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Nolwenn Lemaitre, Hélène Planquette, Frédéric Planchon, Géraldine Sarthou, Stéphanie Jacquet, et al.. Particulate barium tracing of significant mesopelagic carbon remineralisation in the North Atlantic. *Biogeosciences*, 2018, 15 (8), pp.2289-2307. 10.5194/bg-15-2289-2018 . hal-02024247

**HAL Id: hal-02024247**

**<https://amu.hal.science/hal-02024247>**

Submitted on 19 Feb 2019

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## Particulate barium tracing of significant mesopelagic carbon remineralisation in the North Atlantic

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Received: 20 September 2017 – Discussion started: 4 October 2017

Revised: 13 February 2018 – Accepted: 16 March 2018 – Published: 19 April 2018

**Abstract.** The remineralisation of sinking particles by prokaryotic heterotrophic activity is important for controlling oceanic carbon sequestration. Here, we report mesopelagic particulate organic carbon (POC) remineralisation fluxes in the North Atlantic along the GEOTRACES-GA01 section (GEOVIDE cruise; May–June 2014) using the particulate biogenic barium (excess barium;  $Ba_{xs}$ ) proxy. Important mesopelagic (100–1000 m)  $Ba_{xs}$  differences were observed along the transect depending on the intensity of past blooms, the phytoplankton community structure, and the physical forcing, including downwelling. The subpolar province was characterized by the highest mesopelagic  $Ba_{xs}$  content (up to  $727 \text{ pmol L}^{-1}$ ), which was attributed to an intense bloom averaging  $6 \text{ mg chl } a \text{ m}^{-3}$  between January and June 2014 and by an intense 1500 m deep convection in the central Labrador Sea during the winter preceding the sampling. This downwelling could have promoted a deepening of the prokaryotic heterotrophic activity, increasing the  $Ba_{xs}$  content. In comparison, the temperate province, characterized by the lowest  $Ba_{xs}$  content ( $391 \text{ pmol L}^{-1}$ ), was sampled during the bloom

period and phytoplankton appear to be dominated by small and calcifying species, such as coccolithophorids. The  $Ba_{xs}$  content, related to oxygen consumption, was converted into a remineralisation flux using an updated relationship, proposed for the first time in the North Atlantic. The estimated fluxes were of the same order of magnitude as other fluxes obtained using independent methods (moored sediment traps, incubations) in the North Atlantic. Interestingly, in the subpolar and subtropical provinces, mesopelagic POC remineralisation fluxes (up to 13 and  $4.6 \text{ mmol C m}^{-2} \text{ d}^{-1}$ , respectively) were equalling and occasionally even exceeding upper-ocean POC export fluxes, deduced using the  $^{234}\text{Th}$  method. These results highlight the important impact of the mesopelagic remineralisation on the biological carbon pump of the studied area with a near-zero, deep ( $> 1000 \text{ m}$ ) carbon sequestration efficiency in spring 2014.

## 1 Introduction

The ocean represents the largest active CO<sub>2</sub> sink (Sabine et al., 2004) partly materialised by the oceanic biological carbon pump (BCP), which controls the export of carbon and nutrients to the deep ocean through the production of biogenic sinking particles (Boyd and Trull, 2007; Sigman and Boyle, 2000; Volk and Hoffert, 1985). The North Atlantic sustains one of the most productive spring phytoplankton blooms of the world ocean (Esaias et al., 1986; Henson et al., 2009; Longhurst, 2010; Pommier et al., 2009). The high primary productivity in combination with the water mass formation there as part of the thermohaline circulation (Seager et al., 2002) results in a particularly efficient BCP in the North Atlantic (Buesseler et al., 1992; Buesseler and Boyd, 2009; Herndl and Reinthaler, 2013; Honjo and Manganini, 1993; Le Moigne et al., 2013b), estimated to contribute up to 18 % of the global oceanic BCP (Sanders et al., 2014). However, the magnitude of the carbon transfer to the deep ocean depends on many factors including the efficiency of bacterial remineralisation within the mesopelagic layer (100–1000 m depth layer). In this layer, most of the particulate organic carbon (POC) exported from the upper mixed layer is respired or released to the dissolved phase as dissolved organic carbon (DOC; Buesseler et al., 2007; Buesseler and Boyd, 2009; Burd et al., 2016; Herndl and Reinthaler, 2013; Lampitt and Antia, 1997; Martin et al., 1987). Mesopelagic remineralisation has often been reported to balance or even exceed the carbon supply from the surface (i.e. POC and DOC; Arístegui et al., 2009; Baltar et al., 2009; Burd et al., 2010; Collins et al., 2015; Fernández-castro et al., 2016; Giering et al., 2014; Reinthaler et al., 2006), highlighting the impact of mesopelagic processes on bathypelagic carbon sequestration. Unfortunately, studies focusing on the mesopelagic layer are scarce, and the remineralisation process in this part of the water column remains poorly constrained. A variety of methods have been used to assess deep remineralisation. The attenuation of the particulate organic matter concentration with depth can be deduced from POC fluxes recorded by bottom-tethered or free-floating neutrally buoyant sediment traps (e.g. Buesseler et al., 2007; Honjo et al., 2008; Martin et al., 1987) deployed at different depths. Bacterial respiration can be assessed by measuring the rate of dissolved oxygen consumption, but this approach is usually limited to the upper 200 m of depth because of sensitivity issues (Arístegui et al., 2005; Christaki et al., 2014; Lefèvre et al., 2008). However, sediment traps and direct respiration measurements are insufficiently reliable for depths exceeding 200 to 500 m (i.e. the lower mesopelagic area). Earlier work has revealed that the accumulation of particulate biogenic barium (excess barium; Ba<sub>xs</sub>) in the mesopelagic water column (100–1000 m) is related with organic carbon remineralisation. This biogenic Ba is essentially carried by barite (BaSO<sub>4</sub>) microcrystals, which form inside oversaturated micro-environments, mostly aggregates of organic material where prokaryotic activity is

intense (Bishop, 1988; Collier and Edmond, 1984; Dehairs et al., 1980; Ganeshram et al., 2003; Gonzalez-Munoz et al., 2003). Bacterial activity will result in the disruption of these aggregates, thereby releasing the barite crystals in the ambient water. As a result, the concentration of Ba<sub>xs</sub> relates with oxygen consumption rate (Dehairs et al., 1997; Shopova et al., 1995) and can be converted into a remineralisation rate of POC in the mesopelagic layer (Dehairs et al., 1997). Ba<sub>xs</sub> has been successfully used as a proxy of POC remineralisation flux in the Southern Ocean (Cardinal et al., 2005; Jacquet et al., 2008a, b, 2011a, 2015; Planchon et al., 2013) and Pacific Ocean (Dehairs et al., 2008).

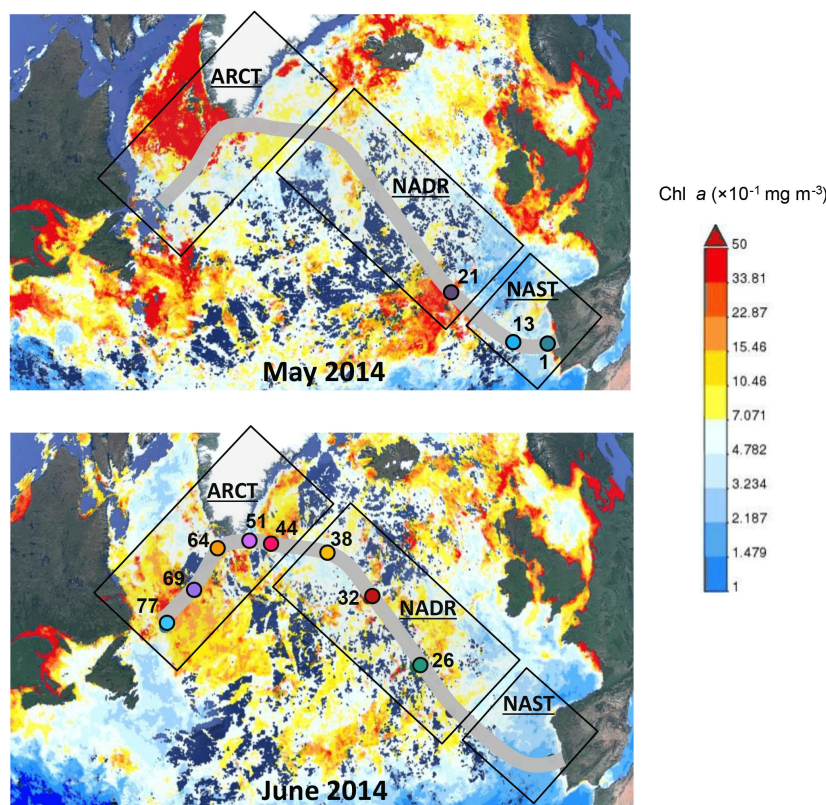
We examined mesopelagic POC remineralisation along the GEOTRACES-GA01 section during the GEOVIDE cruise (15 May–30 June 2014; R/V *Pourquoi Pas?*) by assessing particulate biogenic barium (excess barium; Ba<sub>xs</sub>) contents. This study is the first one to report the use of the Ba<sub>xs</sub> proxy in the North Atlantic. Regional variations in the Ba<sub>xs</sub> distributions along the crossed biogeochemical provinces are discussed regarding the stage and intensity of the bloom, the phytoplankton community structure, and the physical forcing. We reassessed the algorithm between Ba<sub>xs</sub> content and oxygen consumption developed for the Southern Ocean, adapting it for the North Atlantic. We compared the remineralisation fluxes resulting from this new North Atlantic-specific algorithm with those obtained using other methods in the same area. This comparison, in combination with surface primary production (PP) and POC export estimates (Lemaitre et al., 2018; this issue), allowed us to evaluate the fate of POC to the deep ocean and to constrain the BCP in the North Atlantic.

## 2 Methods

### 2.1 Study area

The GEOVIDE section (15 May–30 June 2014; R/V *Pourquoi pas?*) crossed different biogeochemical provinces in the North Atlantic including the North Atlantic subtropical gyre (NAST; Stations 1 and 13), the North Atlantic drift (NADR) covering the West European (Stations 21 and 26) and Icelandic (Stations 32 and 38) basins, and the Atlantic Arctic (ARCT) divided between the Irminger (Stations 44 and 51) and Labrador (Stations 64, 69, and 77) seas (Longhurst, 1995; Figs. 1, 2).

The evolution of chlorophyll *a* (chl *a*) concentrations from satellite imagery (Fig. 1) revealed the decline of the bloom in the NAST and the Labrador Sea and the bloom period within the NADR province and the Irminger Sea. Indeed, the highest daily PP rates were measured in the NADR and in the Irminger Sea (> 150 mmol C m<sup>-2</sup> d<sup>-1</sup>; Fonseca-Batista et al., 2018; this issue; Lemaitre et al., 2018; this issue). The phytoplankton community structure also varied regionally, with diatoms dominating the ARCT province and the West Euro-



**Figure 1.** Satellite-derived chlorophyll *a* concentrations (MODIS Aqua from <http://giovanni.sci.gsfc.nasa.gov/>, last access: September 2017), in milligrams per cubic metre, during the GEOVIDE cruise (May and June 2014). The GEOVIDE transect (grey line) and the main crossed provinces are indicated. NAST: North Atlantic subtropical gyre; NADR: North Atlantic drift; ARCT: Atlantic Arctic. Coloured circles indicate stations sampled at the corresponding month.

pean basin of the NADR, coccolithophorids dominating the Icelandic basin of the NADR, and cyanobacteria dominating the NAST province (Tonnard et al., 2018). Finally, as described elsewhere (Daniault et al., 2016; García-Ibáñez et al., 2015; Kieke and Yashayaev, 2015; Zunino et al., 2017; this issue), these provinces also differ in terms of their hydrographic features. The NADR province is crossed by the subarctic front (SAF), which was located near Station 26 during GEOVIDE (Fig. 2). Strong currents were observed near the Greenland margin (probably influencing Stations 51 and 64), and an intense 1500 m deep convection happened during the winter preceding GEOVIDE in the central Labrador Sea (Station 69) due to the formation of the Labrador Sea Water (LSW) in winter (Fig. 2). These features influenced the magnitude of the carbon export fluxes, as well as the export and transfer efficiencies along the transect (Lemaitre et al., 2018; this issue). The highest POC export fluxes from the upper-ocean (calculated at the depth “*z*” ranging from 40 to 130 m at Stations 44 and 32, respectively) were observed in the NADR province and in the Labrador Sea and reached up to  $10 \text{ mmol C m}^{-2} \text{ d}^{-1}$  at Station 69 (Lemaitre et al., 2018; this issue). Export efficiency (i.e. the ratio of the POC export to the PP) was generally low ( $\approx 10\%$ ), except at Sta-

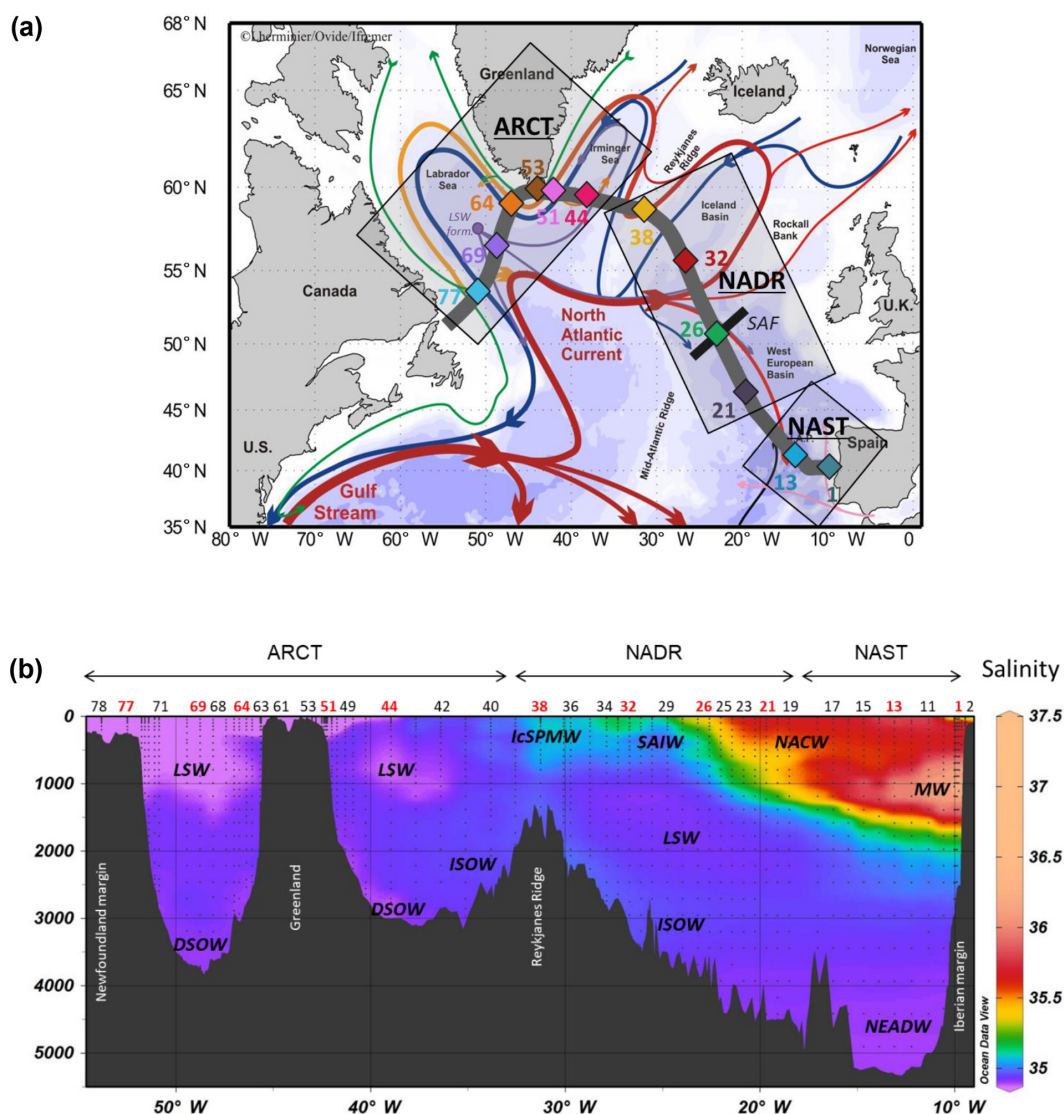
tions 1 and 69 where it reached 35 %. The transfer efficiency (defined as the ratio of the POC export at  $z + 100 \text{ m}$  to the POC export at  $z$ ) was more variable, ranging from 30 % at Station 69 to 78 % at Station 32 (Lemaitre et al., 2018; this issue).

## 2.2 Sampling and analyses

For different objectives, during GEOVIDE, suspended particles were collected using different sampling techniques. The main goal of the Niskin sampling was to derive  $\text{Ba}_{\text{xs}}$  concentrations and, thus, carbon remineralisation fluxes in the mesopelagic zone (high resolution in the 100–1000 m layer) at stations where PP data and carbon export fluxes were also determined. The goal of the Go-Flo sampling was, at first, dedicated to the determination of all dissolved and particulate trace elements and their isotopes. Since particulate Ba and Al were determined on samples collected by both sampling techniques, we took the opportunity to compare both datasets in order to assess the quality of our data.

1.  $\text{Ba}_{\text{xs}}$  concentrations measured in samples collected using a standard CTD rosette equipped with 12 L Niskin bottles. At 11 stations, 18 depths were generally sam-





**Figure 2.** (a) Schematic of the circulation features, adapted from García-Ibáñez et al. (2015). Bathymetry is plotted in colour 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. 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. (b) Salinity along the GEOVIDE section and associated water masses are as follows: LSW: Labrador Sea Water; ISOW: Iceland–Scotland Overflow Water; IcSPMW: Iceland Subpolar Mode Water; SAIW: Subarctic Intermediate Water; NACW: North Atlantic Central Water; MW: Mediterranean water; DSOW: Denmark Strait Overflow Water; NEADW: North East Atlantic Deep Water. Station labels in red indicate sites where Niskin casts were sampled. NAST: North Atlantic subtropical gyre; NADR: North Atlantic drift; ARCT: Atlantic Arctic. Data were plotted using ODV software (Schlitzer, 2017).

pled between the surface and 1500 m in order to cover a high vertical resolution in the mesopelagic layer (Table S1 in the Supplement). An amount of 4 to 8 L of sea-water was filtered on acid-cleaned polycarbonate membranes of 0.4 µm porosity (Nuclepore®, 47 or 90 mm diameter). Filter membranes were rinsed with Milli-Q-grade water (18.2 MΩ cm; ≤ 5 mL) to remove sea salt, dried at ambient temperature under a laminar flow hood,

and finally stored in clean petri slides until analysis in the home-based laboratory.

Filters were totally digested overnight with a concentrated tri-acid mixture (1.5 mL HCl/1 mL HNO<sub>3</sub>/0.5 mL HF; all Merck Suprapur grades) using clean Teflon vials (Saville®) on a hot plate at 90 °C. The acid solution was then evaporated at 110 °C until near dryness and the residue dissolved

in 13 mL 0.32 M  $\text{HNO}_3$  (Merck; distilled Normapur). The solutions were transferred to polypropylene tubes (VWR) and analysed for barium (Ba), aluminium (Al), and other major and minor elements using an inductively coupled plasma quadrupole mass spectrometer (ICP-QMS; X Series 2 Thermo Fisher) equipped with a collision cell technology (CCT). We used a concentric quartz nebulizer ( $1 \text{ mL min}^{-1}$ ) and nickel sample and skimmer cones. During the analyses, internal standards (Ru, In, Re, and Bi) were added to samples in order to monitor and correct the instrumental drift and matrix-dependent sensitivity variations.

Two multi-element artificial standard solutions were prepared for external calibration. The first contained major elements (Na, Mg, Al, Ca, and Ti) and the second was prepared with minor elements (Sr, Ba, REEs, Th, and U). Standards were prepared with dilution of the multi-element mixed standard stock solutions to span the expected range of sample concentrations, with concentrations in the standard curve spaced to cover potential sample variations.

The accuracy and precision of our analyses were assessed using the following Certified Reference Materials (CRM): BHVO-1, JB-3, JGb-1, and SLRS-5 (Table 1).

The detailed procedure for sample preparation and analysis is given in Cardinal et al. (2001).

2.  $\text{Ba}_{\text{xs}}$  concentrations measured in samples collected using the trace metal clean rosette, equipped with 22 12 L Go-Flo bottles at higher spatial resolution (31 stations) but with lower vertical resolution in the mesopelagic layer. Details about filtration, sample processing, and analyses can be found in Gourain et al. (2018; this issue). Briefly, at each depth, two size fractions were investigated:  $0.45\text{--}5 \mu\text{m}$  using polysulfone filters (Supor®) and  $>5 \mu\text{m}$  using mixed ester cellulose filters (Millipore®). Between 2 and 5 L of seawater was filtered for the upper water column (surface to 100 m) and 10 L for depths exceeding 100 m. Excess seawater from the filters was drawn off and then the filters were frozen in acid-cleaned petri dishes until home analysis. In the laboratory, filters were digested with a solution of 8 M  $\text{HNO}_3$  (Ultrapur grade, Merck) and 2.3 M HF (Suprapur grade, Merck). Vials were then refluxed at  $130^\circ\text{C}$  on a hotplate for 4 h. After gentle evaporation, the residue was redissolved with approximately 2 mL of 0.32 M  $\text{HNO}_3$  spiked with  $1 \mu\text{g L}^{-1}$  of indium. Solutions were analysed using a sector field inductively coupled plasma mass spectrometer (Element 2, Thermo) following the method of Planquette and Sherrell (2012). Total Ba and Al concentrations were calculated by summing the two size fractions. The accuracy

**Table 1.** Particulate barium (Ba) and aluminium (Al) concentrations and resulting recoveries of the certified reference materials SLRS-5 (river water), BHVO-1 (basalt powder), JB-3 (basalt powder), and JGb-1 (gabbro powder).

	Ba	Al
SLRS-5 ( $\mu\text{g kg}^{-1}$ )	$13 \pm 1$	$47 \pm 2$
$n = 4$	95 %	95 %
BHVO-1 ( $\mu\text{g g}^{-1}$ )	$129 \pm 1$	$70118 \pm 984$
$n = 4$	93 %	96 %
JB-3 ( $\mu\text{g g}^{-1}$ )	$229 \pm 13$	$92144 \pm 1620$
$n = 4$	94 %	101 %
JGb-1 ( $\mu\text{g g}^{-1}$ )	$68 \pm 15$	$91491 \pm 732$
$n = 4$	106 %	99 %

and precision of these analyses were assessed using the BCR-414 CRM (see Gourain et al., 2018; this issue).

For both Niskin and Go-Flo samples, the  $\text{Ba}_{\text{xs}}$  concentrations were calculated by subtracting the particulate lithogenic barium (pBa-litho) from the total particulate barium (pBa). The pBa-litho was determined by multiplying the particulate aluminium (pAl) concentration by the upper continental crust (UCC) Ba : Al molar ratio ( $0.00135 \text{ mol mol}^{-1}$ ; Taylor and McLennan, 1985). Along the GEOVIDE section, the pBa-litho fraction represented less than 7 % of total barium, except at Stations 1 and 53, close to the Iberian and Greenland margin where pBa-litho accounted for 28 and 44 % of total Ba, respectively. Because of the rather large uncertainty associated with the UCC Ba : Al ratio and because of the high lithogenic particle loads at Stations 1 and 53, those stations were not considered further in this study. Uncertainties on  $\text{Ba}_{\text{xs}}$  concentrations were estimated using error propagation and ranged between 6 and 25 %.

For stations where total pBa and pAl concentrations were available at similar depths, the regression of  $\text{Ba}_{\text{xs}}$  concentrations (100–1000 m layer) from the Go-Flo samples vs. those of the Niskin samples was significant (regression slope: 0.87;  $R^2$ : 0.61;  $p < 0.01$ ;  $n = 66$ ; Fig. S1 in the Supplement) despite some discrepancies, especially in the higher concentration domain. Such discrepancies could have resulted from differences in the chemical protocols and most likely the filters used. The Niskin samples collected on  $0.4 \mu\text{m}$  polycarbonate filters were digested using a tri-acid mix (50 %  $\text{HCl}$  / 33 %  $\text{HNO}_3$  / 17 %  $\text{HF}$ ), while the Go-Flo samples collected on paired  $0.45 \mu\text{m}$  polyestersulfone /  $5 \mu\text{m}$  mixed ester cellulose filters were digested using a 50 %  $\text{HNO}_3$  / 10 %  $\text{HF}$  acid mix. The use of different filter types has been shown to lead to different concentrations, depending on the element of consideration, despite using the same digestion technique (Planquette and Sherrell, 2012). The addition of  $\text{HCl}$  has been shown to not improve elemental recoveries of marine particles (Ohnemus and Lam, 2014) but the larger  $\text{HF}$  con-

centration of the tri-acid mix used for digesting the Niskin samples, likely, dissolved more of the refractory particles, explaining the slightly higher concentrations obtained for these samples.

In addition, filtered suspended matter was also analysed using a field emission scanning electron microscope (FE-SEM; JEOL JSM-7100F) to detect the presence of barite particles (Fig. 3). Because of time-consuming analyses, seven filters from the different basins were scanned: six samples with high mesopelagic  $\text{Ba}_{\text{xs}}$  concentrations (Station 13 at 400 m; Station 38 at 300 m; Station 44 at 300 and 700 m; Station 69 at 600 m, and Station 77 at 300 m) and one sample with high surface  $\text{Ba}_{\text{xs}}$  concentrations (Station 26 at 50 m). For each sample, a filter surface of  $0.5 \text{ cm}^2$  was analysed.

To verify the relationship between  $\text{Ba}_{\text{xs}}$  and barite particles (see Sect. 4.1), we evaluated the contribution of the barite particles to  $\text{Ba}_{\text{xs}}$  concentrations for the sample collected at 600 m at Station 69 and which has a high mesopelagic  $\text{Ba}_{\text{xs}}$  content (see Sect. 3). Using the FE-SEM, 0.003 % of the total filter surface was scanned and size and volume of all detected barite particles present in this surface area were assessed. To this aim, each barite particle was pictured using a magnification setting between 12 000 and 15 000 $\times$ . Images were then analysed with the software ImageJ and, for each barite particle, the longest and shortest axes were measured and pixels were converted to nanometres. Barite particles were then assimilated to ellipses to calculate their volume. Finally, the concentration of pBa of each barite particle was calculated using Eq. (1):

$$\text{pBa in barite} = \frac{\sum [V \times \mu_{\text{BaSO}_4} \times (M_{\text{Ba}}/M_{\text{BaSO}_4})]}{V_{\text{SW}}}, \quad (1)$$

where  $V$  is the volume of the barite particle (between  $0.01$  and  $3.96 \mu\text{m}^3$ ),  $\mu_{\text{BaSO}_4}$  is the density of barite ( $4.45 \text{ g cm}^{-3}$ ),  $M_{\text{Ba}}/M_{\text{BaSO}_4}$  is the molar proportion of barium in  $\text{BaSO}_4$  (0.59), and  $V_{\text{SW}}$  is the volume of seawater filtered (equivalent to  $0.2 \text{ mL}$  for the portion of filter surface analysed).

### 3 Results

#### 3.1 Particulate biogenic $\text{Ba}_{\text{xs}}$ distribution

##### 3.1.1 Section overview

The  $\text{Ba}_{\text{xs}}$  longitudinal section of concentrations (Fig. 4) shows elevated concentrations between 100 and 1000 m, in the mesopelagic layer ( $333 \pm 224 \text{ pmol L}^{-1}$ ; median  $\pm 1 \text{ SD}$ ;  $n = 209$ ). In comparison, the surface ocean (depths  $< 100 \text{ m}$ ) and the deep ocean (depths  $> 1000 \text{ m}$ ) are characterized by lower median values ( $94$  and  $114 \text{ pmol L}^{-1}$ ,  $n = 113$  and  $199$ , respectively). Exceptions can be observed for the upper waters at Stations 25 and 26 and bottom waters at Stations 29, 32, 36, 38, and 71, where high  $\text{Ba}_{\text{xs}}$  concentrations may be attributed to Ba assimilation by phytoplank-

ton and sediment resuspension, respectively (Gourain et al., 2018; this issue). Concentrations ranged from 4 (Station 11, 55 m) to  $24\,643 \text{ pmol L}^{-1}$  (Station 26, 35 m) in surface waters and from 7 (Station 71, 350 m) to 1388 (Station 15, 300 m)  $\text{pmol L}^{-1}$  in the mesopelagic layer (100–1000 m). For the mesopelagic layer, where the maximum  $\text{Ba}_{\text{xs}}$  concentrations were generally observed, the highest  $\text{Ba}_{\text{xs}}$  concentration was observed in the NAST province, reaching  $1388 \text{ pmol L}^{-1}$  at 300 m of Station 15. These maxima occurred between 200 and 600 m but were spread over larger depth intervals in the ARCT province, where high  $\text{Ba}_{\text{xs}}$  values occurred until 1200 m depth at Station 69.

##### 3.1.2 Individual profiles

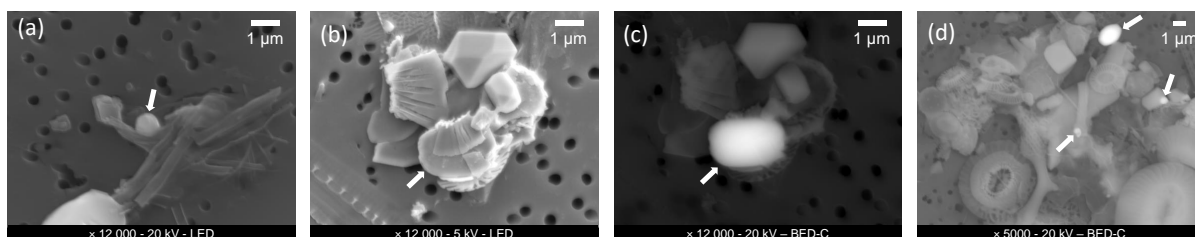
In this section, we only present  $\text{Ba}_{\text{xs}}$  concentrations obtained from Niskin bottles. This is because (i) both data sets converge (regression slope: 0.87;  $R^2$ : 0.61;  $p < 0.01$ ;  $n = 66$ ); (ii) Niskin casts had a better sampling resolution in the 100–1000 m layer; and (iii) Niskin casts were also used for the determination of POC export using the 234-Th deficit method (see Lemaitre et al., 2018; this issue).

All the vertical  $\text{Ba}_{\text{xs}}$  profiles (Fig. 5) show increased concentrations between 100 and 1000 m, followed by lower concentrations deeper that tend to return to a background level of  $180 \pm 54 \text{ pmol L}^{-1}$  ( $n = 10$ ) as the average along the GEOVIDE transect. This background value is quite characteristic for the deep ocean ( $> 1000 \text{ m}$ ) and is considered to represent the residual  $\text{Ba}_{\text{xs}}$  left over after partial dissolution and sedimentation of  $\text{Ba}_{\text{xs}}$  produced during previous phytoplankton growth events (Dehairs et al., 1997).

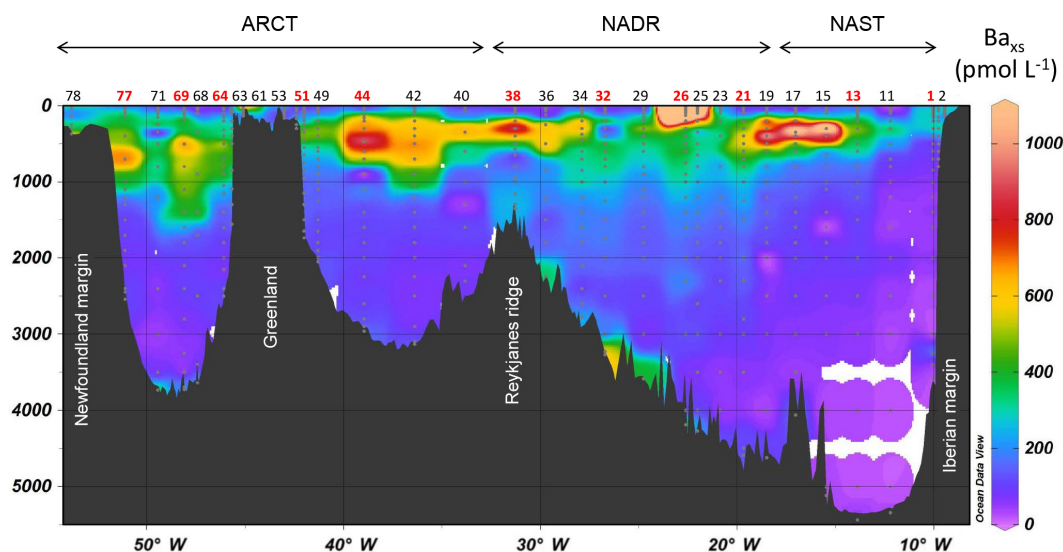
In the NAST province (Station 13), the  $\text{Ba}_{\text{xs}}$  concentrations steadily increased from the surface to 400 m, reaching  $961 \text{ pmol L}^{-1}$ , then decreased with depth, reaching the background level of  $180 \text{ pmol L}^{-1}$  at 1500 m.

In the West European basin of the NADR province, vertical profiles of  $\text{Ba}_{\text{xs}}$  were similar, yet concentrations in the mesopelagic layer were smaller at Station 21 with  $\text{Ba}_{\text{xs}}$  peaking only at  $524 \text{ pmol L}^{-1}$ .  $\text{Ba}_{\text{xs}}$  concentrations returned to the background value at 1200 m.  $\text{Ba}_{\text{xs}}$  concentration in surface waters of Station 26 were the highest of the entire section reaching  $1888 \text{ pmol L}^{-1}$  at 50 m (note that the value for the Go-Flo sample at 35 m reaches  $24\,643 \text{ pmol L}^{-1}$ ; Sect. 3.1.1). Below this depth,  $\text{Ba}_{\text{xs}}$  concentrations decreased back to the background level at 100 m, then increased again, with a second peak of  $451 \text{ pmol L}^{-1}$  at 200 m. In the Icelandic basin of the NADR province,  $\text{Ba}_{\text{xs}}$  concentrations were relatively high, reaching 646 and  $711 \text{ pmol L}^{-1}$  at 200 and 300 m at stations 32 and 38, respectively. Station 38 was characterized by a double  $\text{Ba}_{\text{xs}}$  peak at 300 and 700 m. Below this second maximum,  $\text{Ba}_{\text{xs}}$  concentrations decreased to the background level at 1000 m for both stations.

In the ARCT province, a similar double peak profile was observed at Station 44, in the Irminger Sea, with  $\text{Ba}_{\text{xs}}$  concentrations reaching  $750 \text{ pmol L}^{-1}$  between 200 and 400 m



**Figure 3.** Barite particles observed with the FE-SEM at (a) Station 38 (300 m), (b, c) Station 44 (700 m), and (d) Station 69 (600 m). Panel (c) shows the backscattered electron image of the aggregate in (b) highlighting the shape of the partly hidden barite crystal. White arrows indicate the position of barite crystals.



**Figure 4.** Section of the particulate biogenic barium ( $\text{Ba}_{\text{xs}}$ ) ( $\text{pmol L}^{-1}$ ) determined in samples collected with the Go-Flo bottles. Stations labelled in red are those where profiles were also obtained from Niskin casts. Data were plotted using the ODV software (Schlitzer, 2017).

and  $820 \text{ pmol L}^{-1}$  at 700 m. Then,  $\text{Ba}_{\text{xs}}$  concentrations returned to the background value at 1100 m. Close to the Greenland margin (Station 51),  $\text{Ba}_{\text{xs}}$  concentrations reached a maximum of  $495 \text{ pmol L}^{-1}$  at 300 m, which was lower than the maxima determined at the other stations of the ARCT province.

The  $\text{Ba}_{\text{xs}}$  concentrations of Stations 44 and 51 were compared to those obtained at Station 11 ( $63.5^\circ \text{ N}$ – $324.8^\circ \text{ E}$ ) and Station 5 ( $56.9^\circ \text{ N}$ – $317.2^\circ \text{ E}$ ) of the GEOSECS cruise, in summer 1970 (Brewer et al., unpublished results; Fig. 5). The  $\text{Ba}_{\text{xs}}$  concentrations obtained at GEOSECS Station 11 vary over a similar range to those for GEOVIDE Station 44 ( $173$ – $658 \text{ pmol L}^{-1}$  and  $116$ – $823 \text{ pmol L}^{-1}$ , respectively). Similar ranges were also observed between GEOSECS Station 5 and GEOVIDE Station 51 ( $170$ – $402 \text{ pmol L}^{-1}$  and  $127$ – $359 \text{ pmol L}^{-1}$ , respectively).

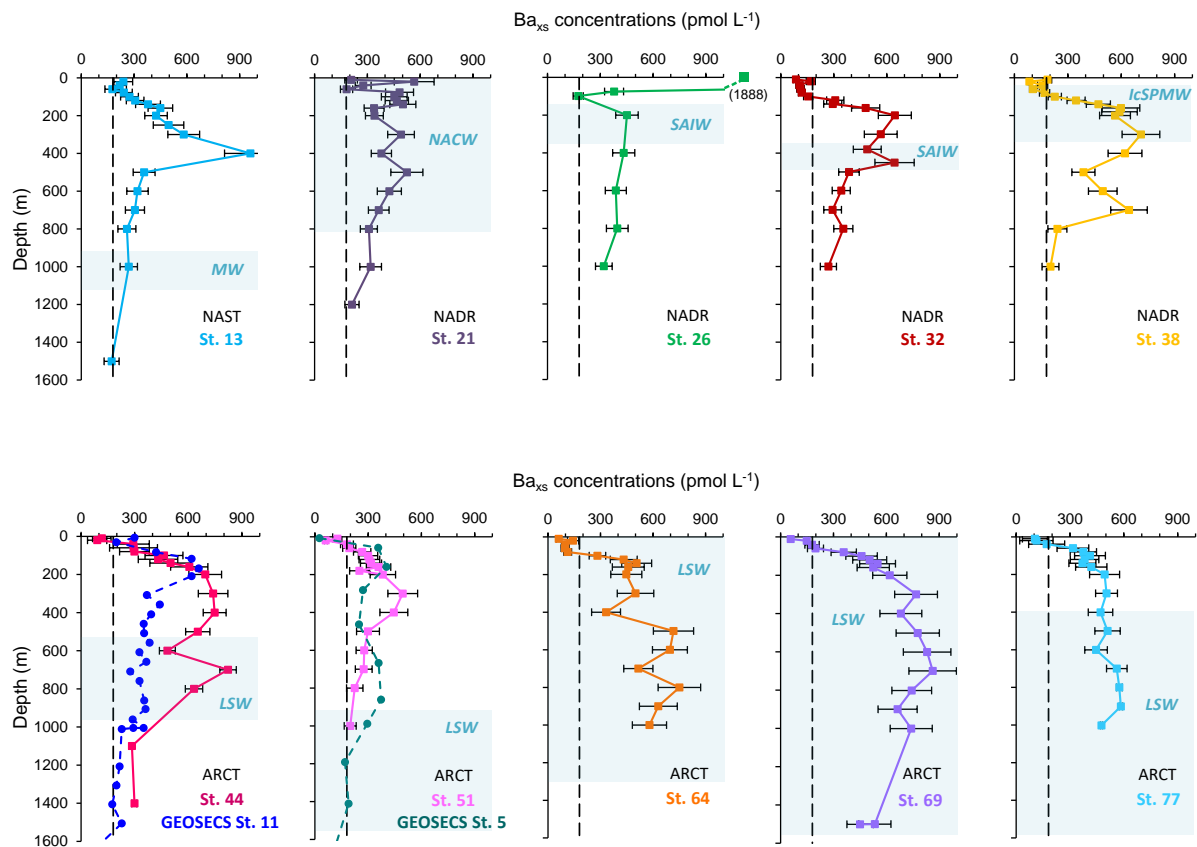
In the Labrador Sea (Stations 64, 69, and 77), high  $\text{Ba}_{\text{xs}}$  concentrations ( $>450$  and up to  $863 \text{ pmol L}^{-1}$  at Station 69) extended to at least 1000 m, without returning to the background level as compared to the other stations out-

side the Labrador Sea. Results for Go-Flo samples indicated that  $\text{Ba}_{\text{xs}}$  concentrations decreased to the background level ( $180 \text{ pmol L}^{-1}$ ) at 1300, 1700, and 1200 m for Stations 64, 69, and 77, respectively.

### 3.2 Mesopelagic $\text{Ba}_{\text{xs}}$

The  $\text{Ba}_{\text{xs}}$  concentrations were integrated (trapezoidal integration) over two depth intervals of the mesopelagic layer (100–500 m and 100–1000 m; Table 2) to obtain depth-weighted average (DWA)  $\text{Ba}_{\text{xs}}$  values.

The DWA  $\text{Ba}_{\text{xs}}$  values between 100 and 500 m ranged from  $399$  to  $672 \text{ pmol L}^{-1}$  and from  $315$  to  $727 \text{ pmol L}^{-1}$  between 100 and 1000 m (Stations 51 and 69, respectively). The DWA  $\text{Ba}_{\text{xs}}$  values varied by less than a factor of 1.4 between both modes of integration. Only for the Labrador Sea (Stations 64, 69, and 77) were the DWA  $\text{Ba}_{\text{xs}}$  values for the 100–1000 m larger than for the 100–500 m interval. For the latter stations, the  $\text{Ba}_{\text{xs}}$  inventories for the interval between 100 m and the depths where concentrations decreased to background level (1300, 1700, and 1200 m for Go-Flo



**Figure 5.** Vertical profiles of  $Ba_{XS}$  concentrations ( $\text{pmol L}^{-1}$ ) determined from Niskin casts during the GEOVIDE (squares) and GEOSECS (circles) cruises. The vertical black dashed line (at  $180 \text{ pmol L}^{-1}$ ) represents the deep-ocean  $Ba_{XS}$  value (or  $Ba_{XS}$  background signal; Dehairs et al., 1997). The approximate depth range of the major water masses is also indicated in blue shading.

**Table 2.** Depth-weighted average (DWA) values of mesopelagic  $Ba_{XS}$  ( $\text{pmol L}^{-1}$ ) for the 100–500 m and 100–1000 m depth intervals. The biogeochemical provinces defined by Longhurst et al. (1995) are also indicated: NAST: North Atlantic subtropical gyre; NADR: North Atlantic drift; ARCT: Atlantic Arctic.

Province	Station	Latitude (° N)	Longitude (° E)	DWA $Ba_{XS}$ 100–500 m ( $\text{pmol L}^{-1}$ )	DWA $Ba_{XS}$ 100–1000 m ( $\text{pmol L}^{-1}$ )
NAST	13	41.4	−13.9	$578 \pm 89$	$419 \pm 71$
NADR	21	46.5	−19.7	$428 \pm 69$	$394 \pm 64$
	26	50.3	−22.6	$405 \pm 59$	$391 \pm 58$
	32	55.5	−26.7	$522 \pm 81$	$413 \pm 66$
	38	58.8	−31.3	$572 \pm 86$	$465 \pm 78$
ARCT	44	59.6	−38.9	$678 \pm 104$	$633 \pm 98$
	51	59.8	−42	$399 \pm 72$	$315 \pm 58$
	64	59.1	−46.1	$464 \pm 95$	$566 \pm 99$
	69	55.8	−48.1	$672 \pm 111$	$727 \pm 118$
	77	53	−51.1	$472 \pm 80$	$505 \pm 83$

casts at Stations 64, 69, and 77, respectively) were somewhat smaller than for the inventories between 100 and 1000 m (up to 1.5 times in the case of Station 77). To facilitate inter-comparison among stations, we consistently considered  $Ba_{XS}$

inventories over the 100–1000 m depth interval in the following discussion.

Within the NAST province, Station 13 was characterized by a relatively low DWA  $Ba_{XS}$  value of  $419 \text{ pmol L}^{-1}$ .



Similarly, low median DWA  $Ba_{xs}$  contents were observed within the NADR province ( $403 \pm 34 \text{ pmol L}^{-1}$ ,  $n = 4$ ), with the lowest DWA  $Ba_{xs}$  observed at Station 26 ( $391 \pm 58 \text{ pmol L}^{-1}$ ).

The highest median DWA  $Ba_{xs}$  value was observed in the ARCT province ( $566 \pm 155 \text{ pmol L}^{-1}$ ,  $n = 5$ ). There, the DWA  $Ba_{xs}$  contents were more variable between stations, ranging from  $315 \text{ pmol L}^{-1}$  at Station 51 to  $727 \text{ pmol L}^{-1}$  at Station 69, with a high DWA  $Ba_{xs}$  also observed at Station 44 ( $633 \text{ pmol L}^{-1}$ ).

## 4 Discussion

### 4.1 Barite is the main carrier of $Ba_{xs}$

Several barite particles were observed associated with or in close proximity to biogenic fragments such as coccoliths (Fig. 3), suggesting they were originally formed inside biogenic micro-environments as proposed by others (Bishop, 1988; Dehairs et al., 1980; Stroobants et al., 1991). However, no barite crystals were observed in the surface waters at Station 26 where very high  $Ba_{xs}$  concentrations were recorded (up to  $1888 \text{ pmol L}^{-1}$ ), most likely the result of Ba uptake and/or adsorption by biota, as reported by Sternberg et al. (2005) for culture experiments. This result was expected as it fits in the concept of barite formation proposed by Stroobants et al. (1991), showing that the barium sulfate in biogenic aggregates of surface waters is not crystallised, whereas below this surface layer, when organic matter degradation occurs, barite is present as discrete micron-sized particles.

Regarding the contribution of the barite particles to the  $Ba_{xs}$  concentration for the sample collected at 600 m of Station 69, we assumed that the small filter portion (only 0.003 % of the total filter surface was analysed by FE-SEM) is representative of the whole filter. The Ba concentration deduced from the FE-SEM particle sizing analysis and using Eq. (1) is  $1260 \text{ pmol L}^{-1}$ . This is of the same order of magnitude, although 1.5 times larger, as the concentration of total  $Ba_{xs}$  obtained by ICP-MS ( $831 \text{ pmol L}^{-1}$ ) after whole filter digestion. The similarity between both values is remarkable considering the limitations of the FE-SEM procedure (the very small fraction of filter analysed). This also confirms that  $Ba_{xs}$  in the mesopelagic layer is carried mostly by barite particles, as observed earlier (Dehairs et al., 1980).

### 4.2 Factors influencing the DWA $Ba_{xs}$ in the North Atlantic

#### 4.2.1 Influence of the intensity and stage of the bloom

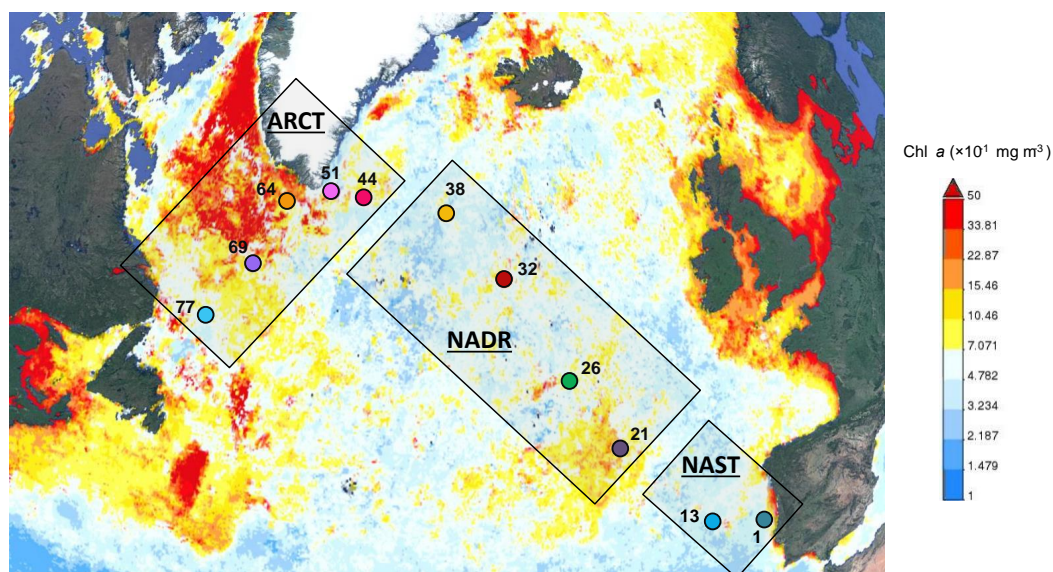
We compared our  $Ba_{xs}$  inventories with the average biomass development from January to June 2014 (Fig. 6), which covers the entire productive period in the North Atlantic, starting from winter till the date of our sampling.

Along the GEOVIDE transect, the most productive area was clearly the Labrador Sea of the ARCT province, where chl *a* concentrations averaged  $6 \text{ mg m}^{-3}$  (Fig. 6). This basin was sampled during the decline of the bloom (Fig. 1; chl *a* concentration was  $> 3 \text{ mg m}^{-3}$  1 month before the sampling, and PP and nutrient concentrations were low during sampling). The high DWA  $Ba_{xs}$  observed in this area (Table 2) likely results from the large biological activity during the period preceding sampling. The West European basin of the NADR province, and in particular the area around Station 21, was also characterized by a high phytoplankton biomass between January and June (Fig. 6), though lower than in the Labrador Sea. Here, the bloom started in May (Fig. 1; chl *a* concentration  $\approx 3 \text{ mg m}^{-3}$ , 1 month before the sampling) and was still in progress during the sampling, as indicated by the high PP ( $135 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ). These features can explain the lower DWA  $Ba_{xs}$  observed at Station 21 (Table 2) compared to the Labrador Sea. The other stations of the NADR (Stations 26, 32, and 38) were sampled during the bloom development (Fig. 1) with high PP reaching  $174 \text{ mmol m}^{-2} \text{ d}^{-1}$  at Station 26. The latter stations were characterized by lower DWA  $Ba_{xs}$  values compared to other stations, pointing to a time lag between the phytoplankton bloom and the build-up of the  $Ba_{xs}$  signal. However, this was not the case for Station 44, in the Irminger Sea of the ARCT province, which was sampled during the bloom (high PP, high chl *a*, and high nutrient concentrations during the sampling period) and characterized by one of the highest DWA  $Ba_{xs}$  values, possibly reflecting an important past bloom.

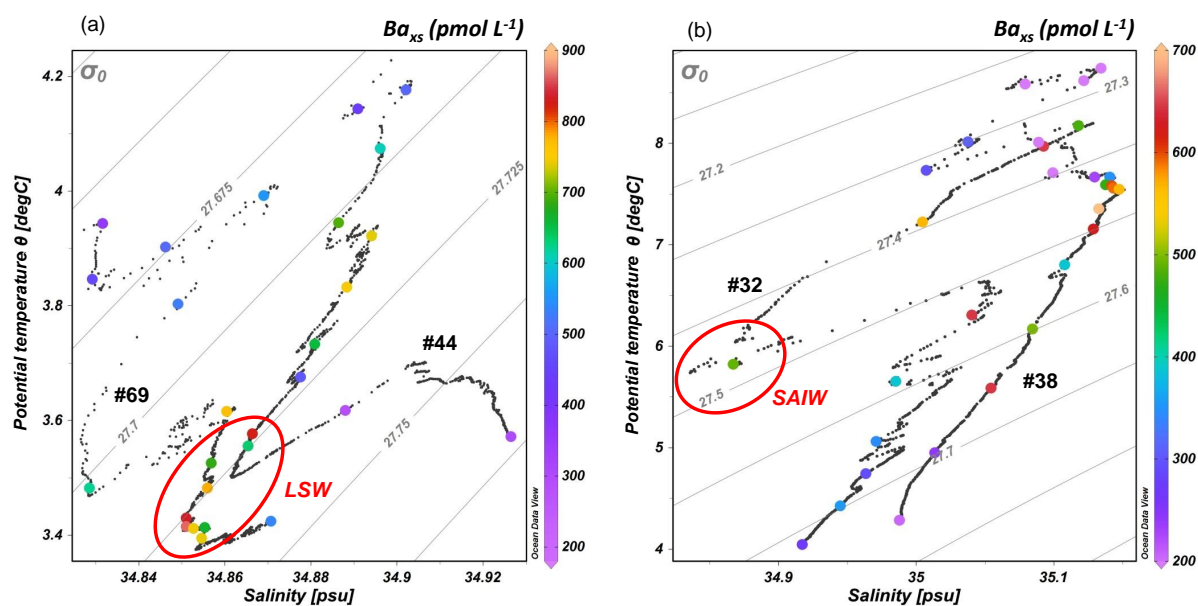
As also indicated by others, the mesopelagic  $Ba_{xs}$  signal builds up during the growth season and therefore integrates effects of past surface production (Dehairs et al., 1997; Cardinal et al., 2001, 2005). The large regional and temporal variability in the bloom development stage thus results in a large variability in the mesopelagic  $Ba_{xs}$  signal in the North Atlantic.

#### 4.2.2 Influence of water masses and physical forcing

The Labrador Sea (Stations 64, 69, and 77) had the largest  $Ba_{xs}$  inventory coinciding with the presence of the Labrador Sea Water (LSW; potential temperature between 2.7 and 3.8 °C and salinity below 34.9; Harvey, 1982; Yashayaev, 2007) in the upper 1500 m. The LSW formation takes place in the central Labrador Sea, where convection reached  $\sim 1700 \text{ m}$  during the winter preceding GEOVIDE (Fig. 2; Kieke and Yashayaev, 2015). The deepening of the mixed layer has been recently shown to represent a major mechanism to convey organic carbon to the mesopelagic zone (from 23 to  $> 100 \%$  in high-latitude regions; Dall'Olmo et al., 2016), supporting the carbon demand of the mesopelagic food web (Burd et al., 2010; Aristegui et al., 2009). Moreover, the highest mesopelagic prokaryotic heterotrophic abundance during GEOVIDE was observed in the central Labrador Sea (Station 69), reaching  $896 \text{ cells } \mu\text{L}^{-1}$  at 500 m,



**Figure 6.** Map of time-averaged chlorophyll *a* concentrations ( $\text{mg m}^{-3}$ ) for the period from January to June 2014 (monthly 4 km MODIS Aqua model; <http://giovanni.sci.gsfc.nasa.gov/>, last access: September 2017).



**Figure 7.** Potential temperature  $\theta$  – salinity plots with isopycnals for Stations (a) 44 and 69 and (b) 32 and 38 of the GEOVIDE cruise, with focus on the 50–2000 m depth interval. Coloured dots represent the discrete samples analysed for  $\text{Ba}_{\text{xs}}$  with the concentration scale on the right. LSW: Labrador Sea Water; SAIW: Subarctic Intermediate Water. Data were plotted using the ODV software (Schlitzer, 2017).

while the median values at the other stations for which bacterial cell numbers were available for the mesopelagic zone (Stations 13, 21, 26, 32, and 38), reached only  $258 \pm 60$  cells  $\mu\text{L}^{-1}$  at similar depth (Julie Laroche, Jennie-Marie Ratten and Ryan Barkhouse, personal communication, 2017). Therefore, the LSW subduction area appears to reinforce the microbial loop by increasing the layer in which the bacteria

can thrive feeding on increased food supplies. This condition appears to increase the  $\text{Ba}_{\text{xs}}$  inventory.

The LSW was also present in the Irminger Sea between 500 and 1000 m at Station 44 (Fig. 2). In the temperature–salinity plot, the high  $\text{Ba}_{\text{xs}}$  concentrations of the second peak ( $823 \text{ pmol L}^{-1}$  at 700 m; Fig. 5) are clearly associated with the presence of LSW (Fig. 7a), suggesting that this second deeper  $\text{Ba}_{\text{xs}}$  maximum represents an advected signal. We cal-

culated the DWA  $Ba_{xs}$  without taking into account the second peak (100–600 m depth interval) and subtracted it from the total DWA  $Ba_{xs}$  (100–1000 m depth interval) to estimate the advected signal. At Station 44, the advected  $Ba_{xs}$  signal represents some  $89 \text{ pmol L}^{-1}$ , or 14 %, of the total signal, which is within the uncertainty of the remineralisation flux calculation (see later below). Similarly, at Station 32 the temperature–salinity plot (Fig. 7b) points out that the second  $Ba_{xs}$  peak (at 450 m; Fig. 5) was related to the presence of the Subarctic Intermediate Water (SAIW; temperature of  $5.6 \pm 0.1^\circ\text{C}$  and salinity of  $34.70 \pm 0.02$ ; Alvarez et al., 2004), which contributes  $14 \text{ pmol L}^{-1}$  (3 %) of the total signal. Association of  $Ba_{xs}$  maxima with water masses is not always clear, as is evident from the case of Station 38 where the second  $Ba_{xs}$  maximum at 700 m (Fig. 5) does not coincide with a specific water mass (Fig. 7). In this case, the deep  $Ba_{xs}$  maximum may possibly result from remineralisation generated by larger or heavier organic aggregates reaching greater depths. At the remaining stations there was no evidence of water mass influence. Overall, lateral transport influencing the local  $Ba_{xs}$  distributions was observed at two stations during GEOVIDE but did not significantly modify the magnitude of the local mesopelagic  $Ba_{xs}$  inventory. However, the subduction occurring in the Labrador Sea resulted in larger mesopelagic DWA  $Ba_{xs}$ , probably due to high organic export and associated prokaryotic heterotrophic activity in these areas.

#### 4.2.3 Influence of the phytoplankton community structure

The different  $Ba_{xs}$  inventories may also be influenced by the differences in phytoplankton community compositions.

The ARCT province was dominated by diatoms (median value:  $63 \pm 19\%$  of the total phytoplankton community taxa; Tonnard et al., 2018) and was characterized by the highest DWA  $Ba_{xs}$  values while the NAST and NADR provinces were characterized by higher abundance of haptophytes (median value:  $43 \pm 16\%$  of the total phytoplankton community taxa; Tonnard et al., 2018) and by lower  $Ba_{xs}$  inventories. Coccolithophorids are part of the haptophyte family and their dominance was confirmed by visual observations on filters (surface down to 400 m) using a FE-SEM. Calcifiers, such as coccolithophorids, have been shown to be more efficient in transferring carbon to the deep ocean compared to diatoms (Francois et al., 2002; Klaas and Archer, 2002; Lam et al., 2011). This difference could result from the low compaction or the high fluffiness of diatom aggregates, the high degree of degradability of organic compounds within diatom aggregates, the greater density of calcite, the resistance of calcite to grazing, and the more refractory nature of the exported organic matter associated with calcite (Bach et al., 2016; Francois et al., 2002; Klaas and Archer, 2002; Lam et al., 2011; Le Moigne et al., 2013a; Ragueneau et al., 2006). Therefore,

enhanced particle degradation when diatoms are predominant seems to increase the mesopelagic DWA  $Ba_{xs}$ .

#### 4.3 Relationship between $Ba_{xs}$ and carbon remineralisation in the North Atlantic

In previous studies focusing on the Southern Ocean,  $Ba_{xs}$ -based mesopelagic carbon remineralisation fluxes were estimated using Eq. (2), which relates the accumulated mesopelagic  $Ba_{xs}$  inventory to the rate of oxygen consumption (Shopova et al., 1995; Dehairs et al., 1997):

$$\text{mesopelagic } Ba_{xs} = 17\,200 \times JO_2 + Ba_{\text{residual}}, \quad (2)$$

where mesopelagic  $Ba_{xs}$  is the DWA in the mesopelagic layer ( $\text{pmol L}^{-1}$ ),  $JO_2$  is the rate of oxygen consumption ( $\mu\text{mol L}^{-1} \text{d}^{-1}$ ), and  $Ba_{\text{residual}}$  is the deep-ocean  $Ba_{xs}$  value observed at zero oxygen consumption (or  $Ba_{xs}$  background signal), which was determined to reach  $180 \text{ pmol L}^{-1}$  (Dehairs et al., 1997).

The oxygen consumption  $JO_2$  can be converted into a C remineralisation flux through Eq. (3):

$$\text{POC mesopelagic remineralisation} = Z \times JO_2 \times (C : O_2)_{\text{Redfield Ratio}}, \quad (3)$$

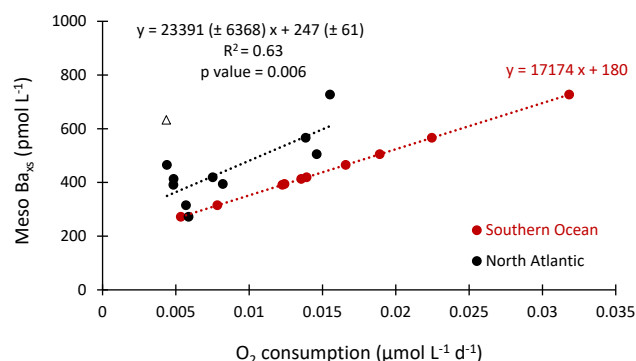
where the POC mesopelagic remineralisation is in  $\text{mmol C m}^{-2} \text{d}^{-1}$ ,  $Z$  is the thickness of the layer in which the mesopelagic  $Ba_{xs}$  is calculated,  $JO_2$  is the rate of oxygen consumption given by Eq. (2), and  $(C : O_2)_{\text{Redfield Ratio}}$  is the stoichiometric molar ratio of carbon to dioxygen (127/175; Broecker et al., 1985).

However, it is of interest to investigate if this relationship can be applied in the North Atlantic. Therefore, we determined the oxygen utilisation rate (OUR;  $\mu\text{mol kg}^{-1} \text{yr}^{-1}$ ), which is obtained by dividing the apparent oxygen utilisation (AOU,  $\mu\text{mol kg}^{-1}$ ) by the water mass age (Table S1). From the Iberian coast to Greenland, the age calculation was based on the CFC-12 distribution (when available, otherwise CFC-11) determined in 2012 (OVIDE CARINA cruise; de la Paz et al., 2017). For the Labrador Sea, the mean age of LSW has been estimated by Rhein et al. (2015) based on a 25-year record of CFC contents. The OUR was then integrated over the 100–1000 m layer. The resulting regression between DWA  $Ba_{xs}$  and OUR is as follows (see Fig. 8):

$$\text{mesopelagic } Ba_{xs} = 23391 (\pm 6368) \times JO_2 + 247 (\pm 61), \quad (4)$$

where mesopelagic  $Ba_{xs}$  and  $JO_2$  are defined in Eq. (2). Here,  $Ba_{\text{residual}}$  is  $247 \text{ pmol L}^{-1}$ .

This regression is significant ( $R^2 = 0.63$ ;  $p$  value = 0.006) when Station 44 is excluded. This latter station was located in the Irminger Gyre (Zunino et al., 2017; this issue) and it is possible that the gyre system induced an accumulation and retention of mesopelagic  $Ba_{xs}$ , which then no longer reflects remineralisation associated with the present growth season.



**Figure 8.** Regression of DWA mesopelagic  $Ba_{xs}$  ( $\text{pmol L}^{-1}$ ) versus  $O_2$  consumption rate ( $\mu\text{mol L}^{-1} \text{d}^{-1}$ ) using the Southern Ocean transfer function from Dehairs et al. (1997; red circles) and the transfer function obtained here for the North Atlantic (black circles). Station 44 (triangle) was excluded from the regression. If station 44 is included,  $R^2 = 0.33$  and the  $p$  value = 0.07.

Figure 8 also shows the oxygen consumption related to the GEOVIDE  $Ba_{xs}$  values using the Southern Ocean regression (Eq. 2). It appears that for a given mesopelagic  $Ba_{xs}$  inventory the oxygen consumption is smaller when using the Southern Ocean regression. However, both regressions are not significantly different when taking into account the errors associated with the slope and intercept of the regression in Eq. (4). The Southern Ocean regression appears to represent a lower limit that seems to overestimate the remineralisation fluxes. Furthermore, the relationship here deduced for the North Atlantic is sensitive to potential errors. Indeed, calculation of OUR has been shown to underestimate the ocean respiration because of the non-proportional diffusive mixing of AOU and water mass age resulting in an excess loss of AOU versus age (Koeve and Kähler, 2016). This would decrease the mismatch between the Southern Ocean and North Atlantic regressions. Errors can also be directly associated with the CFC-based age values of the water masses, which would appear especially critical for LSW. Indeed, the severe winter preceding the cruise (2013/2014) appeared to have strongly ventilated LSW with a mixed-layer depth exceeding 1700 m (Kieke and Yashayaev, 2015), indicating that the mean age (4 years) estimated by Rhein et al. (2015) may have overestimated the real LSW age (Pascale Lherminier, personal communication, 2017). Moreover, in the Labrador Sea, the residence time of LSW strongly varies between the central Labrador Sea (4–5 years) and the boundary currents off the Greenland and Newfoundland coasts (a few months; Deshayes et al., 2007; Straneo et al., 2003). An overestimation of these ages leads to underestimating OUR, resulting in reducing the apparent discrepancy between the both North Atlantic and Southern Ocean regressions.

In the following discussion, carbon remineralisation fluxes are estimated for the North Atlantic (GEOVIDE and GEOSECS cruises) using Eqs. (4) and (3).

## 4.4 Comparison of remineralisation fluxes

### 4.4.1 Remineralisation from the $Ba_{xs}$ proxy

The GEOVIDE remineralisation fluxes are compared with values reported for the World Ocean and also based on  $Ba_{xs}$  inventories (Table 3; Fig. 9). In the North Atlantic, the fluxes obtained during the GEOVIDE and GEOSECS (symbolised by stars in Fig. 9) cruises are of the same order of magnitude, highlighting a relatively constant remineralisation over the last 44 years. The remineralisation fluxes reported for the Southern and Pacific oceans are similar to those in the NAST and NADR provinces of the North Atlantic. However, the fluxes in the ARCT province are clearly higher, highlighting an important remineralisation in the northern part of the North Atlantic compared to other oceans.

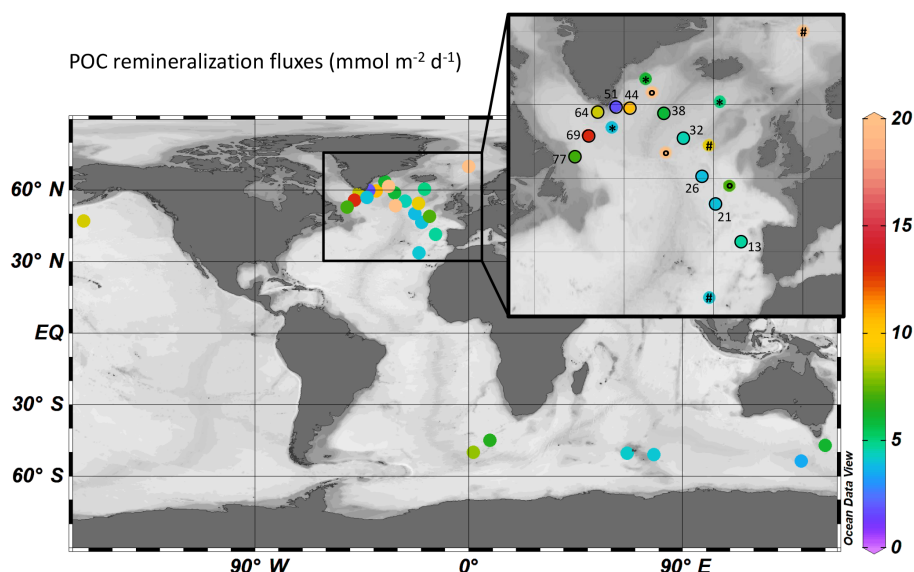
### 4.4.2 Remineralisation from direct measurements

In the North Atlantic, carbon respiration rates were also deduced from surface drifting sediment traps and associated shipboard incubations (Fig. 9). Collins et al. (2015) determined very high respiration rates reaching 39 and 72  $\text{mmol C m}^{-2} \text{d}^{-1}$  at sites located in the NADR and in the ARCT provinces, respectively. Nevertheless, these high fluxes were deduced in the upper mesopelagic layer (50–150 m) where respiration is larger compared to the lower mesopelagic layer (100–1000 m). This difference in depth interval could thus explain the lower remineralisation rates in our study. Also using surface drifting sediment traps and associated-shipboard incubations but supplemented by measurements of zooplankton respiration, Giering et al. (2014) determined respiration rates in the NADR province (PAP site) reaching 7.1  $\text{mmol C m}^{-2} \text{d}^{-1}$  during summer. This flux, determined over the 50–1000 m depth interval, is of the same order of magnitude as our estimates for the NADR province.

### 4.4.3 Remineralisation from the deep sediment traps

The remineralisation flux in the mesopelagic layer can also be derived from the difference between a deep POC export flux and a surface POC export flux. Honjo et al. (2008) compiled deep POC fluxes from bottom-tethered sediment traps and calculated the corresponding export production (upper-ocean POC export flux) using an ecosystem model (Laws et al., 2000) for most world ocean provinces. Then, by difference, the authors estimated an annual average of carbon remineralisation fluxes in the mesopelagic layer, which were converted into daily average fluxes. Remineralisation fluxes reached values of 34  $\text{mmol C m}^{-2} \text{d}^{-1}$  in the ARCT province, 9  $\text{mmol C m}^{-2} \text{d}^{-1}$  in the NADR province, and 4  $\text{mmol C m}^{-2} \text{d}^{-1}$  in the NAST province (Fig. 9). Note that the flux in the ARCT province was one of the highest mesopelagic remineralisation fluxes estimated worldwide, confirming the occurrence of important remineralisation in the northern part of the North Atlantic as compared to other





**Figure 9.** Summary of published POC remineralisation fluxes ( $\text{mmol C m}^{-2} \text{d}^{-1}$ ) in the world ocean. The remineralisation fluxes for the Pacific Ocean (Dehairs et al., 2008) and the Southern Ocean (Cardinal et al., 2005; Jacquet et al., 2008a, b, 2011b, 2015; Planchon et al., 2013) were calculated based on the  $\text{Ba}_{\text{XS}}$  inventories. The insert shows data for the North Atlantic: sites indicated by circles lined in black are from the present study; at sites labelled with # symbols remineralisation was deduced from POC fluxes recorded by moored sediment traps Honjo et al., 2008); at sites labelled by ° remineralisation was obtained from on-board incubations (Collins et al., 2015; Giering et al., 2014); sites labelled with \* are GEOSECS sites for which we calculated remineralisation from existing  $\text{Ba}_{\text{XS}}$  profiles (Brewer et al., unpublished results). Data were plotted using the ODV software (Schlitzer, 2017).

oceans. The values published by Honjo et al. (2008) for the North Atlantic are quite similar to our median values obtained during GEOVIDE. Indeed, mesopelagic remineralisation fluxes based on the  $\text{Ba}_{\text{XS}}$  proxy were similar to the value reported by Honjo et al. (2008) for the NAST province, while they were respectively 2- and 4-fold lower in the NADR and in the ARCT provinces.

Overall, the remineralisation fluxes deduced from the  $\text{Ba}_{\text{XS}}$  proxy are in concordance with those obtained using the other methods, confirming the order of magnitude of the mesopelagic remineralisation fluxes determined in this study of the North Atlantic (Fig. 9).

#### 4.5 The biological carbon pump in the North Atlantic

In order to investigate the efficiency of the biological carbon pump in the North Atlantic, we examined the daily PP (Fonseca-Batista et al., 2018; this issue; Lemaitre et al., 2018; this issue), the upper-ocean POC export (Lemaitre et al., 2008; this issue), and the POC remineralisation in the mesopelagic layer (Table 4; Fig. 10).

During GEOVIDE, low ( $\leq 14\%$ ) export efficiencies (i.e. the ratio between PP and POC export) were observed at most stations, indicating an accumulation of biomass in surface waters or a strong turnover of the exported organic matter due to important remineralisation occurring in the upper water column ( $< 100\text{ m}$ ). Furthermore, mesopelagic POC remineralisation fluxes were relatively high, equalling or exceed-

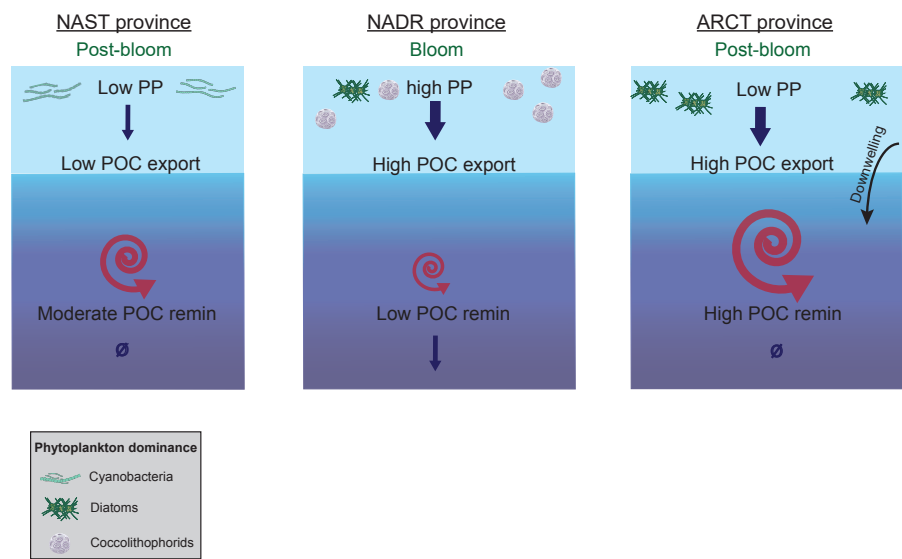
ing the POC export fluxes at some stations. This highlights a strong mesopelagic remineralisation with little or no material left for export to the deep ocean, but above all, it involves an imbalance between carbon supplies and mesopelagic remineralisation.

This imbalance can result from the differences between the time windows over which the PP, POC export, and POC remineralisation fluxes are integrated. Indeed, the measurements of PP represent a snapshot (24 h incubations) while measurements of export ( $^{234}\text{Th}$ ) integrate several weeks (Benitez-Nelson et al., 2001; Buesseler et al., 1992) and remineralisation (from the  $\text{Ba}_{\text{XS}}$  proxy) probably integrates much longer timescales. Moreover, previous studies in the Southern Ocean showed that mesopelagic processing of exported organic carbon, as reflected by  $\text{Ba}_{\text{XS}}$ , has a phase lag relative to the upper-ocean processes (Dehairs et al., 1997; Cardinal et al., 2005). Thus, we do not expect mesopelagic  $\text{Ba}_{\text{XS}}$  to be in phase with coinciding amplitude of PP and subsequent export. Because of the observed high remineralisation fluxes relative to the export fluxes, particularly in the ARCT province, it is likely that particulate organic matter sank out of the surface waters and became subject to mineralisation in the mesopelagic layer during the period preceding the specific time windows for POC export and PP. Such discrepancies between fluxes can be amplified by the spatial and temporal variability in the phytoplankton blooms in this province, generating sudden high export events and



**Table 3.** Comparison of the Baxs inventory ( $\text{pmol L}^{-1}$ ) and related carbon mesopelagic remineralisation fluxes ( $\text{mmol C m}^{-2} \text{d}^{-1}$ ) obtained in the world ocean. Fluxes are calculated with the new North Atlantic regression (Eq. 4) for the GEOVIDE and GEOSECS cruises and with the Southern Ocean regression (Eq. 2) for the other studies. HNLC: high nutrient–low chlorophyll; art. Fe fertilised: artificially Fe fertilised; nat. Fe fertilised: naturally Fe fertilised; PF: Polar Front; NAST: North Atlantic subtropical gyre; NADR: North Atlantic drift; ARCT: Atlantic Arctic.

Cruise (season)	Location	Features	Depth interval, m	DWA Baxs $\text{pmol L}^{-1}$	MR fluxes $\text{mmol C m}^{-2} \text{d}^{-1}$	Reference
CLIVAR SR3 – SAZ98 (spring/summer)	Australian sector Southern Ocean	Spring Summer	150–400	235–554 296–353	0.3–3.0 0.2–3.4	Cardinal et al. (2005)
VERTIGO (summer)	Pacific Ocean	Oligotrophic (Aloha station) Mesotrophic (K2 station)	150–500	157–205 367–713	1.0–3.0 2.7–8.8	Dehairs et al. (2008)
EIFEX (summer)	Atlantic sector Southern Ocean	Art. Fe fertilised (in patch) HNLC (out patch)	150–1000	273–415 233–423	2.6–7.7 1.2–8.0	Jacquet et al. (2008a)
KEOPS (summer)	Indian sector Southern Ocean	Nat. Fe fertilised (A3 station) HNLC (C11 station)	125–450	342–401 309–493	2.1–2.8 1.7–4.0	Jacquet et al. (2008b)
SAZ-SENSE (summer)	Australian sector Southern Ocean	Nat. Fe fertilised (SAZ east) HNLC (SAZ west)	100–600	244–395 199–249	3.0–6.1 2.1–3.1	Jacquet et al. (2011)
BONUS-GoodHope (summer)	Atlantic sector Southern Ocean	North of PF South of PF	125–600	284–497 235–277	2.1–6.4 1.1–1.9	Planchon et al. (2013)
KEOPS 2 (spring)	Indian sector Southern Ocean	Nat. Fe fertilised (A3 station) HNLC (R2 station)	150–400	267–314 572	0.9–1.2 4.2	Jacquet et al. (2015)
GEOSECS II (summer)	North Atlantic	NAST + NADR ARCT	100–1000	199–361 242–413	0.5–4.9 1.7–6.3	Brewer (unpublished values)
GEOVIDE (spring)	North Atlantic	NAST (Station 13) NADR (Station 21) NADR (Station 26) NADR (Station 32) NADR (Station 38) NADR (Station 44) ARCT (Station 51) ARCT (Station 64) ARCT (Station 69) ARCT (Station 77)	100–1000	419 394 391 413 465 633 315 566 727 505	4.6 3.9 3.8 4.4 5.9 10 1.8 8.6 13 6.9	This study



**Figure 10.** General schematic of the biological carbon pump in the NAST, NADR, and ARCT provinces during GEOVIDE. Primary production (PP) data from Fonseca-Batista et al. (2018; this issue) and Lemaitre et al. (2018; this issue); particulate organic carbon (POC) export fluxes from Lemaitre et al. (2018; this issue) and POC remineralisation fluxes from this study. The dominating phytoplankton communities and the stage of the bloom are also indicated.

**Table 4.** Comparison of the mesopelagic POC remineralisation fluxes (Remineralisation) with primary production (PP) and POC export fluxes in the upper water column (Export). All fluxes are expressed in  $\text{mmol C m}^{-2} \text{d}^{-1}$ .

	ARCT – Labrador Sea			ARCT – Irminger Sea		NADR				NAST
Station	77	69	64	51	44	38	32	26	21	13
PP <sup>1</sup>	80	27	54	166	137	68	105	174	135	79
Export <sup>2</sup>	6	10	8	3	1	5	8	7	5	2
Remineralisation	7	13	9	2	10	6	4	4	4	5

<sup>1</sup> PP data from Fonseca-Batista et al. (2018; this issue) and Lemaitre et al. (2018; this issue). <sup>2</sup> Export data from Lemaitre et al. (2018; this issue).

associated remineralisation. In contrast to the above, at Station 32 in the NADR province, a large fraction of exported POC (50 %; Table 4) appears to escape remineralisation. The more efficient POC transfer through the mesopelagic layer of this province may be explained by the fact that sampling took place in an early stage of the bloom and/or by the presence of calcified phytoplankton species, ballasting aggregates thereby increasing their settling velocity (see Sect. 4.2.3).

Overall, the remineralisation in the mesopelagic layer is an important process that needs to be taken into account as our results point to the poor capacity of specific areas within the North Atlantic to sequester carbon at depths below 1000 m in spring 2014.

5 Conclusions

We investigated mesopelagic carbon remineralisation fluxes in the North Atlantic during spring 2014 (GEOVIDE section) using, for the first time, the particulate biogenic barium inventories measured for this area. The excess biogenic barium ( $\text{Ba}_{\text{xs}}$ ) inventories in the mesopelagic layer varied between the different provinces of the North Atlantic. The largest  $\text{Ba}_{\text{xs}}$  inventory was observed in the ARCT province, where high carbon production rates were also observed earlier in the season. The regional variations in the  $\text{Ba}_{\text{xs}}$  inventory may also result from differences with phytoplankton community composition encountered along this transatlantic section. Lower mesopelagic  $\text{Ba}_{\text{xs}}$  contents occurred where smaller calcified phytoplankton species dominated, such as in the NADR province. Finally, the ARCT province was also characterized by important water mass subduction, generating a large transport of organic matter to the deep ocean,

which might have resulted into an important  $Ba_{xs}$  accumulation in the mesopelagic layer.

Using the OUR method, we confirmed that the mesopelagic  $Ba_{xs}$  inventory can be related to the oxygen utilisation rate, but the relationship between both parameters is slightly different compared to the relationship proposed elsewhere for the Southern Ocean. A new relationship is thus proposed for the North Atlantic. This proxy approach provided estimations of mesopelagic remineralisation fluxes of similar magnitude to those obtained by others using independent methods (free-floating and moored sediment traps, incubations) in the North Atlantic.

Overall, in spring 2014, the mesopelagic remineralisation balanced or exceeded POC export in the subtropical and sub-polar provinces of the North Atlantic, highlighting the important impact of the mesopelagic remineralisation on the biological carbon pump and indicating that little to no organic matter was transferred below 1000 m in this region.

*Data availability.* Underlying data are reported in the Supplement.

**The Supplement related to this article is available online at <https://doi.org/10.5194/bg-15-2289-2018-supplement>.**

*Competing interests.* The authors declare that they have no conflict of interest.

*Special issue statement.* This article is part of the special issue “GEOVIDE, an international GEOTRACES study along the OVIDE section in the North Atlantic and in the Labrador Sea (GA01)”. It is not associated with a conference.

*Acknowledgements.* We would like to thank the captain and the crew of the R/V *Pourquoi Pas?*, as well as Fabien Perault and Emmanuel De Saint Léger from the CNRS DT-INSU for their help during the CTD deployments. Pierre Branellec, Floriane Desprez de Gésincourt, Michel Hamon, Catherine Kermabon, Philippe Le Bot, Stéphane Leizour, and Olivier Ménage are also acknowledged for their technical help during the cruise. We acknowledge Lorna Foliot, Raphaëlle Sauzède, Joséphine Ras, Hervé Claustre, and Céline Dimier for the sampling and analysis of pigments. We would like to thank the co-chief scientists Pascale Lherminier and Géraudine Sarthou. We also express our thanks to Pascale Lherminier, Herlé Mercier, Monika Rhein, Julie Deshayes, and Claude Talandier for providing useful help on the characteristics of the Labrador Sea Water. Satellite chlorophyll *a* data and visualisations used in this study were produced with the Giovanni and the Ocean Color (Ocean Biology Processing Group; OBPG) online data system, developed and maintained by NASA.

This work was funded by the Flanders Research Foundation (project G071512N), the Vrije Universiteit Brussel (strategy

research program: project SRP-2), the French National Research Agency (ANR-13-BS06-0014 and ANR-12-PDOC-0025-01), the French National Center for Scientific Research (CNRS-LEFE-CYBER), IFREMER, and the “Laboratoire d’Excellence” Labex-Mer (ANR-10-LABX-19). For this work, Maribel I. Garcia-Ibáñez was supported by the Centre for Climate Dynamics at the Bjerknes Centre and by the Spanish Ministry of Economy and Competitiveness through the BOCATS (CTM2013-41048-P) project co-funded by the Fondo Europeo de Desarrollo Regional 2014–2020 (FEDER).

Edited by: Gilles Reverdin

Reviewed by: two anonymous referees

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