8	0.1	0.0	0.0	nd	nd	3	1	79	9	696	77

**Table 3:** Particulate export fluxes in  $\mu\text{g}/\text{m}^2/\text{d}$  for aluminum (pAl), cadmium (pCd), cobalt (pCo), copper (pCu), iron (pFe), manganese (pMn), nickel (pNi), phosphorus (pP), titanium (pTi), vanadium (pV) and zinc (pZn); in  $\text{mg}/\text{m}^2/\text{d}$  for lithogenic material, iron oxides (Fe(OH)<sub>3</sub>), manganese oxides (MnO<sub>2</sub>), calcium carbonate (CaCO<sub>3</sub>), opal and in  $\text{dpm}/\text{m}^2/\text{d}$  for <sup>234</sup>Th. Standard deviations (sd) were calculated by considering the standard deviations of the <sup>234</sup>Th fluxes and pTE:<sup>234</sup>Th ratios at Eq, with all concentration and activity uncertainties estimated using error propagation law.



**TABLE 4**

Variables	Lithogenic flux	Fe(OH) <sub>3</sub> flux	MnO <sub>2</sub> flux	CaCO <sub>3</sub> flux	Opal flux	POC flux	Al flux	Cd flux	Co flux	Cu flux	Fe flux	Mn flux	Ni flux	P flux	Ti flux	V flux	Zn flux
Lithogenic flux	<b>1</b>																
Fe(OH) <sub>3</sub> flux	0.083	<b>1</b>															
MnO <sub>2</sub> flux		<b>0.769</b>	<b>1</b>														
CaCO <sub>3</sub> flux	0.200	<b>0.633</b>	<b>0.706</b>	<b>1</b>													
Opal flux	0.164		0.028	0.073	<b>1</b>												
POC flux	0.391				0.473	<b>1</b>											
Al flux	<b>1.000</b>	0.083		0.200	0.164	0.391	<b>1</b>										
Cd flux	<b>0.618</b>	0.018	0.037	0.100	0.364	0.273	<b>0.618</b>	<b>1</b>									
Co flux	<b>0.745</b>			0.200		0.282	<b>0.745</b>	0.591	<b>1</b>								
Cu flux	<b>0.845</b>	0.330	0.156	0.255	0.064	0.191	<b>0.845</b>	<b>0.791</b>	<b>0.609</b>	<b>1</b>							
Fe flux	<b>0.855</b>	0.395	0.220	0.273	0.145	0.455	<b>0.855</b>	0.591	0.527	<b>0.900</b>	<b>1</b>						
Mn flux	0.527	0.183	0.440	0.364	0.136	0.473	0.527	<b>0.636</b>	0.527	<b>0.718</b>	<b>0.736</b>	<b>1</b>					
Ni flux	<b>0.764</b>	0.440	0.138	0.491			<b>0.764</b>	0.573	<b>0.673</b>	<b>0.791</b>	<b>0.636</b>	0.345	<b>1</b>				
P flux	0.491			0.073	0.209	0.236	0.491	<b>0.891</b>	<b>0.718</b>	<b>0.627</b>	0.400	<b>0.655</b>	0.473	<b>1</b>			
Ti flux	<b>0.691</b>	0.312		0.018	0.000	0.564	<b>0.691</b>	0.300	0.400	<b>0.627</b>	<b>0.845</b>	0.427	0.409	0.100	<b>1</b>		
V flux			0.119		0.009	0.336		0.200	0.127			0.327		0.445		<b>1</b>	
Zn flux	<b>0.909</b>	0.303	0.000	0.318	0.018	0.245	<b>0.909</b>	0.527	<b>0.764</b>	<b>0.791</b>	<b>0.818</b>	0.464	<b>0.855</b>	0.464	<b>0.718</b>		<b>1</b>

**Table 4:** Spearman rank correlation coefficients between trace element and mineral export fluxes for the large size fraction at the Eq depth. The analysis was conducted on log-transformed export fluxes to ensure that input variables were more normally distributed and to reduce the influence of extreme values. Correlations with  $R < 0.1$  are not shown. Values in bold are correlation coefficients with  $p\text{-value} \leq 0.05$  (t-test; XLStat software).

**TABLE 5**

Basin	Station	Al					Co					Cu					Fe				
		diss. invent.	part. invent.	sinking rate	$\tau_{tot}$		diss. invent.	part. invent.	sinking rate	$\tau_{tot}$		diss. invent.	part. invent.	sinking rate	$\tau_{tot}$		diss. invent.	part. invent.	sinking rate	$\tau_{tot}$	
		$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd
Iberian	1	20847	12741	65	4	0.2	219	13	25	64	3	3718	28	52	236	11	2392	5553	63	2	0.1
	13	7720	6672	5	51	5	124	32	2	269	29	5002	129	4	1033	110	1564	1139	13	20	2
west	21	13038	3628	15	33	1	151	37	5	125	5	6224	186	9	422	19	861	599	66	4	0.2
Europ.	26	6181	1741	7	62	12	195	20	2	598	114	6100	133	1	3646	698	691	741	6	31	6
Icelandic	32	12630	1465	42	30	4	224	22	16	92	11	5539	202	7	534	66	1471	898	135	3	0.3
	38	6007	716	32	23	1	111	9	3	380	19	2859	113	2	944	47	786	539	64	3	0.2
Irminger	44	443	1831	3	15	4	49	7	1	401	111	1281	147	1	512	142	809	996	5	14	4
	51	9983	4558	4	76	5	312	2	7	2125	145	8128	200	1	3191	218	1983	3275	3	52	4
Labrador	64	3525	3049	6	30	2	203	4	1	3427	209	5812	160	3	966	59	2086	1976	20	8	0.5
	69	969	3314	3	15	11	31	9	1	245	175	2150	129	1	996	713	294	1915	3	16	12
	77	2621	4465	1	106	3	122	44	0.1	1873	57	3588	237	0.3	3442	105	864	5128	0.5	147	5

Basin	Station	Mn					Ni					Zn				
		diss. invent.	part. invent.	sinking rate	$\tau_{tot}$		diss. invent.	part. invent.	sinking rate	$\tau_{tot}$		diss. invent.	part. invent.	sinking rate	$\tau_{tot}$	
		$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$	m/d	d	sd
Iberian	1	6726	408	12	130	6	8236	23	37	854	39	5769	1174	16	32	1
	13	2606	332	1	664	70	11488	167	10	789	84	1355	951	4	67	7
west	21	2134	272	3	280	12	27694	816	11	339	15	2736	536	15	44	2
Europ.	26	2868	204	5	330	63	20682	194	1	12374	2369	1647	552	1	271	52
Icelandic	32	2505	175	9	212	26	19375	193	22	597	74	709	679	76	4	0.4
	38	1018	98	6	151	8	8152	88	11	674	33	790	400	22	11	0.1
Irminger	44	361	312	1	89	25	3611	118	2	544	151	658	757	1	99	27
	51	2317	102	2	1080	74	9212	181	4	1240	85	3668	855	3	171	12
Labrador	64	1833	113	8	162	3	15196	97	3	3987	243	4112	536	3	256	16
	69	152	152	1	129	92	4705	202	1	1902	1361	464	345	3	33	24
	77	1353	461	0.1	2626	80	9488	1006	0.05	13297	407	3177	638	1	582	18

**Table 5:** Dissolved inventories (diss. invent. from <sup>69,85</sup> and from Planquette et al., personal communication, 2019), particulate inventories (part. invent. from <sup>65</sup> and from Planquette et al., personal communication, 2019), sinking rates calculated as the inverse of particle residence time multiplied by the Eq depth layer; total residence time ( $\tau_{tot}$ , in days) calculated by dividing the total inventory (dissolved+particulate) by the

particulate flux and its standard deviation (sd) obtained by calculating  $\tau_{\text{tot}}$  at Eq, Eq+20m or Eq-20m (20m being the average error on the determination of the Eq depth).

## ASSOCIATED CONTENT

### Supporting Information

Figure S1: Summary of the different sampling and analytical steps for the  $>53\mu\text{m}$  particle size fraction, collected on in-situ pump (ISP) filters and for total  $^{234}\text{Th}$  activities, collected via standard CTD rosette. In this figure, each filter is defined by a nominal porosity (in  $\mu\text{m}$ ) and a diameter (corresponding to the symbol  $\emptyset$ , in mm).

Figure S2: Mineral fluxes calculated either by using Al (top panel) or Ti (bottom panel) as lithogenic tracers (in  $\text{mg}/\text{m}^2/\text{d}$ ).

Figure S3: Vertical concentration profiles in the upper 400m (see Table S1 for deeper concentrations) of pTEs and minerals for the  $>53\mu\text{m}$  size fraction along the GEOVIDE transect. There are three plots per element: Station #1 (shown alone because of the extreme values observed for few elements); Iberian, west European and Icelandic basins; Irminger and Labrador basins.

Figure S4: Vertical profiles of pTE: $^{234}\text{Th}$  and mineral: $^{234}\text{Th}$  ratios in the upper 400m for the large size fraction ( $>53\mu\text{m}$ ) along the GEOVIDE transect. There are three plots per element: Station #1 (shown alone because of the extreme values observed for few elements); Iberian, west European and Icelandic basins; Irminger and Labrador basins.

Figure S5: Concentration profiles of the pFe:pAl (mol/mol) and pFe:POC (mmol/mol) ratios, with the Eq depth (horizontal black dotted line), the pFe:pAl ratio in the UCC (vertical brown dashed line, from Taylor and McLenan, 1985) and the pFe:POC ratio in phytoplankton bulk (vertical green dashed line, from Twining et al., 2015). Ratios at Eq determined via the concentrations and the fluxes are indicated below each graph.

Table S1: Trace element concentrations (in nmol/L), mineral concentrations (in  $\mu\text{g}/\text{L}$ ) and  $^{234}\text{Th}$  activities (in dpm/L) for the large size fraction ( $>53\mu\text{m}$ ) along the GEOVIDE transect.

The (\*) indicate depths where POC was collected using a separate ISP unit, 10 to 50 m apart from the ISP dedicated to TEs.

Table S2: Particulate TE:<sup>234</sup>Th (in nmol/dpm) and mineral:<sup>234</sup>Th (in µg/dpm or ng/dpm) ratios in the large size fraction (>53µm), estimated at the Eq depth, along the GEOVIDE transect.

## **AUTHOR INFORMATION**

### **Corresponding Author**

\* Nolwenn Lemaitre (nolwenn.lemaitre@erdw.ethz.ch)

### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### **Notes**

The authors declare no competing financial interest.

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