- 1 Early season mesopelagic carbon remineralization and transfer
- 2 efficiency in the naturally iron-fertilized Kerguelen area

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- 4 Jacquet S.H.M.¹, F. Dehairs², D. Lefèvre¹, A.J. Cavagna², F. Planchon³,
- 5 U. Christaki⁴, L. Monin⁵, L. André⁵, I. Closset⁶ and D. Cardinal⁶

6

- ¹Aix Marseille Université, CNRS/INSU, IRD, Mediterranean Institute of
- 8 Oceanography (MIO), UM 110, 13288 Marseille, France

9

- 10 ²Vrije Universiteit Brussel, Analytical, Environmental & Geo-Chemistry
- and Earth System Sciences, Brussels, Belgium

12

- 13 ³Laboratoire des Sciences de l'Environnement Marin (LEMAR),
- 14 Université de Brest, CNRS, IRD, UMR 6539, IUEM; Technopôle Brest
- 15 Iroise, Place Nicolas Copernic, F-29280 Plouzané, France

16

- 17 ⁴INSU-CNRS, UMR8187 LOG, Laboratoire d'Océanologie et de
- 18 Géosciences, Université du Littoral Côte d'Opale, ULCO, 32 avenue
- 19 Foch, 62930 Wimereux, France

20

- 21 ⁵Earth Sciences Department, Royal Museum for Central Africa,
- Leuvensesteenweg 13, Tervuren, B 3080, Belgium

23

- ⁶Sorbonne Universités (UPMC, Univ Paris 06)-CNRS-IRD-MNHN,
- LOCEAN Laboratory, 4 place Jussieu, F-75005 Paris, France

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 $27 \qquad \textbf{Corresponding author:} \ step hanie.jacquet@mio.osupytheas.fr$

Abstract

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We report on the zonal variability of mesopelagic particulate organic carbon remineralization and deep carbon transfer potential during the Kerguelen Ocean and Plateau compared Study 2 expedition (KEOPS 2; Oct.-Nov. 2011) in an area of the Polar Front supporting recurrent massive blooms from natural Fe fertilization. Mesopelagic carbon remineralization (MR) was assessed using the excess, non-lithogenic particulate barium (Baxs) inventories in mesopelagic waters and compared with bacterial production (BP), surface primary production (PP) and export production (EP). Results for this early season study are compared with results obtained during a previous study (2005; KEOPS 1) for the same area at a later stage of the phytoplankton bloom. Our results reveal the patchiness of the season advancement and of the establishment of remineralization processes between plateau (A3) and Polar Front sites during KEOPS 2. For the Kerguelen plateau (A3 site) we observe a similar functioning of the mesopelagic ecosystem during both seasons (spring and summer), with low and rather stable remineralization fluxes in the mesopelagic column (150-400 m). The shallow water column (~500m), the lateral advection, the zooplankton grazing pressure and the pulsed nature of the POC transfer at A3 seem to drive the extend of MR processes on the plateau. For deeper stations (>2000 m) located on the margin, inside a Polar Front meander, as well as in the vicinity of the Polar Front, east of Kerguelen, remineralization in the upper 400 m in general represents a larger part of surface carbon export, but when considering the upper 800 m, in some cases, the entire flux of exported carbon is remineralized. In the Polar Front meander, where successive stations form a time series, two successive events of particle transfer were evidenced by remineralization rates: a first mesopelagic and deep transfer from a past bloom before the cruise, and a second transfer expanding at mesopelagic layers during the cruise. Regarding the deep carbon transfer

efficiency, it appeared that above the plateau (A3 site) the mesopelagic remineralization was not a major barrier to the transfer of organic matter to the sea-floor (close to 500 m). There the efficiency of carbon transfer to the bottom waters (>400 m) as assessed by PP, EP and MR fluxes comparisons reached up to 87% of the carbon exported from the upper 150 m. In contrast, at the deeper locations mesopelagic remineralization clearly limited the transfer of carbon to depths >400 m. For sites at the margin of the plateau (station E-4W) and the Polar front (station F-L), mesopelagic remineralization even exceeded upper 150 m export, resulting in a null transfer efficiency to depths >800 m. In the Polar Front meander (time series), the capacity of the meander to transfer carbon to depth >800 m was highly variable (0 to 73 %). The highest carbon transfer efficiencies in the meander are furthermore coupled to intense and complete deep (>800 m) remineralization, resulting again in a close to zero deep (>2000 m) carbon sequestration efficiency there.

Key Words: particulate barium, mesopelagic carbon remineralization, carbon transfer efficiency, Southern Ocean

1. INTRODUCTION

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While numerous artificial (Boyd et al., 2000, 2004; Gervais et al., 2002; Buesseler et al., 2004, 2005; de Baar et al., 2005; Hoffmann et al., 2006; Boyd et al., 2012; Smetacek et al., 2012) and natural (Blain et al., 2007; Pollard et al., 2009; Zhou et al., 2010, 2013) ocean iron-fertilization experiments in the Southern Ocean demonstrated the role of iron in enhancing the phytoplankton biomass and production in high-nutrient lowchlorophyll (HNLC) regions, determining to what extent fertilization could modify the transfer of particulate organic carbon (POC) to the deep ocean is far from being comprehensively achieved (Lampitt et al., 2008; Morris and Charette, 2013; Le Moigne et al., 2014; Robinson et al., 2014). This is partly due to the short term over which the observations were made, precluding extrapolation to longer time scales. Moreover, when assessing whether Fesupply could induce vertical POC transfer, the magnitude of the export from surface is not the only important parameter to take into account. Indeed, POC fate in the mesopelagic zone (defined as 100-1000 m depth layer) is often largely overlooked although these depth layers are responsible for the remineralization of most of the POC exported from the surface layer (Martin et al., 1987; Longhurst, 1990; Lampitt and Antia, 1997; François et al., 2002; Buesseler et al., 2007b; Buesseler and Boyd, 2009). Only few studies considered mesopelagic carbon (C) remineralization rates (Buesseler et al., 2007a; Jacquet et al., 2008a, 2008b, 2011a, 2011b; Salter et al., 2007) to estimate the response of deep POC export to fertilization. Assessing mesopelagic C remineralization is pivotal to evaluate remineralization length scale as well as the time scale of the C storage in the deep ocean. Indeed the typical depth of the main thermocline, 1000 m (IPCC, WG1, 2007, chp5) is often referred to as the horizon clearly removed from the surface ocean and atmosphere (Passow and Carlson, 2012). Overall, assessing mesopelagic C remineralization will allow to better quantify the ocean's biological carbon

pump and its efficiency in the global C cycle which bears large uncertainty and is currently under debate (e.g. from 5 Gt/yr in Henson et al., 2011 to 21 Gt C/yr in Laws et al., 2000 and 13 Gt/yr in IPPC WG1 report (ch. 6, 2013).

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The present work aims at understanding the impact of a natural ironinduced bloom on the mesopelagic POC remineralization and zonal variability in the Kerguelen area (Southern Ocean). Here, C remineralization was assessed from particulate biogenic Ba (hereafter called excess-Ba or Baxs; mainly forms as barite BaSO₄ crystals) contents in the mesopelagic water column. The link between barite and C remineralization resides in the fact that this mineral precipitates inside oversaturated micro-environments (biogenic aggregates) during the process of prokaryotic degradation of sinking POC (Dehairs et al., 1980, 1992, 1997, 2008; Stroobants et al., 1991, Cardinal et al., 2001, 2005; Jacquet et al., 2007, 2008b, 2011a; Planchon et al., 2013; Sternberg et al. 2007, 2008a, 2008b). Once the aggregates have been remineralized, barites are released and spread over the mesopelagic layer. Overall, earlier work highlights the fact that suspended barite in mesopelagic waters builds up over the growing season and reflects past remineralization activity integrated over several days to weeks (Dehairs et al., 1997; Cardinal et al., 2005; Jacquet et al., 2007, 2008b). An algorithm relating mesopelagic Ba_{xs} contents to oxygen consumption (Shopova et al., 1995; Dehairs et al., 1997) allowed remineralization of POC fluxes to be estimated for the mesopelagic layer. Combined with surface C production and export estimates, mesopelagic Baxs also informs on the efficiency of the system toward deep carbon transfer. From earlier studies, the efficiency of C transfer through the mesopelagic layer was reported to increase under artificially induced (EIFEX; Strass et al., 2005; Smetacek et al., 2012) and natural (KEOPS; Blain et al., 2007) Fe-replete conditions (Jacquet et al., 2008a, 2008b; Savoye et al., 2008) compared to Fe-limited, non-bloom, HNLC reference stations in the Southern Ocean. In contrast, C transfer efficiency through the mesopelagic layer was reported smaller in natural Fe-replete locations during the SAZ-Sense cruise off Tasmania (Jacquet et al., 2011a, 2011b). Differences in plankton community structure and composition (e.g. diatoms vs. flagellates, type of diatoms) were pointed at, as possible causes of such discrepancies in C transfer efficiency through the mesopelagic layer (Jacquet et al., 2008a, 2011a, 2011b). Also, differences in integration time scales for the processes that control the carbon fluxes in artificially vs. naturally Fe fertilized systems, may yield an incomplete picture of the C transfer potential and lead to misleading conclusions.

Here, we examine changes in mesopelagic POC remineralization during the early spring (Oct. -Nov. 2011) KEOPS 2 expedition to the naturally iron fertilized area eastward of Kerguelen Islands. The hydrographic structure of the Kerguelen area generates contrasted environments that are differently impacted by iron availability and mesoscale activity. The specific objectives of the present work are to assess the zonal variability of mesopelagic C remineralization and deep C transfer potential, and to identify possible causes inducing this variability. As the same area was visited earlier in 2005 during summer at a late stage of the bloom (KEOPS 1; Jan.-Feb., 2005), this condition offers a unique opportunity to estimate the main carbon fluxes over most of the growth season. Mesopelagic C remineralization estimates are compared to particle and biological parameters as reported in other papers included in this issue (Cavagna et al., 2014; Christaki et al., 2014; Dehairs et al., 2014; Lasbleiz et al., 2014; Laurenceau-Cornec et al., 2015; Planchon et al., 2014; van der Merve et al., 2015) and in Blain et al., (2007), Christaki et al. (2008), Jacquet et al., (2008a), Park et al., (2008) and Savoye et al., (2008).

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2. EXPERIMENT AND METHODS

2.1. Study area

The KEOPS 2 (Kerguelen Ocean and Plateau compared Study) cruise was conducted in austral spring at the onset of the bloom from 10 October to 20 November aboard the R/V Marion Dufresne (TAAF/IPEV). The KEOPS 2 expedition studied the Kerquelen Plateau area (Indian sector of the Southern Ocean) which is characterized by the passage of the Polar Front (PF), as illustrated in Fig.1a. The Kerguelen Plateau is surrounded by the Antarctic Circumpolar Current (ACC) whose main branch circulates to the north of the plateau (Park et al., 2008). A second branch of the ACC circulates to the south of Kerguelen Islands to further join a branch of the Fawn Trough Current (FTC). The FTC has a main northeast direction, but a minor branch splits away northwestward to join the eastern side of the Kerguelen plateau (Park et al., 2008; Fig1.a). These particular hydrographic features generate a mosaic of recurrent massive bloom patterns in the northeastern part of the Plateau and the possible sources and mechanisms for fertilization were investigated during ANTARES 3 (1995; Blain et al., 2001) and KEOPS 1 cruise, later referred to as KEOPS 1 (Jan.-Feb. 2005, late summer conditions; Blain et al., 2007, 2008). During KEOPS 2 the evolution of Chl-a data based on multi-satellite imagery of the study area revealed the presence of different Chl-a rich plumes (D'ovidio et al., 2015) (Fig.1a; e.g. Chl-a map from 11/11/2011). Stations were sampled in distinct zones covering these different bloom patterns (Fig.1a) (corresponding stations are reported in Fig1.b): (a) on the shallow plateau (station A3; see 1 in Fig.1a). Note that station A3 coincides with a site studied during the KEOPS 1 cruise, and that it was sampled twice over a 27-day period; (b) in a meander formed by a quasipermanent retroflection of the Polar Front (PF) and topographically-steered by the eastern escarpment (Gallieni Spur) of the Kerguelen Plateau (mainly stations E, sampled as a quasi-lagrangian temporal series) (see 2 in Fig.1a); (c) along a North-South Transect (referred to as TNS stations; see 3, grey line in Fig.1a) and a West-East Transect (referred to as TEW stations; see 4, grey

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line in Fig.1a), both crossing the PF; and (d) in the Polar Front Zone (PFZ) in the vicinity (east) of the PF (station F-L; see 5 in Fig.1a). Furthermore we also sampled a reference HNLC/non bloom/non Fe-fertilized station southwest of the Plateau (station R-2; see 6 in Fig.1a). Station locations are given in Table 1.

Detailed descriptions of the complex physical structure of the area, circulation, water masses and fronts are given in Park et al. (2014). Briefly, the main hydrodynamic features observed during the cruise are the following (see θ -S diagram, Fig.2a): (1) North of the PF, stations in the PFZ (TNS-1, TEW-8 and F-L) present Antarctic Surface Waters (AASW; $\theta \approx 4^{\circ}$ C and density <27); θ -S characteristics between 150 to 400 m at station F-L (and to a lesser extent at station TNS-1) reveal the presence of interleaving with waters from northern (subantarctic) origin, centered between the 27.2 and 27.5 density curves, where Antarctic Intermediate Waters (AAIW) are usually found. This contrasts with the situation at station TEW-8, where there is no evidence of interleaving; (2) stations south of the PF exhibit subsurface temperature minima characteristic of Winter Waters (WW); below the WW three water masses can be identified, namely: the Upper (temperature maximum) and Lower (salinity maximum) Circumpolar Deep Water (UCDW and LCDW), and the Antarctic Bottom Water (AABW). Theses water masses are present roughly in the following depth intervals: 700 m<UCDW< 1500 m; 1500 m <LCDW < 2500 m; AABW > 2500 m.

Based on the θ -S characteristics (Fig.2a, -2b) and surface phytoplankton biomasses we can schematically group the stations as follows. The R-2 HNLC reference station (white dot in Fig.1b) is characterized by a very low biomass (with low iron contents; Quéroué et al., 2015). Stations TEW-3 and TNS-8 (black dots) are characterized by a low to moderate biomass and Fe contents. Stations A3 and E-4W (red dots; south of the PF) as well as stations TNS-1, F-L and TEW-8 (blue dots; north of the PF) are

characterized by high biomass and iron contents. Stations in the core of the PF meander (green dots; stations TNS-6, E-1, E-2, E-3, E-4E and E-5 considered as a temporal series) are characterized by moderate biomass and iron contents.

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2.2. Sampling and analyses

22 CTD casts (surface to 500-2000 m) were sampled for particulate barium (Table 1) using a CTD-rosette equipped with 22 12L Niskin bottles. Deep particulate Ba profiles (>1000 m) were not systematically obtained from the same CTD cast, but from successive casts sampled closeby in time and space and having similar θ -S data profiles. In the following, we use both the station and CTD numbers to refer to stations.

4 to 7 L of seawater were filtered onto 47 mm polycarbonate membranes (0.4 µm porosity) under slight overpressure supplied by filtered air (0.4 μ m). The filters were rinsed with Milli-Q grade water (<5 mL) to remove sea salt, dried (50°C) and stored in Petri dishes for later analysis. In the home-based laboratory we performed a total digestion of samples using a tri-acid (0.5 mL HF/1.5 mL HCl/1 mL HNO3; all Suprapur grade) mixture in closed telfon beakers overnight at 90°C in a clean pressurized room. After evaporation close to dryness samples were re-dissolved into around 13 mL of HNO₃ 2%. The solutions were analysed for Ba and other major and minor elements by ICP-QMS (inductively coupled plasma-quadrupole mass spectrometry; X Series 2 ThermoFisher) equipped with a collision cell technology (CCT). To correct instrumental drift and matrix effects, internal standards and matrix-matched calibrations were used. We analysed several certified reference materials which consisted of dilute acid-digested rocks (BHVO-1, JB-3 and JGb-1), natural riverine water (SLRS-5) and multi-element artificial solutions for these external calibrations. Based on analyses of these external standards, accuracy and reproducibility are better than \pm 5%. For more details on sample processing and analysis we refer to Cardinal et al. (2001). Among all elements analysed, particular interest went to Ba and Al. The presence of sea-salt was checked by analysing Na and the sea-salt particulate Ba contribution was found negligible. Average detection limits equal 0.6 nM for Al and 3 pM for Ba. Detection limits were calculated as three times the standard deviation on the blank measured on board and then normalized to an average dilution factor of 385, i.e., particles from around 5 L of Milli-Q water, dissolved in a final volume of 13 mL as for the samples. Biogenic barium (hereafter called excess-Ba or Baxs) was calculated as the difference between total particulate Ba and lithogenic Ba using Al as the lithogenic reference element (Dymond et al., 1992; Taylor and McLennan, 1985). At most sites and depths the biogenic Baxs represented >95% of total particulate Ba. Lithogenic Ba reached up to 20% of total particulate Ba at some depths in the upper 80-100 m, mainly at station R-2 and stations north of the Polar Front (i.e., TEW-8, F-L and TNS-1). The standard uncertainty (Ellison et al., 2000) on Ba_{xs} data ranges between 5 and 5.5%. Ba_{xs} and Al data are reported in Appendix A.

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2.3. O₂ consumption and POC remineralization

The rate of oxygen consumption and particulate organic carbon remineralization rate in the mesopelagic layer (later referred to as MR) can be estimated using an algorithm relating mesopelagic Ba_{xs} contents and oxygen consumption based on earlier observations in the Southern Ocean (Shopova et al., 1995; Dehairs et al., 1997; 2008). The detailed calculations are described in Jacquet et al. (2008a, 2011a). Briefly, we use the following equations:

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$$J_{O_2} = (Ba_{xs} - Ba_{residual})/17450$$
 (Eq.1)

$$C_{respired} = Z \times J_{O_2} \times RR$$
 (Eq.2)

where J_{02} is the O_2 consumption (µmol Γ^{-1} d⁻¹) and $C_{respired}$ is the Mineralization Rate of organic carbon (in mmol C m⁻² d⁻¹; MR); Ba_{xs} is the depth-weighted average Ba_{xs} value (DWAv), i.e. the Ba_{xs} inventory divided by the depth layer considered Z, Ba_{residual} is the residual Ba_{xs} signal (or Ba_{xs} background) at zero oxygen consumption and RR is the Redfield C/O_2 molar ratio (127/175; Broecker et al., 1985). DWAv Ba_{xs} values were calculated both for the 150 to 400 m (Plateau and deep stations) and the 150 to 800 m layers (deep stations only) (see details further below). The residual Ba_{xs} is considered as 'preformed' Ba_{xs}, left-over after partial dissolution and sedimentation of Ba_{xs} produced during a previous phytoplankton growth event. In BaSO₄ saturated waters, such as the ones filling the whole ACC water column (Monnin et al. 1999), this background Ba_{xs} value was considered to reach 180 to 200 pM which is rather characteristic for the deep ocean (>1000m) (see Dehairs et al., 1997; Jacquet et al., 2008a, 2011). In the present study we used a Ba_{xs} background of 180 pM.

We take the opportunity here to also compare O_2 consumption rates for the KEOPS 1 expedition (D. Lefèvre, unpublished data) with KEOPS 1 Ba_{xs} data published earlier (Jacquet et al., 2008a). No such O_2 consumption data are available for KEOPS 2. During KEOPS 1, dark community respiration (DCR) was estimated from changes in the dissolved oxygen concentration over 72 hours incubations. Discrete samples were collected at three depths in the mesopelagic zone from Niskin bottles into 125 cm³ borosilicate glass bottles according to the WOCE procedure, and oxygen concentration was determined by Winkler titrations using a photometric endpoint detector (Williams and Jenkinson, 1982). By integrating DCR data in the water column we estimated the rate of oxygen consumption (later referred to as JO_2 -W). We compared JO_2 -W obtained from incubated oxygen samples with the rate of oxygen consumption based on KEOPS 1 mesopelagic Ba_{xs} contents (Eq.1; later referred to as JO_2 -Ba). Dissolved oxygen was measured three times at

station A3 (same location as during KEOPS2) over a 19-day period (A3 CTD #32, #74 and #119). Dissolved oxygen was also measured at station C11 located off-shelf in less productive HNLC waters (51.65°S, 78.00°E; not shown in Fig.1) and was sampled two times over a 10-day period (C11 CTD#42 and #83). Fig.3 compares JO₂-W and JO₂-Ba for repeat stations A3 (#32, 74 and 119) and C11 (#42 and 83) (integration between 150-300 m). JO_2 -W range from 0.082 to 0.208 mmol m⁻² d⁻¹ at station A3 and from 0.292 to 0.528 mmol m⁻² d⁻¹ at station C11. Although JO₂-Ba rates (from 0.846 to 1.555 mmol m⁻² d⁻¹) are slightly higher than JO₂-W, JO₂ rates are of the same order of magnitude and present a same trend. We observe a significant positive correlation between both JO_2 rates ($R^2=0.90$; p<0.01) with a slope of 0.64. The difference in oxygen consumption rates could be explained by the integration time of both methods (few hours for the incubations vs. few days to weeks for Baxs) and by the fact that KEOPS 1 occurred at the decline of the bloom (late summer; low organic substrates), which would explain the lower JO_2 rates as estimated by the incubation method.

Overall, these results highlight the need for further constraining spatial and temporal variability of deep ocean oxygen utilisation via a combination of direct rate measurements and the Ba_{xs} proxy. In the present work O_2 consumption and POC remineralisation was assessed from Ba_{xs} inventories and Eqs.1 and 2. C remineralization rates are given in Table 1. Relative standard uncertainties (Ellison et al., 2000) on C remineralization ranged between 4 and 20%.

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3. RESULTS

3.1. Particulate biogenic Baxs profiles

 Ba_{xs} profiles in the upper 800 m are reported in Fig.4. The complete whole water column data set is given in Appendix A. From previous studies we know that Ba_{xs} in surface waters is distributed over different, mainly non-

barite biogenic phases (see Stroobants et al., 1991, Jacquet et al., 2007, Cardinal et al., 2005, Sternberg et al., 2005). As such, these do not reflect POC remineralization processes, in contrast to mesopelagic waters where Ba_{xs} is mainly composed of barite (Dehairs et al., 1980) formed during prokaryotic degradation of sinking POC (Martin et al., 1987; Sarmiento et al., 1993; Buesseler et al., 2007b). For KEOPS 2 we observe that Ba_{xs} concentrations generally increase below 150 m (i.e., they increase above the background level set at 180 pM), but some sites have ocean surface Ba_{xs} contents significantly larger than background (E-1,896 pM at 21 m; E4-E, 563 pM at 93 m). Such values are not unusual, and very high surface values have been observed occasionally in earlier Southern Ocean studies. During KEOPS 1, surface Ba_{xs} maxima at the three A3 repeats stations ranged from 1354 to 5930 pM at 50 m, likely associated with phytoplankton derived particles (Jacquet et al., 2008a).

The following part focuses on the mesopelagic zone where most of the remineralization of exported organic matter takes place. The Ba_{xs} profile for station R-2 (CTD #17) displayed a characteristic mesopelagic Ba_{xs} maximum reaching up to 834 pM at 304 m which is actually one of the highest values observed for the whole study (Fig.4a). Ba_{xs} profiles for stations A3 above the Kerguelen plateau (A3-1 CTD #4 and A3-2 CTD #107; Fig.4b) had lower mesopelagic Ba_{xs} contents, with values ranging from about 80 to 350 pM. For both A3 visits, Ba_{xs} values increased close to the seafloor reaching up to 1108 pM (A3-1, 474 m) and 1842 pM (A3-2, 513 m). In contrast, station E-4W (located further north along the margin in deeper waters, but with similar θ -S and Chl-a characteristics as station A3) displayed a large mesopelagic Ba_{xs} maximum reaching up to 627 pM at 252 m (Fig.4c). Station TEW-3 (located on the Kerguelen plateau, in waters with similar θ -S and Chl-a characteristics as station TNS-8) had a profile similar to the one observed at station A3-2, but compared to plateau sites A3-1 and A3-2 no increased Ba_{xs} contents were

observed in bottom water (Fig.4d). The other stations of the study area (Fig.4d-g) have Ba_{xs} profiles similar to the one at station E-4W, showing the characteristic Ba_{xs} maximum between 200 and 500 m. Note that for most of the stations, Ba_{xs} concentrations in waters below the mesopelagic maximum did not systematically decreased to reach the Ba_{xs} background level (180 pM; see above). In some cases Ba_{xs} contents significantly higher than residual Ba_{xs} were observed until below 1000 m (see Appendix A). This is particularly salient at stations TNS-6, E-1, E-2 and F-L where Ba_{xs} values below 1000 m reach 410 pM at 1886 m (TNS-6) and 436 pM at 1498 m (E-1). These cases of high deep Ba_{xs} contents clearly contrasted with the values observed at station E4-E (Fig.4h).

3.2. Depth-weighted average Ba_{xs} content of mesopelagic waters

Since the base of the mixed layer was generally shallower than \leq 150 m, this depth is taken as the upper boundary of the mesopelagic domain. The depth-weighted average (DWAV) Ba_{xs} contents, calculated for the 150-400 m and 150-800 m depth intervals, are given in Table 1. For the profiles on the plateau (500 m water column) bottom waters with evidence of sediment resuspension were not taken into account when calculating DWAV Ba_{xs} values (\geq 400 m). Particle size spectra indicated that sediment resuspension occurred especially at stations A3 and TEW-3 (Jouandet et al., 2014; Lasbleiz et al., 2014; van der Merve et al., 2015;). Thus, at site A3 (Fig.4b) DWAV Ba_{xs} was calculated for the layer between 150 and 354 m for A3-1 (CTD #4) and between 150 and 405 m for A3-2 (CTD#107). For station TEW-3 (CTD #38) DWAV Ba_{xs} was calculated for the water layer between 150 and 400 m (Fig.4d). For the deep sites, we considered both, the 150-400 m and the 150-800 m depth intervals, when calculating the DWAV Ba_{xs} contents. Depth weighted average Ba_{xs} values were translated into carbon remineralization

rates using equation (1) and (2) given above. These rates ranged from 2 to $395 - 91 \text{ mgC m}^{-2} \text{ d}^{-1}$ (Table 1).

DWAV Ba_{xs} values range from 199 to 572 pM (Table 1) and fit within the range reported for Polar Front areas during previous studies (Cardinal et al., 2001, 2005; Jacquet et al., 2005, 2008a, 2008b, 2011; Planchon et al., 2013). For the KEOPS 2 cruise the main observed features are:

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(a) Unexpectedly, the highest DWAV Baxs value of the whole study area (572 pM; 150-400 m) was observed at the reference R-2 site. Bowie et al. (2014), Quéroué et al. (2015) and van der Merve et al. (2015) reported for R-2 local maxima in particulate and dissolved trace metals at 500 m and deeper, reflecting lateral transport of lithogenic matter possibly originating from the Leclaire Rise (a large seamount located west of R-2). Similarly, Lasbleiz et al. (2014) observed a maximum of lithogenic silica (LSi) at 500 m, confirming lithogenic inputs there. However, we note that the mesopelagic Baxs maximum at R-2 occurs at shallower depths, around 300 m, and that there is no evidence for elevated values at 500 m where the previous authors reported higher trace element and silica concentrations. Also, as reported above (see section 2.2 and Appendix A), the higher lithogenic Ba fractions at R-2 (up to 20% of the total Ba) occur only in the upper 80 m. Moreover, we do note that surface waters at R-2 experienced already some nitrate consumption as compared to subsurface Winter Waters (Tmin waters). Indeed, surface waters had 10% less nitrate than Winter Water (26 µM at 5 m vs. 29 µM at 200 m) and the isotopic enrichment of this surface nitrate confirmed an imprint of uptake (see Dehairs et al., 2014). Also, Lasbleiz et al. (2014) report relatively low Si:C and Si:N ratios for surface ocean suspended matter) pointing to the development of a diatom assemblage just prior the sampling, consistent with the high dissolution rates of biogenic silica (BSi) Closset et al. (2014) report for R-2 surface waters. It is therefore likely that the mesopelagic Baxs content at R-2 indeed reflects remineralization of organic material that was fuelled by an important past early spring production and export event. Similarly, F. Dehairs (unpublished results) observed the presence of significant numbers of barite microcrystals in mesopelagic waters at the KERFIX time series station (50°40′S, 68°25′E) located east of R-2 during late winter (Nov. 1993). Results would thus suggest the occurrence in this HNLC area of recurrent brief early spring diatom productive period pulses and subsequent export and remineralization activity in the underling layers. Chla satellite images (Giovani online Visualization and Analysis system, NASA GES DISC) corroborate that the R-2 and KERFIX area is occasionally subject to enhanced biomass during early spring;

(b) The two successive visits (27-day interval) at site A3 yielded relatively low DWAV Baxs values of 267 and 316 pM, and a quite similar value was observed for the shallow station TEW-3 (324 pM), located further north on the plateau, but north of the PF. Note that for comparison purposes, we recalculated the DWAV Baxs and MR values of KEOPS 1 by considering upper and lower mesopelagic layer boundaries of 150 and 400 m rather than 125 and 450 m, as in Jacquet et al. (2008a). Also, in the latter study the high Ba_{xs} contents observed near the seafloor were not excluded from the calculations, while they are here. These increased benthic boundary layer Ba_{xs} contents (observed also during KEOPS 2) are due to sediment resuspension which extended up to 70 m above the seafloor during KEOPS 1 (Blain et al., 2008; Venchiarutti et al., 2008; Armand et al., 2008). Because of these slightly different depth intervals over which Baxs values were integrated, the KEOPS 1 values discussed here will be slightly different from those reported in Jacquet et al. (2008a). At the other depths the lithogenic Ba contribution at A3 (KEOPS 2) was only minor;

(c) The time series stations in the Polar Front meander had DWAV Ba_{xs} contents ranging from 258 to 427 pM (150-400 m), so reaching values exceeding those on the plateau. For these time series stations values

decreased between day 0 (TNS-6) and 12 (E-3), and then increased again at days 22 (E-4E) and 27 (E-5). Stations E-4W and TNS-8 above the plateau but in deeper waters close to the Kerguelen margin, at the edge the high biomass plume (Figure 1) had the highest DWAV Ba_{xs} values (468 and 473 pM, respectively; 150-400 m), not considering the R-2 reference station. The Polar Front F-L site, although located within the eastern part of the high biomass plume had a smaller DWAV Ba_{xs} value of 345 pM (150-400 m) and the close by station TEW-8 had the lowest DWAV Ba_{xs} value of the whole study area (199 pM; 150-400 m).

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4. DISCUSSION

4.1. Mesopelagic Ba_{xs} and bacterial production

Previous studies revealed that the shape of the column-integrated bacterial production (BP) profile (i.e. the attenuation length scale) was important in setting the Baxs signal in the mesopelagic zone (Dehairs et al., 2008; Jacquet et al., 2008a, 2011a). Mesopelagic Baxs content is smaller when most of the column integrated BP is restricted to the upper mixed layer (indicating an efficient, close to complete remineralization within the surface), compared to situations where a significant part of integrated BP was located deeper in the water column (reflecting significant deep bacterial activity and POC export). During KEOPS 2 the incorporation of ³H-leucine was used to estimate bacterial production. BP data are described in Christaki et al. (2014). In Fig.5 we compare column-integrated BP at 150 m over 400 m (BP150/400) and DWAV Ba_{xs} for the 150-400 m depth interval, next to the relation obtained during KEOPS 1 (BP200/125 and 150-450 m DWAV Baxs; Jacquet et al., 2008a; Christaki et al., 2008). Excluding stations A3, E-1, E-2 and E-3, KEOPS 2 data presented a significant correlation (R^2 =0.88; p<0.01) and a similar trend to the one reported for KEOPS 1. A similar picture was obtained when integrating DWAV Baxs and BP up to 800 m (not shown). The time series

"E" stations in the meander revealed a shift from stations E-1, E-2 and E-3 to stations E-4E and E-5, i.e. towards the trend reported above. A shift was also apparent at station A3 from KEOPS 2 (early spring) to KEOPS 1 (late summer). It is thus possible that results reflect the occurrence of different stage of bloom advancement. The large variability of Ba_{xs} and BP relationship during KEOPS 2, especially at A3 site and in the meander, could reflect the temporal evolution and patchiness of the establishment of mesopelagic remineralization processes in this Polar Front area.

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4.2. Fate of exported organic C in the mesopelagic zone and deep water column

An important question relates to the fate of the exported POC: how much of this POC is respired in the mesopelagic waters and how much escapes remineralization and is exported to deeper layers where longer term sequestration is likely (see e.g. Passow and Carlson, 2012; Robinson et al., 2014; Schneider et al., 2008). To address these questions, we defined two ratios: (1) the mesopelagic C remineralization efficiency (r-ratio in Table 2) which is the ratio of mesopelagic C remineralization (MR, based on the DWAV Ba_{xs} concentrations) over C export (EP) from the 150 m horizon (based on ²³⁴Th, see Planchon et al., 2014), and (2) the C transfer efficiency at 400 and 800 m (i.e., T400, T800 in Table 2) which is the fraction of C export (EP) at 150 m passing through the 400 m (T400) or the 800 m (T800) horizons (e.g., T400 = EP400/EP150 = 1-(MR/EP150), with MR/EP150 = r-ratio; see above). This approach is similar to the one developed by Buesseler and Boyd (2009) stating that a conventional curve-fitting of particle flux data (i.e., power law or exponential) skews our interpretation of the mesopelagic processes. They recommended the use of combined metrics to capture and compare differences in flux attenuation. In the following, we compare MR fluxes for the different KEOPS 2 areas (Reference site; Plateau sites; Polar Front and Polar Front Meander) and discuss remineralization and transfer efficiencies for those sites for which MR, primary production (PP) and/or EP data (Table 2) were available. PP data were estimated from uptake experiments including 24-hour incubations at different PAR levels over the euphotic layer i.e., up to the 0,01% PAR level (Cavagna et al., 2014). EP data were estimated from ²³⁴Th activities and ²³⁴Th /POC ratios and are discussed in Planchon et al. (2014). The thorium method integrates POC export over a 1 month period (²³⁴Th half live equals 24.1 days). We remind here that MR fluxes as based on mesopelagic Ba_{xs} reflect past remineralization activity integrated over several days to a few weeks (Dehairs et al., 1997; Cardinal et al., 2005; Jacquet et al., 2007, 2008b). In order to compare EP with MR (r-ratio and transfer efficiency) we consider EP fluxes from 150 m. Results are compared with late summer KEOPS 1 results. For KEOPS 1, PP data are detailed in Lefèvre et al. (2008) and Mosseri et al. (2008), EP data are detailed in Savoye et al. (2008) and Ba_{xs} data are described in Jacquet et al. (2008a).

4.2.1. Reference station R-2

Since station R-2 had the highest DWAV Ba_{xs} content it yielded the highest MR flux of the whole study area (91 mgC m⁻² d⁻¹; 150-800 m; Table 2). In contrast, both PP and EP fluxes at R-2 were very low (132 and 10 mgC m⁻² d⁻¹, respectively) and the calculated MR flux exceeded EP (Table 2). The resulting export efficiency (EP/PP) was high, and T400 and T800 value (the fraction of EP exported deeper than 400 m and 800 m, as defined above) equal 0 (i.e., no export of POC beyond 400 and 800 m; note that >100% values, i.e., MR>EP, were set to zero in Fig.7a and Table 2). The fact that MR exceeds EP therefore implies a non-steady state condition at the R-2 site. As reported above, R-2 probably experienced a brief early spring diatom production pulse days to a few weeks before the start of the KEOPS 2 cruise,

followed by subsequent export and quite important remineralization activity in the underling layers as depicted by MR data.

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4.2.2. Station A3 on the Plateau

542 The MR fluxes on the plateau varied little between the two visits 27 543days apart (Table 1) and as discussed below they were moreover similar to 544 summer values obtained during KEOPS 1 (see Jacquet et al., 2008a) when the 545 same A3 site was sampled 3 times over a 19-day period. While during KEOPS 2 (spring) MR fluxes at A3 ranged from 11 to 14 mgC m⁻² d⁻¹ (with a standard 546 547 uncertainty around 5%) they were slightly larger during KEOPS 1 (summer; 17 to 23 mgC m⁻² d⁻¹) (Fig.5). We observed differences in the mesopelagic 548 549 POC remineralization efficiency between the two seasons (r-ratio, blue values 550 in Fig.6, Table 2). During KEOPS 1 r-ratios (MR/EP) remained low, ranging 551 from 7 to 9% of EP at A3, while during KEOPS 2 r-ratios were slightly higher 552 but decreased from 29% (A3-1; first visit) to 13%, 27 days later (A3-2; 553 second visit). This variation in r-ratio during KEOPS 2 is mostly due to an increase of EP (from 47 to 85 mgC m⁻² d⁻¹; Planchon et al., 2014) over the 554 555 same period while MR showed little change. Although at this early stage of the season (spring) PP at A3-2 had already reached 2172 mgC m⁻² d⁻¹ (Cavagna 556 et al., 2014), EP remained relatively low (85 mgC m⁻² d⁻¹). Here EP accounted 557 558 for only about 4% of PP (low export efficiency; see green data points in 559 Fig.5). This condition suggested that phytoplankton biomass 560 accumulating in the surface waters without significant export yet, or that C 561was channeled to higher trophic levels as suggested by Christaki et al. 562 (2014). Note that a negative relationship between primary productivity and 563 surface carbon export efficiency has already been reported from previous 564 studies in the Southern Ocean (Lam et al., 2007; Morris et al., 2007; Savoye 565 et al., 2008; Jacquet et al., 2011a, 2011b). Among possible explanations for 566 the occurrence of high productivity-low export efficiency regimes in high

latitude systems Maiti et al. (2013) mentioned differences in trophic structure, grazing intensity, recycling efficiency, high bacterial activity, or increase in DOC export, but the exact reason remain unclear. In contrast, during KEOPS 1 (summer), EP fluxes reached 250 mgC m⁻² d⁻¹ at 125 m (14-31% of PP) while PP ranged from 865 to 1872 mgC m⁻² d⁻¹, reflecting enhanced export efficiency (Jacquet et al., 2008a; Savoye et al., 2008).

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It is important to underline the fact that MR at station A3 was only slightly higher in summer than in spring especially considering the large differences in export efficiency between seasons. According to results from sediment traps deployed over one year at the A3 site, Rembauville et al. (2014) reported that 60% of the annual POC export at the base of the mixed layer occurred over a short periods of time representing <4% of the years and was composed by small highly silicified, fast sinking, resting spores of diatoms that bypass grazing pressure. According to these authors, the pulses are linked to nutrient depletion dynamics inducing resting spore formation. During the rest if the year, the flux was composed of small diatoms (empty frustules) and small fecal pellets, with efficient C retention in the surface layer or transfer to trophic levels. If we consider that export conditions during KEOPS 2 are more similar to those prevailing most of the year, it is surprising that during KEOPS 1 (that would reflect an export event toward the end of the growth season) MR is not more important. This would indicate that fast sinking- highly silicified- and pulsed material was directly transferred to the bottom without major remineralization. Note for example that at the complex R-2 reference station, a small export event (Laurenceau-Cornec et al.; 2015) held heavily silicified diatoms (Lasbleiz et al.; 2014), and that the material was efficiently remineralized in the upper mesopelagic layer as witnessed by the high MR values we observe for that station. For the KEOPS 2 A3 site Laurenceau-Cornec et al. (2015) report that the sinking flux collected in the upper layer using gel-filled sediment traps was composed by phytodetrital aggregates that held slightly silicified diatoms (Lasbleiz et al., 2014). Even considering the shift from slightly- to highly-silicified material transfer between spring (KEOPS2) and summer (KEOPS 1), MR only slightly increases between both periods. Also, the mesozooplankton biomass at A3-2 was one of the highest of the KEOPS2 cruise, with a doubling from KEOPS 2 (early spring) to KEOPS 1 (late summer) (Carlotti et al., 2015). It is thus possible that at A3 the export event reported above, combined with a lasting grazing pressure would have induced this rather low and perduring mesopelagic remineralization. We also wonder whether the shallow water column at A3 combined with lateral advection above the plateau would play a role in triggering the mesopelagic POC remineralization activity and in setting its efficiency. For KEOPS 1, Venchiarutti et al. (2008) report that lateral advection over the plateau could significantly impact particle dynamics. During KEOPS 1, station B1 (CTD68) located on the plateau upstream from A3 according to the plateau circulation (Park et al., 2008) exhibited a very similar Ba_{xs} distribution as station A3: low mesopelagic Ba_{xs} and important bottom resuspension (not shown here; see Jacquet et al., 2008a). These strong similarities in Baxs profiles shape would indicate that next to the pulsed nature of the events, the dynamics on the shallow plateau play an important role in limiting the extend of mesopelagic POC remineralization processes.

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In Fig.7a is shown for both KEOPS cruises the ratio of EP over PP (export efficiency) vs. the fraction of EP exported deeper than 400m (i.e. T400; defined above). Note that for station A3-1 (KEOPS 2), there are no PP data. The A3 site shows increasing EP/PP ratios from spring (KEOPS 2) to late summer (KEOPS 1), and so do the T400 values (A3-1: 70%; A3-2: 87%; KEOPS 1 A3 site: $92\pm1\%$). Station E-4W located in waters with similar θ -S and Chl-a characteristics as the A3 plateau site but has a deeper water column (1384 m has PP and EP fluxes of the same order of magnitude (Table 2). However, MR values (36 mgC m⁻² d⁻¹; 150-400 m) are larger at E-4W,

625 resulting in a lower T400 value of around 33%, compared to 87% for A3-2 626 (Fig. 7a). When integrating down to 800 m, T800 at E-4W equals 0 (i.e., no 627 export of POC beyond 800 m; Fig. 7a and Table 2). Station F-L (in the vicinity 628 of the PF; 74.7°E) appears to function in a similar way as observed for E-4W (71.4°E). PP at station F-L is relatively high (3380 mgC m⁻² d⁻¹), while EP is 629 quite low (43 mgC m⁻² d⁻¹), reflecting the fact that the biomass was not yet 630 631 exported from the surface waters or was transferred to higher trophic levels. 632 Since MR fluxes are slightly lower (21 mgC m⁻² d⁻¹; 150-400 m) at F-L than at 633 E-4W, resulting T400 values are higher (52%) there. 634 Overall, during KEOPS 2 it appears that biomass at stations A3, E-4W 635 and F-L (sites of high productivity) was accumulating in surface waters (e.g. 636 transfer to higher trophic levels) and export did not start yet considering the 637 early stage of the season during KEOPS 2. Our observations allow us to 638 conclude the following: 639 (1) Both seasons (KEOPS 1 and KEOPS 2) showed a similar functioning of the 640 mesopelagic ecosystem at A3. The rather low and perduring MR fluxes under 641 high production and variable export regimes (high export efficiency during 642 KEOPS 1 and low export efficiency during KEOPS 2) indicated that here

643 mesopelagic remineralization does not represent a major resistance to organic 644 matter transfer to the sea-floor at A3. On average (considering both seasons, 645 but excluding A3-1) the C transfer efficiency into the deep (>400 m) as 646 assessed by PP, EP and MR fluxes comparisons reached 91±3% at A3; 647 (2) In contrast to A3, E-4W and F-L showed important mesopelagic 648 remineralization rates, reducing the efficiency of C transfer beyond 400 m to 649 33 and 52%, respectively, and to zero for both stations beyond 800 m. 650 Bottom depth, lateral advection, zooplankton grazing pressure and the pulsed 651 nature of the POC transfer at A3 were the particular conditions that could 652 drive the differences in C transfer efficiency between A3 and E4-W and F-L 653 and limit the extend of MR processes at A3.

4.3. Stations in the meander

Temporal short term changes for the stations TNS-6, E-1, E-2, E-3, E-4E and E-5, located in the Polar front meander, will be discussed in this section. Note that no PP or EP data exist for TNS-6. From Table 2 it appears that PP almost doubled between E-1 and E-5 but this increase was not paralleled by an increase of EP and MR, except for the 30% EP increase from E-1 to E-3. In fact overall EP shows a decreasing trend with time, while MR (150-400 m) stays rather constant, except for the decrease between E-1 and E-3 (Table 2). As reported above such a mismatch may result from differences in time scales characterizing the different processes that were compared. The most likely explanation is that in this early stage of the growth season, phytoplankton biomass was accumulating in the surface layer and export was lagging behind.

The ratio of EP over PP vs. T400 and T800 showed a large variability in transfer efficiency inside the meander (Fig.7b). PP and EP fluxes increased by about 30% from E-1 to E-3, but a concomitant decrease of mesopelagic MR yielded to an enhanced transfer efficiency, from 74 to 92%, through the 400 m boundary and from 52 to 73% through the 800 m boundary. This suggests that significant remineralization should have occured at greater depths (even > 1000 m) and it is also reflected by the presence of Ba_{xs} maxima below 1000 m (see Fig.4h and Appendix A). This was particularly salient when plotting Ba_{xs} contents vs. depths over the 27-day observation period (Fig.8). The high deep water Ba_{xs} values in Figure 8 were not taken into account when integrating TNS-6 and E-1 profiles between 150 and 400 or even 150 and 800 m (Fig. 5e). Considering that the seafloor in the meander area is at about 2000 m depth, it seems unlikely that these high Ba_{xs} contents at depths >1000 m were due to sediment resuspension. Also, particle spectra for these sites do not reveal any bottom resuspension (Jouandet et al., 2014; Lasbleiz

et al., 2014; van der Merve et al., 2015). Therefore, the high deep (>1000 m) Ba_{xs} contents at TNS-6 and E-1 most likely reflected the fact that here significant remineralization of POC material did occur in the bathypelagic domain and even down to the sea-floor. Note that suspended particles in the depth range containing the deep Ba_{xs} maxima were dominated by the <2 μ m size fraction (Zhou et al., pers. comm.). When integrating the Ba_{xs} contents from 150 m to the sea-floor at stations TNS-6 and E-1, MR fluxes increase to 156 and 184 mgC m⁻² d⁻¹ respectively. Such C fluxes were similar to the EP values (maximum value of 130 mgC m⁻² d⁻¹ at E-3) and suggested that the exported POC was entirely remineralized in the water column leaving no C for transfer to the sediments.

Overall, the temporal pattern of mesopelagic remineralization described above reflects two successive events of particle transfer: a first transfer from a previous bloom (occurred before visiting TNS-6 and perduring at E-1) and a second transfer from E-4E to E-5. The first transfer was evident by the downward (up to the bottom) propagation of the mesopelagic Baxs maximum signal, which mostly weakens at E-2. The second event was reflected by the occurrence again of important mesopelagic Baxs build-up at E-4E and E-5. Overall, our results indicated the large capacity of the Polar Front Meander to transfer POC material to depth, but in contrast to station A3 on the Plateau, this transfer was coupled to intense and near to complete POC remineralization (as also observed at E-4W and F-L). Between-sites changes in mesopelagic carbon remineralization due to unequal biomass productivity and iron fertilization over the Kerguelen Plateau were thus relatively complex. Furthermore, the situation in the Meander area seems to corroborate results obtained in the iron-replete Subantarctic Zone east of the Tasman Plateau (Australian sector of the Southern Ocean; SAZ-Sense cruise; Jacquet et al., 2011a, 2011b), where the mesopelagic remineralization efficiency was reported relatively high (on average 91%) and the deep (>600 m) carbon

transfer weak (<10%). Finally, the important Ba_{xs} contents reported between 1000 and 2000 m during the first stages of the meander time-series strengthen recent results indicating for the Southern Ocean that 1000 m is insufficient as an ocean-wide reference for carbon transfer and sequestration potential (Robinson et al., 2014).

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5. Conclusion

Based on spatially and temporally well resolved mesopelagic excess particulate Ba inventories this work estimated mesopelagic remineralization above the Kerguelen Plateau and inside a permanent meander of the Polar Front to the east of Plateau, areas. The observed variability of mesopelagic remineralization reflects differences in the fate of the biomass that is exported to the deep ocean, between Plateau and Polar Front. Results also reveal the patchiness of the season advancement and of the establishment of remineralization processes between theses sites. Our results indicate that the reference station R-2 experienced few days to weeks before the start of the cruise an export event that was efficiently remineralized in the upper mesopelagic layer. In terms of deep ocean carbon transfer efficiency, our results highlight that above the plateau (A3 site) mesopelagic remineralization is not a major barrier to organic matter transfer to the sea-floor, with carbon transfer beyond 400 m reaching up to 87% of EP during KEOPS 2, while in the Polar Front Meander remineralization of exported organic carbon in the upper 400 m is more efficient than above the plateau. In the Meander area remineralization may even balance export when including its effect in the deeper waters (till 800 m and even deeper), thus resulting in a close to zero carbon transfer to sediment. A similar condition is also observed for sites at the margin of the plateau (E-4W) and the Polar front (F-L).

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Acknowledgements

742We thank the officers and crew of R/V Marion Dufresne for their 743 assistance during work at sea. We are indebted to chief scientist S. Blain and 744voyage leader B. Quéquiner for skillful leadership during the cruise and to the 745CTD team for managing rosette operation and CTD data. This research was 746 supported by the French Agency of National Research grant (project KEOPS 2, 747 #ANR-10-BLAN-0614), the Belgian Science Policy (BELSPO) project 748'BIGSOUTH' (SD/CA/05A), Flanders Research Foundation (FWO Project G071512N), the European Union Seventh Framework Programme (Marie Curie 749 750 CIG 'MuSiCC' under grant agreement no 294146 to D.C.) and the Strategic 751Research Programme at Vrije Universiteit Brussel.

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Figure captions

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Figure 1: (a) Kerguelen Island area in the Southern Ocean with KEOPS 2 sampling zones and MODIS Chlorophyll concentrations (mg m⁻³) (Chl-a map from 11/11/2011, courtesy F. d'Ovidio) superposed. 1 refers to station A3; 2 to stations E; 3 to the South-North Transect; 4 to the West-East Transect; 5 to station F-L and 6 to reference station R-2; (b) Corresponding stations location. Colors indicate stations with near similar θ -S and Chl-a characteristics.

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763 Figure 2: (a) Potential temperature θ – salinity S plots and isopycnals for 764KEOPS 2 profiles, (b) Focus on the upper 200 m water column. AASW= 765Antarctic Surface Waters, AAIW= Antarctic Intermediate Waters, WW= Winter Waters, UCDW and LCDW= Upper and Lower Circumpolar Deep Water, 766 767 AABW= Antarctic Bottom Water. Graph constructed using Ocean Data View 768 (Schlitzer, 2002; Ocean Data View; http://www.awi-769 bremerhaven.de/GEO/ODV).

770 Figure 3: Rates of oxygen consumption (mmol m⁻² d⁻¹) during KEOPS 1 as 771772 directly measured (JO_2 -W) and from mesopelagic Ba_{xs} contents (JO_2 -Ba). 773 Rates are integrated between 150-300 m. 774775Figure 4: Particulate biogenic Ba_{xs} profiles (pM) in the upper 800 m (Fig.4a-g) 776 and in the upper 2500 m (Fig.4h). Stations are identified by CTD cast 777 numbers. BKG= Ba_{xs} background (180 pM). 778 779 Figure 5: Regression of the ratio of integrated bacterial production (BP) in the 780 upper 150 m over integrated BP in the upper 400 m versus depth weighted 781 average (DWAv) mesopelagic Baxs (pM; 150-400 m) during KEOPS 2. KEOPS 782 1 data (dots) are reported for comparison. 783 784Figure 6: Schematic, comparing the fate of POC at station A3 during KEOPS 1 785 and KEOPS 2 cruises. PP= primary production, EP= export production at 150 786 m depth and MR= mesopelagic POC remineralization deduced from the Baxs 787 maxima and integrated between 150-400 m; all fluxes in mgC m⁻² d⁻¹. EP/PP 788 (green values), MR/PP (red values) and MR/EP (r-ratio, blue values) ratios 789 shown as %. 790 791 Figure 7: Y-axis: EP/PP = POC flux at 150 m (EP150) as a fraction of primary 792 production (PP); X-axis: EPx/EP150 = POC flux at defined depths (EPx; here 793 400 and 800 m) as a fraction of POC flux at 150 m (EP150). The green cross 794 (Fig. 5a) is for station A3-1 (KEOPS-2). Since no PP data is available for that

station, the EP/PP value has been arbitrarily set to 0. Isolines represent the

modeled 1, 5, 10, 20 and 30% of PP export to depths >at 400 or 800 m, and

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represent export efficiency.

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799	Figure 8: Temporal evolution of particulate biogenic Ba (Ba $_{xs}$; pM) in the
800	upper 2000 m water column in the Polar Front meander. Graph constructed
801	using Ocean Data View (Schlitzer, 2002; Ocean Data View; http://www.awi-
802	bremerhaven.de/GEO/ODV).
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804	Table captions
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806	<u>Table 1</u> : Station locations, CTD cast number and bottom depth during KEOPS
807	2. Depth-weighted average values (DWAv) of mesopelagic \mbox{Ba}_{xs} (pM) and \mbox{Ba}_{xs}
808	based mesopelagic POC remineralization (MR; $mgC m^{-2} d^{-1}$) integrated
809	between 150-400 and 150-800 m depths. See text for further information on
810	calculation.
811	
812	<u>Table 2</u> : Comparison of mesopelagic POC remineralization (MR) with primary
813	production (PP) and export production (EP). All fluxes in mg C m^{-2} d^{-1} . r-ratio
814	is the ratio of MR over EP. EP/PP is the export efficiency. The C transfer
815	efficiency at 400 and 800 m (T400, T800) is the fraction of C export (EP) at
816	150 m exiting through the 400 m (T400) or the 800 m (T800) horizons. See
817	text for further information on calculation.
818	
819	Appendix A: Excess particulate biogenic Ba (Ba _{xs} ; pM) and particulate Al (nM)
820	during KEOPS 2.
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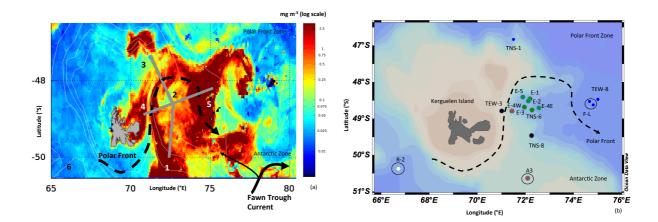
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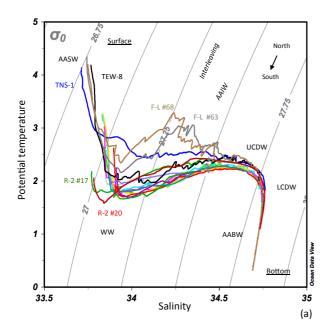
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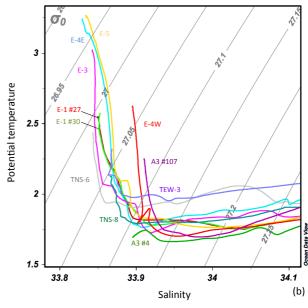
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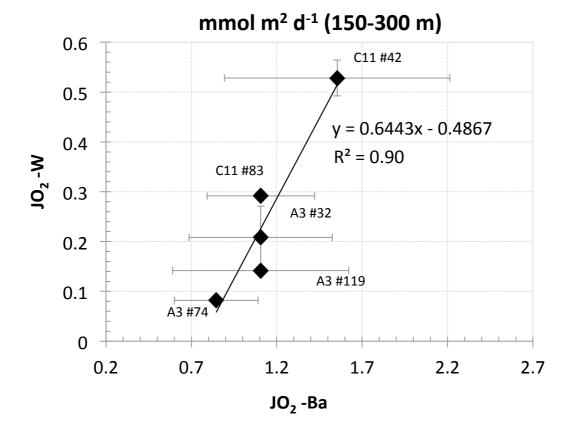
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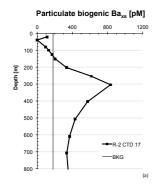
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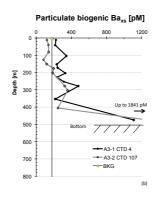


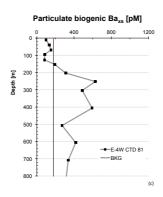


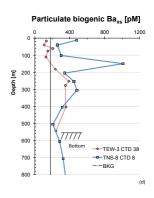


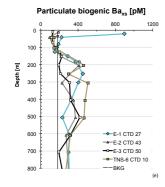


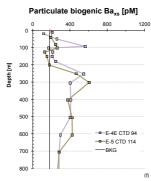


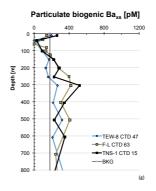


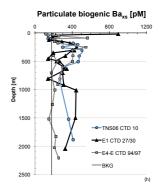


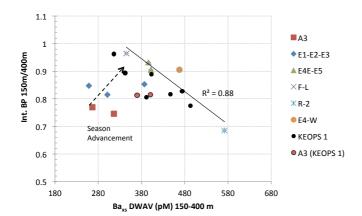






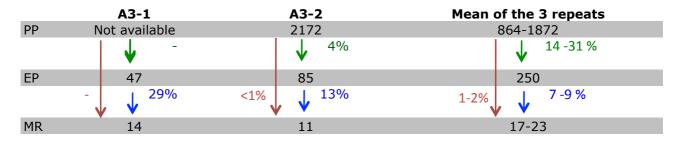






KEOPS 2 (Early spring 2011)

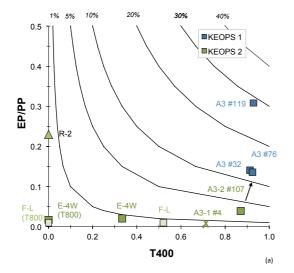
KEOPS 1 (Late summer 2005)

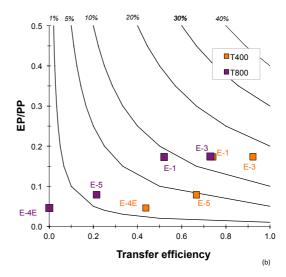


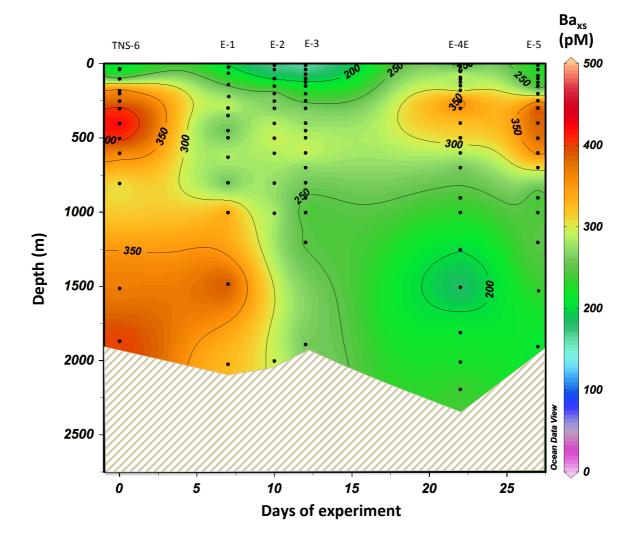
All fluxes in mgC $\mathrm{m^{-2}\,d^{-1}}$

Blue values: r-ratio, mesopelagic remineralization efficiency (MR/EP)

Grenn values: EP/PP Red values: MR/PP







Station	CTD cast #	Long (°E)	Lat (°S)	Date of sampling	Seafloor [m]	DWAv° Ba _{xs} [pM] 150- 400 m	DWAv Ba _{xs} [pM] 150- 800 m	MR°° 150- 400 m [mgC/m²/d]	MR Stnd Uncertainty %	MR 150- 800 m [mgC/m²/d]	MR Stnd Uncertainty %
Plateau											
A3-1	4*	72.080	50.629	20/10	530	316	/	14	4	/	/
A3-2	107*	72.056	50.624	16/11	527	267	/	11	5	,	/
TEW-3	38	71.018	48.799	31/10	560	324	/	28	8	/	/
Meander time series											
TNS-6	10	72.277	48.779	22/10	1885	427	389	31	7	69	17
E-1	27/30	72.187	48.458	29,30/10	2056	387	325	26	6	48	14
E-2	43	72.077	48.523	1/11	2003	301	309	15	5	42	13
E-3	50/55	71.967	48.702	03,04/11	1915	258	286	10	4	35	12
E-4E	94/97	72.563	48.715	13,14/11	2210	395	357	27	7	58	15
E-5	113/114	71.900	48.412	18/11	1920	402	380	28	7	66	17
Polar Front Zone											
TNS-1	15	71.501	46.833	23/10	2280	350	315	22	6	45	14
TEW-8	47	74.999	48.471	2/11	2786	199	240	2	4	20	11
F-L	63/68	74.659	48.532	06,07/11	2695	345	328	21	6	49	14
Polar Front											
E-4W	81/87	71.425	48.765	11,12/11	1384	468	411	36	8	76	18
Antarctic Zone											
R-2 (Reference site)	17/20	66.717	50.359	25,26/10	2300	572	456	50	10	91	20
TNS-8	8	72.240	49.463	21/10	1030	473	358	37	8	59	15

^{*}Station A3 (CTD #4 and #107); integration up to 354 and 405 m DWAV $^\circ$ = Depht weighted average value MR $^\circ$ = Mesopelagic C remineralization

Station	CTD	MLD [m]	Ez** [m]	PP° Ez EP°° 150 m		MR 150-400 m	MR 150-800 m	EP/PP	r-ratio	r-ratio	T400	T800
	CID	MED [III]	EZ. · [III]	[mgC/m²/d]	[mgC/m2/d]	[mgC/m²/d]	[mgC/m²/d]	LP/PP	150-400 m	150-800 m	1400	1600
Plateau												
A3-1	4*	161	/	/	47	14	/	/	0.29	/	0.70	/
A3-2	107*	165	38	2172	85	11	/	0.04	0.13	/	0.87	/
Reference sit	te											
R-2	17/20	111	92	132	30	50	91	0.23	1.65	3.02	0	0
Meander time	e series											
E-1	27/30	84	64	578	100	26	48	0.17	0.26	0.48	0.74	0.52
E-3	50/55	41	68	748	130	10	35	0.17	0.08	0.27	0.92	0.73
E-4E	94/97	77	34	1037	48	27	58	0.05	0.57	1.21	0.43	0.00
E-5	113/114	36	54	1064	84	28	66	0.08	0.33	0.78	0.67	0.22
Polar Front 2	Polar Front Zone											
F-L	63/68	21	29	3380	43	21	49	0.01	0.48	1.13	0.52	0
Polar Front												
E-4W	81/87	67	31	3287	54	36	76	0.02	0.67	1.41	0.33	0

^{*}Station A3 (CTD4 and 107); MR integrated up to 354 and 405 m **EZ euphotic layer (till 1% PAR level) ° PP data from Cavagna et al. (this issue) °° EP data from PLanchon et al. (this issue)

Station A	43							Station RK2							
A3-1 CTI Niskin	D4 Depth [m]	Ba _{xs} [pM]	Al [nM]	A3-2 CTD 10 Niskin	7 Depth [m]	Ba _{xs} [pM]	Al [nM]	R-2 CTD17 Niskin	Depth [m]	Ba _{xs} [pM]	Al [nM]	R-2 CTD 20 Niskin	Depth [m]	Ba _{xs} [pM]	Al [nM]
23 21 19 17 15 13 11 9 7 5	11 42 104 152 173 204 227 253 279 354 474	224 217 345 234 244 333 235 315 480 216 1108	35 64 65 19 19 17 8 6 8 21 155	23 21 19 17 15 13 11 9 7 5	11 40 81 126 151 176 202 277 303 405 513	122 140 141 82 119 186 323 359 247 1842	16 12 10 27 14 9 14 24 32 19 186	24 23 22 20 18 16 14 13 12 10 9 7	21 40 80 100 126 151 203 253 304 404 507 608 708 911	110 0 95 131 168 205 334 616 834 573 430 367 337 368	107 693 49 27 5 4 3 6 16 9 10 4 10	17 15 13 11 10 8 6	356 507 609 812 1011 1520 1832 2473	546 239 226 267 189 201 184 286	12 17 7 3 2 4 2 3
Station E															
24	Depth [m] 21	896	Al [nM]	Niskin 17	Depth [m] 303	Ba _{xs} [pM]	Al [nM]	Niskin 23	Depth [m]	Ba _{xs} [pM]	Al [nM]	E-3 CTD 50 Niskin 24	Depth [m]	Ba _{xs} [pM]	Al [nM] 45
23 22 20 18 16 14 13 12 10 9 7	41 81 101 125 151 182 253 303 403 505 605 707 913	221 190 172 150 290 375 450 402 327 230 305 298 309	131 161 102 10 9 5 12 9 10 6 10 10	16 15 13 11 10 8 6	353 455 505 636 808 1011 1498 2042	195 143 268 343 138 442 436 326	25 6 7 2 4 9 7	21 18 16 14 12 10 8 7 6 5 4	41 102 153 204 254 305 406 507 609 813 1016 2020	93 143 215 408 311 227 353 371 271 297 350 302	152 17 57 9 6 4 5 9 10 14 35	23 22 20 18 16 14 13 12 10 9 7 5	42 71 102 125 153 203 252 304 404 505 606 707 912	117 130 160 201 225 193 210 309 316 419 320 193 265	93 28 22 11 18 3 2 6 7 64 14 12 5
Station E	E (continue	d)													
Niskin 17	55 Depth [m] 404	Ba _{xs} [pM]	Al [nM]	Niskin 24	Depth [m]	Ba _{xs} [pM]	Al [nM]	E-4W CTD 87 Niskin 17	Depth [m]	Ba _{xs} [pM]	Al [nM]	E-4E CTD 94 Niskin 24	Depth [m]	Ba _{xs} [pM]	Al [nM] 32
16 15 13 11 10 8 6	455 505 605 810 910 1012 1214 1908	103 2772 176 378 258 172 184 228 237	5 6 5 3 2 3 6 9	23 22 20 18 16 14 13 12 10 9 7	10 41 70 94 126 153 203 252 304 406 507 607 708 909	134 152 86 84 193 312 628 488 594 272 418 338 294	17 5 18 7 8 4 17 12 11 11 12 21 14	16 15 13 11 10 8 6	354 453 606 811 910 1011 1214 1384	250 233 182 186 187 268 249 250	10 7 9 5 7 61 29 30	23 22 20 18 16 14 13 12 10 9 7	93 103 126 152 181 253 305 404 505 606 706 912	260 563 170 215 210 247 547 403 408 403 298 285 245	11 223 5 9 6 7 4 78 26 26 13 8
Station E	E (continue	d)													
E-4E CTC Niskin 21 18 13 8 7 6 5 4 1	D 97 Depth [m] 404 505 706 1012 1265 1518 1827 2027 2212	Ba _{xs} [pM] 199 242 175 212 189 149 225 212 254	Al [nM] 2 3 1 111 2 2 43 12 9	E-5 CTD 113 Niskin 10 10 8 6 1	Depth [m] 911 1011 1214 1922	Ba _{ss} [pM] 111 266 256 208	Al [nM] 3 16 15 5	E-5 CTD 114 Niskin 24 23 22 20 18 16 14 13 12 10 9 7 5 1	Depth [m] 11 41 82 102 126 152 202 252 302 404 507 606 707 910	Ba _{ss} [pM] 210 219 245 264 131 153 181 469 606 377 422 425 281 281	Al [nM] 5 14 4 14 6 5 2 6 9 13 11 7 12 6				
Transect	t West-East	•						Station F-L							
TEW-3 C Niskin 23 21 19 17 13 11 9 7 5	Depth [m] 16 41 61 76 112 183 253 277 404 545	Ba _{xs} [pM] 133 107 209 148 128 235 391 348 356 242	Al [nM] 40 112 45 20 13 8 11 9 8 13	TEW-8 CTD 4 Niskin 23 21 18 16 14 12 10 8 7 6 5 4	Depth [m] 10 41 102 152 202 254 304 405 507 609 809 1011 2812	Ba _{xx} [pM] 196 0 92 169 134 164 268 217 319 209 330 334 11179	Al [nM] 31 251 41 45 9 5 12 5 8 14 22 826	F-L CTD 63 Niskin 24 23 22 20 18 16 14 13 12 10 9 7 5 1	Depth [m] 11 35 61 82 101 126 151 202 252 303 404 506 707 911	Ba _{sc} [pM] 146 97 0 1441 134 185 221 280 399 420 305 408 247 282	Al [nM] 37 41 228 36 5 5 7 8 7 26 7 10 11	F-L CTD 68 Niskin 17 16 15 13 11 10 8 6 1	Depth [m] 405 456 506 607 910 1013 1215 1772 2741	Ba _{ss} [pM] 264 233 339 265 718 257 316 225 2999	Al [nM] 6 9 12 3 7 5 8 7 131
	Transect North-South														
TNS-1 CT Niskin 23 21 18 16 14 12 10 8 7 6 5 4	TD15 Depth [m] 11 41 102 153 202 253 304 405 506 607 809 1520 2282	Ba _{ss} [pM] 262 30 93 225 289 228 521 346 230 352 234 127 211	Al [nM] 62 90 15 17 5 2 4 3 1 13 4 6 19	TNS-6 CTD 1 Niskin 21 18 16 14 12 10 8 7 6 5 4	Depth [m] 35 42 103 184 204 255 306 407 509 610 813 1526 1886	Ba _{ss} [pM] 182 141 143 413 461 298 505 474 464 315 269 362 410	Al [nM] 26 12 14 11 8 5 7 4 9 15 9 13 21	TNS-8 CTD8 Niskin 21 18 16 14 12 10 8 7 6 5 4	Depth [m] 12 41 102 150 205 254 305 405 505 606 707 910 1000	Ba _{ss} [pM] 478 258 303 1008 341 447 481 312 208 283 3225 376 294	Al [nM] 45 53 32 33 10 6 4 3 7 11 35 28				