Interactive comment on "Early season mesopelagic carbon remineralization and transfer efficiency in the naturally iron-fertilized Kerguelen area" by S. H. M. Jacquet et al.

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Dr Jacquet and co-workers report an interesting study variability of the mesopelagic barite in excess along a broad N-S transect in the Kerguelen area, from which they deduce the zonal variability of the POC export. They also performed this study within a meander east of the Kerguelen plateau, transect allowing them to follow the temporal evolution of these oceanic parameters. They eventually compare some of their results (when possible) to earlier data obtained at the same location but at fall, which provides an insight on the seasonal variability of the Baxs distribution, POC export (EP) and their remineralization rate estimate, that they compare to primary production (PP and EP being published in companion papers of the same issue). The set of data is of good quality, the complexity of the area made the interpretation challenging, difficulty which is honorably overcame by the authors. This work deserves to be published in Biogeosciences, but not without some improvements proposed below.

#### **General Comments**

**Reviewer:** The whole paper is based on the use of Baxs as proxy of the POC remineralization, proxy that was well described by many preceding works of the same authors and oth- ers. Indeed, the Baxs mesopelagic maxima is ubiquist; Bishop, Dehairs and others demonstrated that micro-crystals of barite precipitates in biological microenvironments (fecal pellets, aggregates. . .), and that the release of these micro-crystals yielding the observed maximum corresponds to the disintegration of this biological material, con- comitant to the maximum consumption of oxygen, the latter being related to POC oxi- dation. However, this reasoning and the empirical relationship allowing relating Baxs to POC remineralization is based on one dimensional approach. The Kerguelen plateau is particularly dynamic, and several preceding works discuss (and even propose a modelling, for the Pa/Th distribution, Venchiarutti et al, 2008) the importance of the advection on the fate of Trace Elements and isotopes on the plateau and around. I am concerned by the fact that the impact of advection and internal tides is never dis- cussed in this work. For example, the maximum of Baxs at the reference station is considered only as a remnant signal from a preceding bloom, occurring in late winter. Other works are observing maxima of LSi, particulate Fe, Mn and Al (van de Merwe, Lasbleiz et al) that could be advected from the Leclaire Rise, located 75 km north west of R-2. . .knowing that resuspended sediments are also enriched in Baxs (as shown in this work at stations A3 for ex) why is the hypothesis of such horizontal transport not discussed here? On the plateau, what is the importance of horizontal versus vertical transport? This should be more deeply considered in the present manuscript.

#### **Reply:**

First, to estimate POC remineralization rates we used an algorithm relating Baxs contents to the rate of oxygen consumption that was deduced via a 1-D advection diffusion model applied on highly resolved, precises dissolved O2 profiles along 6°W in the Southern Ocean (Shopova et al., 1995, Dehairs et al., 1997). During the KEOPS 1 cruise, by comparing mesopelagic oxygen consumption rate obtained using the Winkler method and this obtain using Baxs contents and the above-mentioned algorithm, the correlation was significative ( $R^2$ =0,90, p<0.05). We concluded in the validity of the algorithm in the Kerguelen area. This correlation and discussion about oxygen consumption rate have been added in the ms.

Then, Baxs peak at the K2 reference station is surprising in that in "HNLC / no bloom / low productivity / low export" conditions we observe a signal that we attributed to a previous/ winter production and export event. Nitrate contents and isotopic enrichment also relate an imprint of winter uptake (Dehairs et al., this issue), and low Si:C and Si:N ratios potentially reflect a previous diatoms development (Lableiz et al., this issue), which is consistent with high dissolution rates of BSi in surface (Closset et al., this issue). Both results suggest the occurrence of a winter production and

remineralization event. In Bowie et al., Quéroué et al. and van der Merve et al., (both this issue), authors report that lateral transport of lithogenic matter from the Leclaire Rise (a large seamount located west of station R) would explain local maximum at 500 m depth and deeper, in particulate and dissolved trace metals. This is also corroborated in Lasbleiz et al. (this issue) with LSi data exhibiting a maximum at R station at 500m reflecting particulate lithogenic input. However, the Baxs maximum at K2 is relatively shallower (maximum at 300 m). Also, the size fractions of particles above and below 500 m depths are different at this station. We don't think that the upper 500 m Baxs signal (and maximum at 300 m) could be related to major Ba advection. We can however not exclude the impact of advection on the whole Baxs profile, even if salient Ba peak are not present deeper 500 m. Also, the Baxs was calculated as the difference between total Ba and lithogenic Ba using Al as the lithogenic reference element. During KEOPS2, at most of sites and depths the biogenic Baxs represented >95% of total Ba. At K2, the lithogenic Ba reached up to 20% solely in the upper 80 m.

Concerning station A3 on the Plateau, the lithogenic contribution is relatively important, mainly below 400 m where we observe important Ba and Al peaks. Particles size spectra clearly indicated at A3 sediment resuspension. We mentioned in the ms. that for profiles at station on the plateau, bottom waters with evidence of lithogenic input were not taken into account when calculation DWAv Baxs values. As also reported for station R-2, the lithogenic part at A3 on the Ba signal was minor (expect near the bottom due to sediment resuspension). Concerning the importance of lateral advection on the plateau in setting the Baxs signal, we added a discussion in the ms. (we referred to the work of Venchiarutti et al., 2008 and to Baxs profiles obtained on the plateau during KEOPS 1).

Sentences have been added in paragraphs first mentioned to as 4.1 and 4.2. These paragraphs moved to the results section.

#### Detailed comments

**<u>Reviewer:</u>** In the abstract, it should be explicitly written that the "mesopelagic POC remineralisa- tion" reported here is deduced from Baxs proxy: this would be more precise **<u>Reply</u>**: Done

**<u>Reviewer:</u>** -In the introduction and section 3.2, no reference is made to E. Sternberg work, who also demonstrated (with F Morel) that Baxs in the surface water is "scavenged Ba" but not immediately crystallized as barite, and brought some clues on the seasonal "rhythm" of the barite formation by studying a "short time series" in the Mediterranean Sea. This could be added.

*Reply:* Three references related to the works of E. Sternberg (2005, 2007 and 2008) have been added in the introduction and in section 3.1.

**<u>Reviewer:</u>**-At the end of the introduction, I found question 1) not clearly written, please explicit better what was this first motivation.

*Reply:* Question has been reformulated, and explanations have been added in the introduction and section 2.1.

**<u>Reviewer:</u>**-Sampling and analyses: neither the blanks, nor the reproducibility are given, should be added.

*Reply:* Details have been added in section 2.2.

**<u>Reviewer:</u>**--In the result section, the surface maxima observed at E1 and the pic at 100 m at E4-E are not described. Could be done.

*Reply:* The surface Baxs signal at E1 and E4 has been described (paragraph 3.1)

**<u>Reviewer:</u>**-Paragraph 4.1: the first sentence is not clear as it is written: the link between "low productivity, low export and highest DWAV is not direct, which appears to be the case at the first reading of the sentence: rephrase.

*Reply:* the sentence has been revised.

**<u>Reviewer:</u>**- End of the same paragraph: about the hypothesis of "recurrent winter production" that might explain the R-2 maximum. . .was such phenomena visible and already observed with the satellites?

**<u>Reply:</u>** We checked Chla satellite image from the Giovani online Visualization and Analysis system (NASA GES DISC). It appears that for different years, the R-2 and KERFIX area could indeed be subject to enhanced productivity during early spring periods, but it is not salient for winter period. The sentence has been revised in the ms.

**<u>Reviewer:</u>**- Discussion, station in the meander (4.3): I appreciated the evolution of the different ratios considered here, that allows following an interesting temporal evolution of the biogeochemical dynamic in this "recirculation". Fig 5b and the related discussion would be easier to follow if the authors could add an inset to the Fig3, inset showing the full depth profile of Baxs at the stations TNS-6 and E-1 where bathypelagic processes are suspected.

*Reply:* Fig3h has been added showing the full depth profile of Baxs at TNS6 and E-1 vs. E4-E. Fig3h is referred in the ms in section 3.1 and 4.2.3.

**Reviewer:**-Table 1: in the date of sampling, the precision "2011" is perhaps not useful *Reply:* "2011" has been removed from the dates of sampling.

**<u>Reviewer:</u>**--Figures: None of the figure proposes a circulation scheme, that could be helpful (in connection with my general comment)

*<u>Reply:</u>* The two branches of the Fawn trough Current have been added in Fig1a. Sentences have been added in section 2.1.

**<u>Reviewer:</u>**-In the caption of fig 4: the authors could add "POC, deduced from the Baxs maxima" <u>*Reply:*</u> Done

Interactive comment on "Early season mesopelagic carbon remineralization and transfer efficiency in the naturally iron-fertilized Kerguelen area" by S. H. M. Jacquet et al.

Anonymous Referee #1 Received and published: 4 July 2014

Review of Early season mesopelagic carbon remineralization and transfer efficiency in the naturally iron-fertilized Kerguelen area by Jacquet et al.

## Overview and major comments

This study is part of the KEOPS2 special issue investigating the downward flux of car- bon in a naturally iron fertilized bloom in the southern ocean (Kerguelen). Although we recently gained knowledge on how POC is exported out of the sunlit layer of the ocean following natural fertilizations (Blain et al., 2007; Chever et al., 2010; Morris and Charette, 2013; Pollard et al., 2009; Le Moigne et al., 2014), a major unknown remains about the fate of the particulate organic carbon further down in the water column. This process is critical to understand if one wants to assess the genuine effect of Fe fertil- ization of atmospheric CO2 concentrations. Jacquet et al present mesopelagic carbon remineralization rate data in the vicinity of the Kerguelen Islands. The paper focuses primarily on the differences in carbon remineralization rate between high and low iron regions and at different stage of the bloom evolution with emphasis on the efficiency with which POC is transferred into the ocean's interior. While I am not an expert in the "Barium" technique, my feeling is that the methods employed to derive estimates car- bon remineralisation rate are well developed and sound, as are the estimates of POC export and primary production estimates presented elsewhere. Nevertheless, before I can recommend the manuscript for publication, significant mod- ifications and improvement are necessary. The discussion lacks substance and only focuses on a basic description on the differences between difference sites sampled and the KEOPS1 results.

**<u>Reviewer:</u>** The authors do not clearly assess to which extent their metrics (r ratio, T400/800) are impacted by the integration time of the various technique they used. The PP, the Th- POC export and the Baxs C remineralisation rate are all express as daily rates (g C m-2d-1). However, PP (likely from bottle incubation, although the information is not available to the reader yet as Cavagna et al is not published) is integrated over a day (24or 12 hours incubation I assume) while the Th-POC export over a month (Le Moigne et al., 2013;Henson et al., 2011). The Baxs integration time seems less constrained and may well be over that of the Th-POC export. To overcome that problem, (Henson et al., 2011) integrated PP over a month which is comparable with the time-period which the Th technique integrates the POC-fluxes over. For instance, this has relevance to explain why the largest remineralisation rates (and subsequent r ratios, and Ts) are observed in the HNLC zone and why Ts (400 or 800) are on occasions larger than 100%. This needs to be assessed and discussed. *Reply:* As detailed further below this has been discussed and revised in the ms.

**<u>Reviewer:</u>** Also, the manuscript would benefit of integrating recent observations about the mechanisms responsible driving the transfer efficiency in high latitude with highlights from some of the paper listed below (non exhaustive list though)(Henson et al., 2012;Le Moigne et al., 2012;Lam et al., 2011;Lam and Bishop, 2007;Maiti et al., 2013;Wilson et al., 2012;Buesseler et al., 2007;Morris and Sanders, 2012) etc... These propos dif- ferent processes as potential mechanisms to explain patterns in POC export/transfer efficiency in high latitude. It would be valuable to examine and discuss the dataset presented here regarding how the various locals Fe supply observed around the Ker- guelen Islands impact patterns in POC export/transfer efficiency in high latitude. I do understand that this paper is part of a special issue and that a more comprehensive overview paper including this dataset might be put together later on. Nonetheless, a more thorough discussion of the results and their implications would be welcome to meet the publication criteria defined by Biogeosciences. *Reply:* Discussion and references have been added in the ms.

**<u>Reviewer</u>:** Finally, the manuscript would benefit from serious improvement regarding language. It needs to be very thoroughly revised by a native english speaker, the text (including references list) is currently littered with typos and awkward sentences which makes the paper hard to read and sometimes confusing.

*<u>Reply:</u> Language has been revised* 

**<u>Reviewer:</u>** Also, some manuscripts referenced in the text do not appear in the references list and the acronyms are not consistently used throughout the text. *<u>Reply:</u>* References will be revised

# Minor comments

*P4*\_P9038, L10: Please refer to (Le Moigne et al., 2014) for most recent advance on the topic *Reply:* the reference has been added in the text.

*P4*\_P9038, L21: "and, and," rephrase. See general comment about language *Reply*: the sentence has been rephrased.

*P5*\_PP9039, L13: Any feeling on how long the Baxs technique intergrates the C remineralisation rate for?

**<u>Reply:</u>** The time window integration of the Ba signal ranges from few (1-3) days to few (1-2) weeks.

*P5\_*P9039, L25: references *Reply:* done

*P6*\_P9040, L19: Dates please *Reply:* dates have been added in the text

*P9*\_P9043, L10: please specify "rates" after remineralization. *Reply:* done

*P11* P9045, L9: What are you referring to?

*Reply:* We referred to section 3.1. Note that these sentences have been rephrased as requested by the second reviewer. Some sentences about the surface Baxs signal have been added in section 3.1.

*P11\_*P9045, L15: Four or for? needs rephrasing *Reply:* we rephrased

*P11\_*P9045, L28: The two *Reply:* done

*P12\_*P9046, L20 : Include (Robinson et al., 2014) *Reply:* done

*P13\_*P9047; L6: Sequestration efficiency refers to the sequestration efficiency (the excess of POC export divided by the excess of DFe supply) as defined in (Blain et al., 2007) and re-used in (Pollard et al., 2009;Morris and Charette, 2013;Chever et al., 2010;Le Moigne et al., 2014). Please stick to the established terminology to avoid confusion. *Reply:* done

*P13\_*P9047, L8: untill !!!! ("up to" would be adequate here). *Reply:* done

P13\_P9047, L10 and Table 2: EP/PP is called export efficiency (Buesseler, 1998)

## *<u>Reply:</u>* OK we mentioned it.

*P13\_*P9047, L14: You imply here that remineralisation rates are a function of PP and export here (low PP/export; high remineralisation). Why C remineralisation rates would be negatively correlated with PP and export in the HNLC region?

*Reply:* The negative relationship between PP and PP and differences in EP/PP vs. MR have been discussed. The main reasons to explain the differences are the time delay between signals and differences in diatoms and sinking material.

*P13\_*P9047, L16: Could you specify sampling depth? Trull et al and Laurenceau et al are not available yet.

# **<u>Reply:</u>** done

*P13\_P9047*, L22: Please provide information or references on what mechanism could potentially lead to an important winter production and subsequent export, *P13\_P9047*, L27: you mean a previous winter bloom? and *P14\_P9048*, L3, Is November in the Southern hemi- sphere wintertime? I believe not. The argument (or the date indicated) is not valid. Comparing that to previous estimation of C remineralization rate (from Baxs and other technique) estimated in other HNLC regions (and perhaps a bit further in the season) would provide valuable information on whether the HNLC region has intrinsically a more active heterotrophic community early in the season or whether the high C remineralisation rate observed here are a artefact of the Baxs technique integration time.

**<u>Reply</u>** (P13\_P9047, L22, P13\_P9047, L27 P14\_P9048, L3): We checked Chla satellite image from the Giovani online Visualization and Analysis system (NASA GES DISC). It appears that for different years, the R-2 and KERFIX area could indeed be subject to enhanced productivity during early spring periods, but it is not salient for winter period. The sentence has been revised in the ms. Also, as reported above the integration time of Ba ranges from several days to week and we can exclude a potential artefact of the Ba technique. According to results from Christaki et al. (this issue), the prokaryotic activity at station R-2 was low but column-integrated bacterial production (BP) below 150 m represents 41% of the 900 m column-integrated value, indicating that important mineralization of material transferred from the surface occurs at mesopelagic depths. Other parameters also show that an export event occurs at R-2 (Lasbleiz et al., this issue- Si:C, Laurenceau et al., this issue- particle composition, Dehairs et al., this issue- nitrate isotopes). Discussion has been revised.

*P18\_P9052*: Nothing about the large remineralisation rate at the reference HNLC site in the conclusion?

*<u>Reply:</u> Conclusion has been revised.* 

1 Early season mesopelagic carbon remineralization and transfer 2efficiency in the naturally iron-fertilized Kerguelen area 3 Jacquet S.H.M.<sup>1</sup>, F. Dehairs<sup>2</sup>, D. Lefèvre<sup>1</sup>, A.J. Cavagna<sup>2</sup>, F. Planchon<sup>3</sup>, 4  $\mathbf{5}$ U. Christaki<sup>4</sup>, L. Monin<sup>5</sup>, L. André<sup>5</sup>, I. Closset<sup>6</sup> and D. Cardinal<sup>6</sup> 6 <sup>1</sup>Aix Marseille Université, CNRS/INSU, IRD, Mediterranean Institute of 78 Oceanography (MIO), UM 110, 13288 Marseille, France 9 10 <sup>2</sup>Vrije Universiteit Brussel, Analytical, Environmental & Geo-Chemistry 11 and Earth System Sciences, Brussels, Belgium 1213<sup>3</sup>Laboratoire des Sciences de l'Environnement Marin (LEMAR), 14Université de Brest, CNRS, IRD, UMR 6539, IUEM; Technopôle Brest Iroise, Place Nicolas Copernic, F-29280 Plouzané, France 1516<sup>4</sup>INSU-CNRS, UMR8187 LOG, Laboratoire d'Océanologie et de 1718 Géosciences, Université du Littoral Côte d'Opale, ULCO, 32 avenue 19 Foch, 62930 Wimereux, France 2021<sup>5</sup>Earth Sciences Department, Royal Museum for Central Africa, 22Leuvensesteenweg 13, Tervuren, B 3080, Belgium 2324<sup>6</sup>Sorbonne Universités (UPMC, Univ Paris 06)-CNRS-IRD-MNHN, 25LOCEAN Laboratory, 4 place Jussieu, F-75005 Paris, France 26

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#### 29 Abstract

30 We report on the zonal variability of mesopelagic particulate organic carbon 31 remineralization and deep carbon transfer potential during the Kerguelen 32Ocean and Plateau compared Study 2 expedition (KEOPS 2; Oct.-Nov. 2011) 33 in an area of the Polar Front supporting recurrent massive blooms from 34natural Fe fertilization. Mesopelagic carbon remineralization (MR) was 35assessed using the excess, non-lithogenic particulate barium  $(Ba_{xs})$ 36 inventories in mesopelagic waters and compared with bacterial production 37 (BP), surface primary production (PP) and export production (EP). Results for 38 this early season study are compared with results obtained during a previous 39 study (2005; KEOPS 1) for the same area at a later stage of the 40 phytoplankton bloom. Our results reveal the patchiness of the season 41 advancement and of the establishment of remineralization processes between 42plateau (A3) and Polar Front sites during KEOPS 2. For the Kerguelen plateau 43(A3 site) we observe a similar functioning of the mesopelagic ecosystem 44 during both seasons (spring and summer), with low and rather stable 45remineralization fluxes in the mesopelagic column (150-400 m). The shallow 46 water column (~500m), the lateral advection, the zooplankton grazing 47pressure and the pulsed nature of the POC transfer at A3 seem to drive the 48extend of MR processes on the plateau. For deeper stations (>2000 m) 49 located on the margin, inside a Polar Front meander, as well as in the vicinity 50of the Polar Front, east of Kerguelen, remineralization in the upper 400 m in 51general represents a larger part of surface carbon export, but when 52considering the upper 800 m, in some cases, the entire flux of exported 53carbon is remineralized. In the Polar Front meander, where successive 54stations form a time series, two successive events of particle transfer were 55evidenced by remineralization rates: a first mesopelagic and deep transfer 56from a past bloom before the cruise, and a second transfer expanding at 57mesopelagic layers during the cruise. Regarding the deep carbon transfer

58efficiency, it appeared that above the plateau (A3 site) the mesopelagic 59remineralization was not a major barrier to the transfer of organic matter to 60 the sea-floor (close to 500 m). There the efficiency of carbon transfer to the 61 bottom waters (>400 m) as assessed by PP, EP and MR fluxes comparisons 62reached up to 87% of the carbon exported from the upper 150 m. In contrast, 63 at the deeper locations mesopelagic remineralization clearly limited the 64 transfer of carbon to depths >400 m. For sites at the margin of the plateau 65(station E-4W) and the Polar front (station F-L), mesopelagic remineralization 66 even exceeded upper 150 m export, resulting in a null transfer efficiency to 67 depths >800 m. In the Polar Front meander (time series), the capacity of the 68 meander to transfer carbon to depth >800 m was highly variable (0 to 73 %). 69 The highest carbon transfer efficiencies in the meander are furthermore 70 coupled to intense and complete deep (>800 m) remineralization, resulting 71again in a close to zero deep (>2000 m) carbon sequestration efficiency 72there.

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

#### 77 **1. INTRODUCTION**

78While numerous artificial (Boyd et al., 2000, 2004; Gervais et al., 79 2002; Buesseler et al., 2004, 2005; de Baar et al., 2005; Hoffmann et al., 80 2006; Boyd et al., 2012; Smetacek et al., 2012) and natural (Blain et al., 81 2007; Pollard et al., 2009; Zhou et al., 2010, 2013) ocean iron-fertilization 82experiments in the Southern Ocean demonstrated the role of iron in 83 enhancing the phytoplankton biomass and production in high-nutrient low-84 chlorophyll (HNLC) regions, determining to what extent fertilization could 85 modify the transfer of particulate organic carbon (POC) to the deep ocean is 86 far from being comprehensively achieved (Lampitt et al., 2008; Morris and 87 Charette, 2013; Le Moigne et al., 2014; Robinson et al., 2014). This is partly 88 due to the short term over which the observations were made, precluding 89 extrapolation to longer time scales. Moreover, when assessing whether Fe-90 supply could induce vertical POC transfer, the magnitude of the export from 91 surface is not the only important parameter to take into account. Indeed, POC 92fate in the mesopelagic zone (defined as 100-1000 m depth layer) is often 93 largely overlooked although these depth layers are responsible for the 94 remineralization of most of the POC exported from the surface layer (Martin et 95 al., 1987; Longhurst, 1990; Lampitt and Antia, 1997; François et al., 2002; 96 Buesseler et al., 2007b; Buesseler and Boyd, 2009). Only few studies 97 considered mesopelagic carbon (C) remineralization rates (Buesseler et al., 98 2007a; Jacquet et al., 2008a, 2008b, 2011a, 2011b; Salter et al., 2007) to 99 estimate the response of deep POC export to fertilization. Assessing 100 mesopelagic C remineralization is pivotal to evaluate remineralization length 101 scale as well as the time scale of the C storage in the deep ocean. Indeed the 102 typical depth of the main thermocline, 1000 m (IPCC, WG1, 2007, chp5) is 103 often referred to as the horizon clearly removed from the surface ocean and 104 atmosphere (Passow and Carlson, 2012). Overall, assessing mesopelagic C 105remineralization will allow to better quantify the ocean's biological carbon

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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).

109 The present work aims at understanding the impact of a natural iron-110 induced bloom on the mesopelagic POC remineralization and zonal variability 111 in the Kerguelen area (Southern Ocean). Here, C remineralization was 112assessed from particulate biogenic Ba (hereafter called excess-Ba or  $Ba_{xs}$ ; 113 mainly forms as barite BaSO<sub>4</sub> crystals) contents in the mesopelagic water 114 column. The link between barite and C remineralization resides in the fact that 115this mineral precipitates inside oversaturated micro-environments (biogenic 116 aggregates) during the process of prokaryotic degradation of sinking POC 117 (Dehairs et al., 1980, 1992, 1997, 2008; Stroobants et al., 1991, Cardinal et 118 al., 2001, 2005; Jacquet et al., 2007, 2008b, 2011a; Planchon et al., 2013; 119 Sternberg et al. 2007, 2008a, 2008b). Once the aggregates have been 120remineralized, barites are released and spread over the mesopelagic layer. 121Overall, earlier work highlights the fact that suspended barite in mesopelagic 122waters builds up over the growing season and reflects past remineralization 123 activity integrated over several days to weeks (Dehairs et al., 1997; Cardinal 124et al., 2005; Jacquet et al., 2007, 2008b). An algorithm relating mesopelagic 125Ba<sub>xs</sub> contents to oxygen consumption (Shopova et al., 1995; Dehairs et al., 126 1997) allowed remineralization of POC fluxes to be estimated for the 127mesopelagic layer. Combined with surface C production and export estimates, 128mesopelagic Baxs also informs on the efficiency of the system toward deep 129carbon transfer. From earlier studies, the efficiency of C transfer through the 130 mesopelagic layer was reported to increase under artificially induced (EIFEX; 131 Strass et al., 2005; Smetacek et al., 2012) and natural (KEOPS; Blain et al., 1322007) Fe-replete conditions (Jacquet et al., 2008a, 2008b; Savoye et al., 1332008) compared to Fe-limited, non-bloom, HNLC reference stations in the 134 Southern Ocean. In contrast, C transfer efficiency through the mesopelagic

135layer was reported smaller in natural Fe-replete locations during the SAZ-136Sense cruise off Tasmania (Jacquet et al., 2011a, 2011b). Differences in 137 plankton community structure and composition (e.g. diatoms vs. flagellates, 138 type of diatoms) were pointed at, as possible causes of such discrepancies in 139C transfer efficiency through the mesopelagic layer (Jacquet et al., 2008a, 140 2011a, 2011b). Also, differences in integration time scales for the processes 141 that control the carbon fluxes in artificially vs. naturally Fe fertilized systems, 142may yield an incomplete picture of the C transfer potential and lead to 143misleading conclusions.

144 Here, we examine changes in mesopelagic POC remineralization 145during the early spring (Oct. -Nov. 2011) KEOPS 2 expedition to the naturally 146iron fertilized area eastward of Kerguelen Islands. The hydrographic structure 147of the Kerguelen area generates contrasted environments that are differently 148 impacted by iron availability and mesoscale activity. The specific objectives of 149the present work are to assess the zonal variability of mesopelagic C 150remineralization and deep C transfer potential, and to identify possible causes 151inducing this variability. As the same area was visited earlier in 2005 during 152summer at a late stage of the bloom (KEOPS 1; Jan.-Feb., 2005), this 153condition offers a unique opportunity to estimate the main carbon fluxes over 154most of the growth season. Mesopelagic C remineralization estimates are 155compared to particle and biological parameters as reported in other papers 156included in this issue (Cavagna et al., 2014; Christaki et al., 2014; Dehairs et 157al., 2014; Lasbleiz et al., 2014; Laurenceau-Cornec et al., 2014; Planchon et 158al., 2014; Van der Merve et al., 2015) and in Blain et al., (2007); Christaki et 159al. (2008); Jacquet et al., (2008a); Park et al., (2008); Savoye et al., (2008). 160

## 161 **2. EXPERIMENT AND METHODS**

162 **2.1. Study area** 

163 The KEOPS 2 (Kerguelen Ocean and Plateau compared Study) cruise 164 was conducted in austral spring at the onset of the bloom from 10 October to 165 20 November aboard the R/V Marion Dufresne (TAAF/IPEV). The KEOPS 2 166 expedition studied the Kerguelen Plateau area (Indian sector of the Southern 167 Ocean) which is characterized by the passage of the Polar Front (PF), as 168 illustrated in Fig.1a. The Kerguelen Plateau is surrounded by the Antarctic 169 Circumpolar Current (ACC) whose main branch circulates to the north of the 170 plateau (Park et al., 2008). A second branch of the ACC circulates to the 171south of Kerguelen Islands to further join a branch of the Fawn Trough 172Current (FTC). The FTC has a main northeast direction, but a minor branch 173splits away northwestward to join the eastern side of the Kerguelen plateau 174(Park et al., 2008; Fig1.a). These particular hydrographic features generate a 175mosaic of recurrent massive bloom patterns in the northeastern part of the 176 Plateau and the possible sources and mechanisms for fertilization were 177investigated during ANTARES 3 (1995; Blain et al., 2001) and KEOPS 1 cruise, 178later referred to as KEOPS 1 (Jan.-Feb. 2005, late summer conditions; Blain 179 et al., 2007, 2008). During KEOPS 2 the evolution of Chl-a data based on 180 multi-satellite imagery of the study area revealed the presence of different Chl-a rich plumes (D'ovidio et al., 2014) (Fig.1a; e.g. Chl-a map from 181 18211/11/2011). Stations were sampled in distinct zones covering these different 183 bloom patterns (Fig.1a) (corresponding stations are reported in Fig1.b): (a) 184 on the shallow plateau (station A3; see 1 in Fig.1a). Note that station A3 185coincides with a site studied during the KEOPS 1 cruise, and that it was 186 sampled twice over a 27-day period; (b) in a meander formed by a quasi-187 permanent retroflection of the Polar Front (PF) and topographically-steered by 188 the eastern escarpment (Gallieni Spur) of the Kerguelen Plateau (mainly 189 stations E, sampled as a quasi-lagrangian temporal series) (see 2 in Fig.1a); 190 (c) along a North-South Transect (referred to as TNS stations; see 3, grey line 191 in Fig.1a) and a West-East Transect (referred to as TEW stations; see 4, grey

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.

197 Detailed descriptions of the complex physical structure of the area, 198circulation, water masses and fronts are given in Park et al. (2014). Briefly, 199the main hydrodynamic features observed during the cruise are the following 200(see  $\theta$ -S diagram, Fig.2a): (1) North of the PF, stations in the PFZ (TNS-1, 201TEW-8 and F-L) present Antarctic Surface Waters (AASW;  $\theta \approx 4^{\circ}$ C and density 202 <27);  $\theta$ -S characteristics between 150 to 400 m at station F-L (and to a 203lesser extent at station TNS-1) reveal the presence of interleaving with waters 204from northern (subantarctic) origin, centered between the 27.2 and 27.5 205density curves, where Antarctic Intermediate Waters (AAIW) are usually 206 found. This contrasts with the situation at station TEW-8, where there is no 207 evidence of interleaving; (2) stations south of the PF exhibit subsurface 208 temperature minima characteristic of Winter Waters (WW); below the WW 209 three water masses can be identified, namely: the Upper (temperature 210maximum) and Lower (salinity maximum) Circumpolar Deep Water (UCDW 211and LCDW), and the Antarctic Bottom Water (AABW). Theses water masses 212are present roughly in the following depth intervals: 700 m<UCDW< 1500 m; 2131500 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., 2014). 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.

225

## 226 **2.2. Sampling and analyses**

227 22 CTD casts (surface to 500-2000 m) were sampled for particulate 228 barium (Table 1) using a CTD-rosette equipped with 22 12L Niskin bottles. 229 Deep particulate Ba profiles (>1000 m) were not systematically obtained from 230 the same CTD cast, but from successive casts sampled closeby in time and 231 space and having similar  $\theta$ -S data profiles. In the following, we use both the 232 station and CTD numbers to refer to stations.

233 4 to 7 L of seawater were filtered onto 47 mm polycarbonate 234membranes (0.4 µm porosity) under slight overpressure supplied by filtered 235air (0.4  $\mu$ m). The filters were rinsed with Milli-Q grade water (<5 mL) to 236 remove sea salt, dried (50°C) and stored in Petri dishes for later analysis. In 237the home-based laboratory we performed a total digestion of samples using a 238tri-acid (0.5 mL HF/1.5 mL HCl/1 mL HNO<sub>3</sub>; all Suprapur grade) mixture in 239 closed telfon beakers overnight at 90°C in a clean pressurized room. After 240evaporation close to dryness samples were re-dissolved into around 13 mL of HNO<sub>3</sub> 2%. The solutions were analysed for Ba and other major and minor 241242elements by ICP-QMS (inductively coupled plasma-quadrupole mass 243spectrometry; X Series 2 ThermoFisher) equipped with a collision cell 244technology (CCT). To correct instrumental drift and matrix effects, internal 245standards and matrix-matched calibrations were used. We analysed several 246certified reference materials which consisted of dilute acid-digested rocks 247(BHVO-1, JB-3 and JGb-1), natural riverine water (SLRS-5) and multi-element 248artificial solutions for these external calibrations. Based on analyses of these 249external standards, accuracy and reproducibility are better than  $\pm$  5%. For

250more details on sample processing and analysis we refer to Cardinal et al. 251(2001). Among all elements analysed, particular interest went to Ba and Al. 252The presence of sea-salt was checked by analysing Na and the sea-salt 253particulate Ba contribution was found negligible. Average detection limits 254equal 0.6 nM for Al and 3 pM for Ba. Detection limits were calculated as three 255times the standard deviation on the blank measured on board and then 256normalized to an average dilution factor of 385, i.e., particles from around 5 L 257of Milli-Q water, dissolved in a final volume of 13 mL as for the samples. 258Biogenic barium (hereafter called excess-Ba or Baxs) was calculated as the 259difference between total particulate Ba and lithogenic Ba using Al as the 260lithogenic reference element (Dymond et al., 1992; Taylor and McLennan, 2611985). At most sites and depths the biogenic  $Ba_{xs}$  represented >95% of total 262particulate Ba. Lithogenic Ba reached up to 20% of total particulate Ba at 263 some depths in the upper 80-100 m, mainly at station R-2 and stations north 264of the Polar Front (i.e., TEW-8, F-L and TNS-1). The standard uncertainty 265(Ellison et al., 2000) on  $Ba_{xs}$  data ranges between 5 and 5.5%.  $Ba_{xs}$  and Al 266 data are reported in Appendix A.

267

# 268 **2.3. O**<sub>2</sub> 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<sub>xs</sub> 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:

276

$$J_{O_{2}} = (Ba_{rs} - Ba_{residual})/17450$$
 (Eq.1)

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

where  $J_{02}$  is the  $O_2$  consumption (µmol  $l^{-1} d^{-1}$ ) and  $C_{respired}$  is the 278Mineralization Rate of organic carbon (in mmol C  $m^{-2} d^{-1}$ ; MR); Ba<sub>xs</sub> is the 279280depth-weighted average Ba<sub>xs</sub> value (DWAv), i.e. the Ba<sub>xs</sub> inventory divided by 281the depth layer considered Z,  $Ba_{residual}$  is the residual  $Ba_{xs}$  signal (or  $Ba_{xs}$ 282background) at zero oxygen consumption and RR is the Redfield C/O<sub>2</sub> molar ratio (127/175; Broecker et al., 1985). DWAv Baxs values were calculated both 283284for the 150 to 400 m (Plateau and deep stations) and the 150 to 800 m layers 285(deep stations only) (see details further below). The residual  $Ba_{xs}$  is 286 considered as 'preformed' Baxs, left-over after partial dissolution and 287sedimentation of Baxs produced during a previous phytoplankton growth 288event. In BaSO<sub>4</sub> saturated waters, such as the ones filling the whole ACC 289water column (Monnin et al. 1999), this background Baxs value was 290considered to reach 180 to 200 pM which is rather characteristic for the deep 291ocean (>1000m) (see Dehairs et al., 1997; Jacquet et al., 2008a, 2011). In 292the present study we used a  $Ba_{xs}$  background of 180 pM.

293We take the opportunity here to also compare  $O_2$  consumption rates 294for the KEOPS 1 expedition (D. Lefèvre, unpublished data) with KEOPS 1  $Ba_{xs}$ 295data published earlier (Jacquet et al., 2008a). No such O<sub>2</sub> consumption data 296are available for KEOPS 2. During KEOPS 1, dark community respiration 297(DCR) was estimated from changes in the dissolved oxygen concentration 298over 72 hours incubations. Discrete samples were collected at three depths in the mesopelagic zone from Niskin bottles into 125 cm<sup>3</sup> borosilicate glass 299 300 bottles according to the WOCE procedure, and oxygen concentration was 301 determined by Winkler titrations using a photometric endpoint detector 302 (Williams and Jenkinson, 1982). By integrating DCR data in the water column 303 we estimated the rate of oxygen consumption (later referred to as  $JO_2$ -W). We 304 compared JO<sub>2</sub>-W obtained from incubated oxygen samples with the rate of 305oxygen consumption based on KEOPS 1 mesopelagic Ba<sub>xs</sub> contents (Eq.1; 306 later referred to as JO<sub>2</sub>-Ba). Dissolved oxygen was measured three times at

307 station A3 (same location as during KEOPS2) over a 19-day period (A3 CTD 308 #32, #74 and #119). Dissolved oxygen was also measured at station C11 309 located off-shelf in less productive HNLC waters (51.65°S, 78.00°E; not 310 shown in Fig.1) and was sampled two times over a 10-day period (C11 311 CTD#42 and #83). Fig.3 compares  $JO_2$ -W and  $JO_2$ -Ba for repeat stations A3 312(#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<sup>-2</sup> d<sup>-1</sup> at station A3 and from 0.292 313 314 to 0.528 mmol  $m^{-2} d^{-1}$  at station C11. Although JO<sub>2</sub>-Ba rates (from 0.846 to 1.555 mmol m<sup>-2</sup> d<sup>-1</sup>) are slightly higher than  $JO_2$ -W,  $JO_2$  rates are of the same 315316 order of magnitude and present a same trend. We observe a significant 317 positive correlation between both  $JO_2$  rates (R<sup>2</sup>=0.90; p<0.01) with a slope of 318 0.64. The difference in oxygen consumption rates could be explained by the 319 integration time of both methods (few hours for the incubations vs. few days 320 to weeks for  $Ba_{xs}$ ) and by the fact that KEOPS 1 occurred at the decline of the 321bloom (late summer; low organic substrates), which would explain the lower 322 $JO_2$  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<sub>xs</sub> proxy. In the present work O<sub>2</sub> consumption and POC remineralisation was assessed from Ba<sub>xs</sub> 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%.

330

## **331 3. RESULTS**

# **332 3.1. Particulate biogenic Ba<sub>xs</sub> profiles**

333 Ba<sub>xs</sub> profiles in the upper 800 m are reported in Fig.4. The complete 334 whole water column data set is given in Appendix A. From previous studies we 335 know that  $Ba_{xs}$  in surface waters is distributed over different, mainly non-

336 barite biogenic phases (see Stroobants et al., 1991, Jacquet et al., 2007, 337 Cardinal et al., 2005, Sternberg et al., 2005). As such, these do not reflect 338 POC remineralization processes, in contrast to mesopelagic waters where Baxs 339 is mainly composed of barite (Dehairs et al., 1980) formed during prokaryotic 340 degradation of sinking POC (Martin et al., 1987; Sarmiento et al., 1993; 341Buesseler et al., 2007b). For KEOPS 2 we observe that  $Ba_{xs}$  concentrations 342 generally increase below 150 m (i.e., they increase above the background 343 level set at 180 pM), but some sites have ocean surface Baxs contents 344 significantly larger than background (E-1,896 pM at 21 m; E4-E, 563 pM at 93 345 m). Such values are not unusual, and very high surface values have been 346 observed occasionally in earlier Southern Ocean studies. During KEOPS 1, 347 surface  $Ba_{xs}$  maxima at the three A3 repeats stations ranged from 1354 to 348 5930 pM at 50 m, likely associated with phytoplankton derived particles 349 (Jacquet et al., 2008a).

350 The following part focuses on the mesopelagic zone where most of the 351remineralization of exported organic matter takes place. The Baxs profile for 352 station R-2 (CTD #17) displayed a characteristic mesopelagic Baxs maximum 353 reaching up to 834 pM at 304 m which is actually one of the highest values 354 observed for the whole study (Fig.4a).  $Ba_{xs}$  profiles for stations A3 above the 355Kerguelen plateau (A3-1 CTD #4 and A3-2 CTD #107; Fig.4b) had lower 356 mesopelagic Baxs contents, with values ranging from about 80 to 350 pM. For 357 both A3 visits,  $Ba_{xs}$  values increased close to the seafloor reaching up to 1108 358pM (A3-1, 474 m) and 1842 pM (A3-2, 513 m). In contrast, station E-4W 359 (located further north along the margin in deeper waters, but with similar  $\theta$ -S 360 and Chl-a characteristics as station A3) displayed a large mesopelagic  $Ba_{xs}$ 361 maximum reaching up to 627 pM at 252 m (Fig.4c). Station TEW-3 (located 362 on the Kerguelen plateau, in waters with similar  $\theta$ -S and Chl-a characteristics 363 as station TNS-8) had a profile similar to the one observed at station A3-2, 364 but compared to plateau sites A3-1 and A3-2 no increased  $Ba_{xs}$  contents were

365 observed in bottom water (Fig.4d). The other stations of the study area 366 (Fig.4d-g) have Ba<sub>xs</sub> profiles similar to the one at station E-4W, showing the 367 characteristic Baxs maximum between 200 and 500 m. Note that for most of 368 the stations, Baxs concentrations in waters below the mesopelagic maximum 369 did not systematically decreased to reach the  $Ba_{xs}$  background level (180 pM; 370 see above). In some cases  $Ba_{xs}$  contents significantly higher than residual  $Ba_{xs}$ 371were observed until below 1000 m (see Appendix A). This is particularly 372 salient at stations TNS-6, E-1, E-2 and F-L where  $Ba_{xs}$  values below 1000 m 373 reach 410 pM at 1886 m (TNS-6) and 436 pM at 1498 m (E-1). These cases 374 of high deep  $Ba_{xs}$  contents clearly contrasted with the values observed at 375station E4-E (Fig.4h).

376

## 377 3.2. Depth-weighted average Ba<sub>xs</sub> content of mesopelagic waters

378 Since the base of the mixed layer was generally shallower than  $\leq 150$ 379 m, this depth is taken as the upper boundary of the mesopelagic domain. The 380 depth-weighted average (DWAV) Baxs contents, calculated for the 150-400 m 381 and 150-800 m depth intervals, are given in Table 1. For the profiles on the 382plateau (500 m water column) bottom waters with evidence of sediment 383 resuspension were not taken into account when calculating DWAv  $Ba_{xs}$  values 384 $(\geq 400 \text{ m})$ . Particle size spectra indicated that sediment resuspension occurred 385 especially at stations A3 and TEW-3 (Jouandet et al., 2014; Lasbleiz et al., 386 2014; Van der Merve et al., 2015;). Thus, at site A3 (Fig.4b) DWAV Baxs was 387 calculated for the layer between 150 and 354 m for A3-1 (CTD #4) and 388 between 150 and 405 m for A3-2 (CTD#107). For station TEW-3 (CTD #38) 389 DWAV Baxs was calculated for the water layer between 150 and 400 m 390 (Fig.4d). For the deep sites, we considered both, the 150-400 m and the 150-391 800 m depth intervals, when calculating the DWAV  $Ba_{xs}$  contents. Depth 392 weighted average Baxs values were translated into carbon remineralization

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

DWAV Ba<sub>xs</sub> 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., Solution 2013). For the KEOPS 2 cruise the main observed features are:

399 (a) Unexpectedly, the highest DWAV  $Ba_{xx}$  value of the whole study area 400 (572 pM; 150-400 m) was observed at the reference R-2 site. Bowie et al. 401 (2014), Quéroué et al. (2014) and van der Merve et al. (2015) reported for R-402 2 local maxima in particulate and dissolved trace metals at 500 m and deeper, 403 reflecting lateral transport of lithogenic matter possibly originating from the 404 Leclaire Rise (a large seamount located west of R-2). Similarly, Lasbleiz et al. 405(2014) observed a maximum of lithogenic silica (LSi) at 500 m, confirming 406 lithogenic inputs there. However, we note that the mesopelagic Baxs 407 maximum at R-2 occurs at shallower depths, around 300 m, and that there is 408 no evidence for elevated values at 500 m where the previous authors 409 reported higher trace element and silica concentrations. Also, as reported 410 above (see section 2.2 and Appendix A), the higher lithogenic Ba fractions at 411 R-2 (up to 20% of the total Ba) occur only in the upper 80 m. Moreover, we 412do note that surface waters at R-2 experienced already some nitrate 413 consumption as compared to subsurface Winter Waters (Tmin waters). 414 Indeed, surface waters had 10% less nitrate than Winter Water (26  $\mu$ M at 5 m 415vs. 29  $\mu$ M at 200 m) and the isotopic enrichment of this surface nitrate 416 confirmed an imprint of uptake (see Dehairs et al., 2014). Also, Lasbleiz et al. 417(2014) report relatively low Si:C and Si:N ratios for surface ocean suspended 418 matter) pointing to the development of a diatom assemblage just prior the 419 sampling, consistent with the high dissolution rates of biogenic silica (BSi) 420 Closset et al. (2014) report for R-2 surface waters. It is therefore likely that 421the mesopelagic Baxs content at R-2 indeed reflects remineralization of

422 organic material that was fuelled by an important past early spring production 423and export event. Similarly, F. Dehairs (unpublished results) observed the 424 presence of significant numbers of barite microcrystals in mesopelagic waters 425 at the KERFIX time series station (50°40'S, 68°25'E) located east of R-2 426during late winter (Nov. 1993). Results would thus suggest the occurrence in 427 this HNLC area of recurrent brief early spring diatom productive period pulses 428and subsequent export and remineralization activity in the underling layers. 429 Chla satellite images (Giovani online Visualization and Analysis system, NASA 430 GES DISC) corroborate that the R-2 and KERFIX area is occasionally subject 431to enhanced biomass during early spring;

432(b) The two successive visits (27-day interval) at site A3 yielded 433 relatively low DWAV Baxs values of 267 and 316 pM, and a quite similar value 434 was observed for the shallow station TEW-3 (324 pM), located further north 435 on the plateau, but north of the PF. Note that for comparison purposes, we 436 recalculated the DWAV Baxs and MR values of KEOPS 1 by considering upper 437 and lower mesopelagic layer boundaries of 150 and 400 m rather than 125 438 and 450 m, as in Jacquet et al. (2008a). Also, in the latter study the high  $Ba_{xs}$ 439 contents observed near the seafloor were not excluded from the calculations, 440 while they are here. These increased benthic boundary layer  $Ba_{xs}$  contents 441 (observed also during KEOPS 2) are due to sediment resuspension which 442 extended up to 70 m above the seafloor during KEOPS 1 (Blain et al., 2008; 443 Venchiarutti et al., 2008; Armand et al., 2008). Because of these slightly 444 different depth intervals over which  $Ba_{xs}$  values were integrated, the KEOPS 1 445values discussed here will be slightly different from those reported in Jacquet 446 et al. (2008a). At the other depths the lithogenic Ba contribution at A3 447 (KEOPS 2) was only minor;

448 (c) The time series stations in the Polar Front meander had DWAV Ba<sub>xs</sub> 449 contents ranging from 258 to 427 pM (150-400 m), so reaching values 450 exceeding those on the plateau. For these time series stations values

451decreased between day 0 (TNS-6) and 12 (E-3), and then increased again at 452days 22 (E-4E) and 27 (E-5). Stations E-4W and TNS-8 above the plateau but 453in deeper waters close to the Kerguelen margin, at the edge the high biomass 454plume (Figure 1) had the highest DWAV Ba<sub>xs</sub> values (468 and 473 pM, 455respectively; 150-400 m), not considering the R-2 reference station. The 456 Polar Front F-L site, although located within the eastern part of the high 457biomass plume had a smaller DWAV Baxs value of 345 pM (150-400 m) and 458the close by station TEW-8 had the lowest DWAV Baxs value of the whole 459study area (199 pM; 150-400 m).

460

## **461 4. DISCUSSION**

# 462 **4.1.** Mesopelagic Ba<sub>xs</sub> and bacterial production

463 Previous studies revealed that the shape of the column-integrated 464 bacterial production (BP) profile (i.e. the attenuation length scale) was 465 important in setting the  $Ba_{xs}$  signal in the mesopelagic zone (Dehairs et al., 466 2008; Jacquet et al., 2008a, 2011a). Mesopelagic Baxs content is smaller 467 when most of the column integrated BP is restricted to the upper mixed layer 468 (indicating an efficient, close to complete remineralization within the surface), 469 compared to situations where a significant part of integrated BP was located 470 deeper in the water column (reflecting significant deep bacterial activity and POC export). During KEOPS 2 the incorporation of <sup>3</sup>H-leucine was used to 471472estimate bacterial production. BP data are described in Christaki et al. (2014). 473In Fig.5 we compare column-integrated BP at 150 m over 400 m (BP150/400) 474and DWAV  $Ba_{xs}$  for the 150-400 m depth interval, next to the relation 475obtained during KEOPS 1 (BP200/125 and 150-450 m DWAV Baxs; Jacquet et 476 al., 2008a; Christaki et al., 2008). Excluding stations A3, E-1, E-2 and E-3, 477KEOPS 2 data presented a significant correlation ( $R^2=0.88$ ; p<0.01) and a 478similar trend to the one reported for KEOPS 1. A similar picture was obtained 479 when integrating DWAV Baxs and BP up to 800 m (not shown). The time series

480 "E" stations in the meander revealed a shift from stations E-1, E-2 and E-3 to 481 stations E-4E and E-5, i.e. towards the trend reported above. A shift was also 482 apparent at station A3 from KEOPS 2 (early spring) to KEOPS 1 (late 483 summer). It is thus possible that results reflect the occurrence of different 484 stage of bloom advancement. The large variability of Baxs and BP relationship 485during KEOPS 2, especially at A3 site and in the meander, could reflect the 486 temporal evolution and patchiness of the establishment of mesopelagic 487 remineralization processes in this Polar Front area.

488

# 489 4.2. Fate of exported organic C in the mesopelagic zone and deep490 water column

491 An important question relates to the fate of the exported POC: how 492much of this POC is respired in the mesopelagic waters and how much 493 escapes remineralization and is exported to deeper layers where longer term 494 sequestration is likely (see e.g. Passow and Carlson, 2012; Robinson et al., 4952014; Schneider et al., 2008). To address these questions, we defined two 496 ratios: (1) the mesopelagic C remineralization efficiency (r-ratio in Table 2) 497 which is the ratio of mesopelagic C remineralization (MR, based on the DWAV 498 $Ba_{xs}$  concentrations) over C export (EP) from the 150 m horizon (based on 499<sup>234</sup>Th, see Planchon et al., this issue), and (2) the C transfer efficiency at 400 500and 800 m (i.e., T400, T800 in Table 2) which is the fraction of C export (EP) 501at 150 m passing through the 400 m (T400) or the 800 m (T800) horizons 502(e.g., T400= EP400/EP150 = 1-(MR/EP150), with MR/EP150 = r-ratio; see 503above). This approach is similar to the one developed by Buesseler and Boyd 504(2009) stating that a conventional curve-fitting of particle flux data (i.e., 505power law or exponential) skews our interpretation of the mesopelagic 506 processes. They recommended the use of combined metrics to capture and 507compare differences in flux attenuation. In the following, we compare MR 508fluxes for the different KEOPS 2 areas (Reference site; Plateau sites; Polar

509Front and Polar Front Meander) and discuss remineralization and transfer 510efficiencies for those sites for which MR, primary production (PP) and/or EP 511data (Table 2) were available. PP data were estimated from uptake 512experiments including 24-hour incubations at different PAR levels over the 513euphotic layer i.e., up to the 0,01% PAR level (Cavagna et al., 2014). EP data were estimated from <sup>234</sup>Th activities and <sup>234</sup>Th /POC ratios and are discussed 514515in Planchon et al. (2014). The thorium method integrates POC export over a 1 516month period (<sup>234</sup>Th half live equals 24.1 days). We remind here that MR 517fluxes as based on mesopelagic Ba<sub>xs</sub> reflect past remineralization activity 518integrated over several days to a few weeks (Dehairs et al., 1997; Cardinal 519et al., 2005; Jacquet et al., 2007, 2008b). In order to compare EP with MR (r-520ratio and transfer efficiency) we consider EP fluxes from 150 m. Results are 521compared with late summer KEOPS 1 results. For KEOPS 1, PP data are 522detailed in Lefèvre et al. (2008) and Mosseri et al. (2008), EP data are 523detailed in Savoye et al. (2008) and  $Ba_{xs}$  data are described in Jacquet et al. 524(2008a).

525

## 526 4.2.1. Reference station R-2

527Since station R-2 had the highest DWAV Ba<sub>xs</sub> content it yielded the 528highest MR flux of the whole study area (91 mgC m<sup>-2</sup> d<sup>-1</sup>; 150-800 m; Table 5292). In contrast, both PP and EP fluxes at R-2 were very low (132 and 10 mgC 530  $m^{-2} d^{-1}$ , respectively) and the calculated MR flux exceeded EP (Table 2). The 531resulting export efficiency (EP/PP) was high, and T400 and T800 value (the 532fraction of EP exported deeper than 400 m and 800 m, as defined above) 533equal 0 (i.e., no export of POC beyond 400 and 800 m; note that >100% 534values, i.e., MR>EP, were set to zero in Fig.7a and Table 2). The fact that MR 535 exceeds EP therefore implies a non-steady state condition at the R-2 site. As 536reported above, R-2 probably experienced a brief early spring diatom 537production pulse days to a few weeks before the start of the KEOPS 2 cruise,

538 followed by subsequent export and quite important remineralization activity in 539 the underling layers as depicted by MR data.

540

# 541 4.2.2. Station A3 on the Plateau

542The 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 544summer values obtained during KEOPS 1 (see Jacquet et al., 2008a) when the 545same 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 546547uncertainty around 5%) they were slightly larger during KEOPS 1 (summer; 17 to 23 mgC m<sup>-2</sup> d<sup>-1</sup>) (Fig.5). We observed differences in the mesopelagic 548549POC remineralization efficiency between the two seasons (r-ratio, blue values 550in Fig.6, Table 2). During KEOPS 1 r-ratios (MR/EP) remained low, ranging 551from 7 to 9% of EP at A3, while during KEOPS 2 r-ratios were slightly higher 552but decreased from 29% (A3-1; first visit) to 13%, 27 days later (A3-2; 553second 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 554555same 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<sup>-2</sup> d<sup>-1</sup> (Cavagna 556et al., 2014), EP remained relatively low (85 mgC m<sup>-2</sup> d<sup>-1</sup>). Here EP accounted 557558for only about 4% of PP (low export efficiency; see green data points in 559Fig.5). This condition suggested that phytoplankton biomass was 560accumulating 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 563surface carbon export efficiency has already been reported from previous 564 studies in the Southern Ocean (Savoye et al., 2008; Morris et al., 2007; 565Jacquet et al., 2011a; 2011b; Lam et al., 2007). Among possible explanations 566 for 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<sup>-2</sup> d<sup>-1</sup> at 125 m (14-31% of PP)
while PP ranged from 865 to 1872 mgC m<sup>-2</sup> d<sup>-1</sup>, reflecting enhanced export
efficiency (Jacquet et al., 2008a; Savoye et al., 2008).

573It is important to underline the fact that MR at station A3 was only 574slightly higher in summer than in spring especially considering the large 575differences in export efficiency between seasons. According to results from 576 sediment traps deployed over one year at the A3 site, Rembauville et al. (this 577issue-b) reported that 60% of the annual POC export at the base of the mixed 578layer occurred over a short periods of time representing <4% of the years 579 and was composed by small highly silicified, fast sinking, resting spores of 580diatoms that bypass grazing pressure. According to these authors, the pulses 581are linked to nutrient depletion dynamics inducing resting spore formation. 582During the rest if the year, the flux was composed of small diatoms (empty 583frustules) and small fecal pellets, with efficient C retention in the surface layer 584or transfer to trophic levels. If we consider that export conditions during 585KEOPS 2 are more similar to those prevailing most of the year, it is surprising 586 that during KEOPS 1 (that would reflect an export event toward the end of the 587growth season) MR is not more important. This would indicate that fast 588sinking- highly silicified- and pulsed material was directly transferred to the 589bottom without major remineralization. Note for example that at the complex 590 R-2 reference station, a small export event (Laurenceau-Cornec et al.; this 591issue) held heavily silicified diatoms (Lasbleiz et al.; 2014), and that the 592material was efficiently remineralized in the upper mesopelagic layer as 593 witnessed by the high MR values we observe for that station. For the KEOPS 2 594A3 site Laurenceau-Cornec et al. (2014) report that the sinking flux collected 595in the upper layer using gel-filled sediment traps was composed by

596 phytodetrital aggregates that held slightly silicified diatoms (Lasbleiz et al., 5972014). Even considering the shift from slightly- to highly-silicified material 598 transfer between spring (KEOPS2) and summer (KEOPS 1), MR only slightly 599increases between both periods. Also, the mesozooplankton biomass at A3-2 600 was one of the highest of the KEOPS2 cruise, with a doubling from KEOPS 2 601 (early spring) to KEOPS 1 (late summer) (Carlotti et al., 2014). It is thus 602 possible that at A3 the export event reported above, combined with a lasting 603 grazing pressure would have induced this rather low and perduring 604 mesopelagic remineralization. We also wonder whether the shallow water 605 column at A3 combined with lateral advection above the plateau would play a 606 role in triggering the mesopelagic POC remineralization activity and in setting 607 its efficiency. For KEOPS 1, Venchiarutti et al. (2008) report that lateral 608 advection over the plateau could significantly impact particle dynamics. 609 During KEOPS 1, station B1 (CTD68) located on the plateau upstream from A3 610 according to the plateau circulation (Park et al., 2008) exhibited a very similar 611  $Ba_{xs}$  distribution as station A3: low mesopelagic  $Ba_{xs}$  and important bottom 612 resuspension (not shown here; see Jacquet et al., 2008a). These strong 613 similarities in Baxs profiles shape would indicate that next to the pulsed nature 614 of the events, the dynamics on the shallow plateau play an important role in 615 limiting the extend of mesopelagic POC remineralization processes.

616 In Fig.7a is shown for both KEOPS cruises the ratio of EP over PP 617 (export efficiency) vs. the fraction of EP exported deeper than 400m (i.e. 618 T400; defined above). Note that for station A3-1 (KEOPS 2), there are no PP 619 data. The A3 site shows increasing EP/PP ratios from spring (KEOPS 2) to late 620 summer (KEOPS 1), and so do the T400 values (A3-1: 70%; A3-2: 87%; 621 KEOPS 1 A3 site:  $92\pm1\%$ ). Station E-4W located in waters with similar  $\theta$ -S 622 and Chl-a characteristics as the A3 plateau site but has a deeper water 623 column (1384 m has PP and EP fluxes of the same order of magnitude (Table 2). However, MR values (36 mgC m<sup>-2</sup> d<sup>-1</sup>; 150-400 m) are larger at E-4W, 624

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<sup>-2</sup> d<sup>-1</sup>), 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<sup>-2</sup> d<sup>-1</sup>; 150-400 m) at F-L than at 633 E-4W, resulting T400 values are higher (52%) there.

Overall, during KEOPS 2 it appears that biomass at stations A3, E-4W and F-L (sites of high productivity) was accumulating in surface waters (e.g. transfer to higher trophic levels) and export did not start yet considering the early stage of the season during KEOPS 2. Our observations allow us to 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  $91\pm3\%$  at A3;

(2) In contrast to A3, E-4W and F-L showed important mesopelagic remineralization rates, reducing the efficiency of C transfer beyond 400 m to 33 and 52%, respectively, and to zero for both stations beyond 800 m. Bottom depth, lateral advection, zooplankton grazing pressure and the pulsed nature of the POC transfer at A3 were the particular conditions that could drive the differences in C transfer efficiency between A3 and E4-W and F-L and limit the extend of MR processes at A3.

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#### 655 **4.3. Stations in the meander**

656 Temporal short term changes for the stations TNS-6, E-1, E-2, E-3, E-657 4E and E-5, located in the Polar front meander, will be discussed in this 658 section. Note that no PP or EP data exist for TNS-6. From Table 2 it appears 659 that PP almost doubled between E-1 and E-5 but this increase was not 660 paralleled by an increase of EP and MR, except for the 30% EP increase from 661 E-1 to E-3. In fact overall EP shows a decreasing trend with time, while MR 662 (150-400 m) stays rather constant, except for the decrease between E-1 and 663 E-3 (Table 2). As reported above such a mismatch may result from 664 differences in time scales characterizing the different processes that were 665 compared. The most likely explanation is that in this early stage of the growth 666 season, phytoplankton biomass was accumulating in the surface layer and 667 export was lagging behind.

668 The ratio of EP over PP vs. T400 and T800 showed a large variability in 669 transfer efficiency inside the meander (Fig.7b). PP and EP fluxes increased by 670 about 30% from E-1 to E-3, but a concomitant decrease of mesopelagic MR 671 yielded to an enhanced transfer efficiency, from 74 to 92%, through the 400 672 m boundary and from 52 to 73% through the 800 m boundary. This suggests 673 that significant remineralization should have occured at greater depths (even 674 > 1000 m) and it is also reflected by the presence of Ba<sub>xs</sub> maxima below 1000 675 m (see Fig.4h and Appendix A). This was particularly salient when plotting 676  $Ba_{xs}$  contents vs. depths over the 27-day observation period (Fig.8). The high 677 deep water Baxs values in Figure 8 were not taken into account when 678 integrating TNS-6 and E-1 profiles between 150 and 400 or even 150 and 800 679 m (Fig. 5e). Considering that the seafloor in the meander area is at about 680 2000 m depth, it seems unlikely that these high  $Ba_{xs}$  contents at depths 681 >1000 m were due to sediment resuspension. Also, particle spectra for these 682 sites do not reveal any bottom resuspension (Jouandet et al., 2014; Lasbleiz

683 et al., 2014; Vandermerve et al., 2015;). Therefore, the high deep (>1000 m) 684  $Ba_{xs}$  contents at TNS-6 and E-1 most likely reflected the fact that here 685 significant remineralization of POC material did occur in the bathypelagic 686 domain and even down to the sea-floor. Note that suspended particles in the 687 depth range containing the deep  $Ba_{xs}$  maxima were dominated by the <2  $\mu$ m 688 size fraction (Zhou et al., pers. comm.). When integrating the  $Ba_{xs}$  contents 689 from 150 m to the sea-floor at stations TNS-6 and E-1, MR fluxes increase to 690 156 and 184 mgC m<sup>-2</sup> d<sup>-1</sup> 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 691 692 exported POC was entirely remineralized in the water column leaving no C for 693 transfer to the sediments.

694 Overall, the temporal pattern of mesopelagic remineralization 695 described above reflects two successive events of particle transfer: a first 696 transfer from a previous bloom (occurred before visiting TNS-6 and perduring 697 at E-1) and a second transfer from E-4E to E-5. The first transfer was evident 698 by the downward (up to the bottom) propagation of the mesopelagic  $Ba_{xs}$ 699 maximum signal, which mostly weakens at E-2. The second event was 700 reflected by the occurrence again of important mesopelagic Ba<sub>xs</sub> build-up at E-701 4E and E-5. Overall, our results indicated the large capacity of the Polar Front 702 Meander to transfer POC material to depth, but in contrast to station A3 on 703 the Plateau, this transfer was coupled to intense and near to complete POC 704 remineralization (as also observed at E-4W and F-L). Between-sites changes 705 in mesopelagic carbon remineralization due to unequal biomass productivity 706 and iron fertilization over the Kerguelen Plateau were thus relatively complex. 707 Furthermore, the situation in the Meander area seems to corroborate results 708 obtained in the iron-replete Subantarctic Zone east of the Tasman Plateau 709 (Australian sector of the Southern Ocean; SAZ-Sense cruise; Jacquet et al., 710 2011a, 2011b), where the mesopelagic remineralization efficiency was 711 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).

717

# **5.** Conclusion

719 Based on spatially and temporally well resolved mesopelagic excess 720 particulate Ba inventories this work estimated mesopelagic POC 721remineralization above the Kerguelen Plateau and inside a permanent 722meander of the Polar Front to the east of Plateau, areas. The observed 723 variability of mesopelagic remineralization reflects differences in the fate of 724 the biomass that is exported to the deep ocean, between Plateau and Polar 725 Front. Results also reveal the patchiness of the season advancement and of 726 the establishment of remineralization processes between theses sites. Our 727 results indicate that the reference station R-2 experienced few days to weeks 728 before the start of the cruise an export event that was efficiently 729 remineralized in the upper mesopelagic layer. In terms of deep ocean carbon 730 transfer efficiency, our results highlight that above the plateau (A3 site) 731 mesopelagic remineralization is not a major barrier to organic matter transfer 732 to the sea-floor, with carbon transfer beyond 400 m reaching up to 87% of EP 733 during KEOPS 2, while in the Polar Front Meander remineralization of exported 734 organic carbon in the upper 400 m is more efficient than above the plateau. 735 In the Meander area remineralization may even balance export when including 736 its effect in the deeper waters (till 800 m and even deeper), thus resulting in 737 a close to zero carbon transfer to sediment. A similar condition is also 738 observed for sites at the margin of the plateau (E-4W) and the Polar front (F-739 L).

740

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752

# 753 Figure captions

754

Figure 1: (a) Kerguelen Island area in the Southern Ocean with KEOPS 2 sampling zones and MODIS Chlorophyll concentrations (mg m<sup>-3</sup>) (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  $\theta$ -S and Chl-a characteristics.

762

763 Figure 2: (a) Potential temperature  $\theta$  – salinity S plots and isopycnals for 764 KEOPS 2 profiles, (b) Focus on the upper 200 m water column. AASW= 765 Antarctic 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-769bremerhaven.de/GEO/ODV).

770

771Figure 3: Rates of oxygen consumption (mmol m<sup>-2</sup> d<sup>-1</sup>) during KEOPS 1 as772directly measured (JO<sub>2</sub>-W) and from mesopelagic Ba<sub>xs</sub> contents (JO<sub>2</sub>-Ba).773Rates are integrated between 150-300 m.

774

775Figure 4: Particulate biogenic  $Ba_{xs}$  profiles (pM) in the upper 800 m (Fig.4a-g)776and in the upper 2500 m (Fig.4h). Stations are identified by CTD cast777numbers. BKG=  $Ba_{xs}$  background (180 pM).

778

Figure 5: Regression of the ratio of integrated bacterial production (BP) in the
upper 150 m over integrated BP in the upper 400 m versus depth weighted
average (DWAv) mesopelagic Ba<sub>xs</sub> (pM; 150-400 m) during KEOPS 2. KEOPS
1 data (dots) are reported for comparison.

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Figure 6: Schematic, comparing the fate of POC at station A3 during KEOPS 1 and KEOPS 2 cruises. PP= primary production, EP= export production at 150 m depth and MR= mesopelagic POC remineralization deduced from the Ba<sub>xs</sub> maxima and integrated between 150-400 m; all fluxes in mgC m<sup>-2</sup> d<sup>-1</sup>. EP/PP (green values), MR/PP (red values) and MR/EP (r-ratio, blue values) ratios shown as %.

790

Figure 7: Y-axis: EP/PP = POC flux at 150 m (EP150) as a fraction of primary production (PP); X-axis: EPx/EP150 = POC flux at defined depths (EPx; here 400 and 800 m) as a fraction of POC flux at 150 m (EP150). The green cross (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 represent export efficiency.

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Figure 8: Temporal evolution of particulate biogenic Ba (Ba<sub>xs</sub>; pM) in the upper 2000 m water column in the Polar Front meander. Graph constructed using Ocean Data View (Schlitzer, 2002; Ocean Data View; <u>http://www.awi-</u> bremerhaven.de/GEO/ODV).

803

#### 804 Table captions

805

806Table 1: Station locations, CTD cast number and bottom depth during KEOPS8072. Depth-weighted average values (DWAv) of mesopelagic Ba<sub>xs</sub> (pM) and Ba<sub>xs</sub>808based mesopelagic POC remineralization (MR; mgC m<sup>-2</sup> d<sup>-1</sup>) integrated809between 150-400 and 150-800 m depths. See text for further information on810calculation.

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Table 2: Comparison of mesopelagic POC remineralization (MR) with primary production (PP) and export production (EP). All fluxes in mg C m<sup>-2</sup> d<sup>-1</sup>. r-ratio is the ratio of MR over EP. EP/PP is the export efficiency. The C transfer efficiency at 400 and 800 m (T400, T800) is the fraction of C export (EP) at 150 m exiting through the 400 m (T400) or the 800 m (T800) horizons. See text for further information on calculation.

818

<u>Appendix A</u>: Excess particulate biogenic Ba (Ba<sub>xs</sub>; pM) and particulate Al (nM)
during KEOPS 2.

821

# 822 **References**

Armand, L.K., Crosta, X., Quéguiner, B., Mosseri, J., Garcia, N. : Diatoms
preserved in surface sediments of the northeastern Kerguelen Plateau,
Deep- Sea Res. Pt. II, 55, 677–692, 2008.

826 de Baar, H. J. W., Boyd, P. W., Coale, K. H., Landry, M.R., Tsud, A., Assmy, 827 P., Bakker, D.C.E, Bozec, Y., Barber, R.T., Brzezinski, M.A., Buesseler, 828 K.O., Boyé, M., Croot, P.L., Gervais, F., Gorbunov, Y., Harrison, P.J., 829 Hiscock, W.T., Laan, P., Lancelot, C., Law, C.S., Levasseur, M., Marchetti, 830 A., Millero, F.J., Nishika, J., Nojiri, Y., van Oijen, T., Riebesell, U., 831 Rijkenberg, M.J.A., Saito, H., Takeda, S., Timmermans, K.R., Veldhuis, 832 J.W., Waite, A.M., Wong, C.S.: Synthesis of iron fertilization experiments: 833 From the iron age in the age of enlightenment, J. Geophys. Res., 110, 834 C09S16, doi:10.1029/2004JC002601, 2005.

- Blain, S., Tréguer, P., Belviso, S., Bucciarelli, E., Denis, M., Desabre, S., Fiala,
  M., Martin Jézéquel, V., Le Fèvre, J., Mayzaud, P., Marty, J.- C., and
  Razouls, S.: A biogeochemical study of the island mass effect in the
  context of the iron hypothesis: Kerguelen Islands, Southern Ocean, DeepSea Res. Pt. I, 48, 163-187, 2001.
- 840 Blain, S., Queguiner, B., Armand, L., Belviso, S., Bombled, B., Bopp, L., 841 Bowie, A., Brunet, C., Brussaard, C., Carlotti, F., Christaki, U., Corbiere, 842 A., Durand, I., Ebersbach, F., Fuda, J. -L., Garcia, N., Gerringa, L., 843 Griffiths, B., Guigue, C., Guillerm, C., Jacquet, S., Jeandel, C., Laan, P., 844 Lefevre, D., Lo Monaco, C., Malits, A., Mosseri, J., Obernosterer, I., Park, 845 Y. -H., Picheral, M., Pondaven, P., Remenyi, T., Sandroni, V., Sarthou, G., 846 Savoye, N., Scouarnec, L., Souhaut, M., Thuiller, D., Timmermans, K., 847 Trull, T., Uitz, J., van Beek, P., Veldhuis, M., Vincent, D., Viollier, E., Vong, 848 L., and Wagener, T.: Effect of natural iron fertilization on carbon 849 sequestration in the Southern Ocean, Nature, 446, 1070-1074, 2007.
- Blain, S., Quéguiner, B., and Trull, T.: The natural iron fertilization experiment
  keops (kerguelen ocean and plateau compared study): An overview,
  Deep-Sea Res. Pt. II, 55, 559–565, 2008.

Boyd, P. W., Bakker, D. C. E., Chandler, C.: A new database to explore the
findings from large-scale ocean iron enrichments experiments,
Oceanography, 25, 64–71, doi:10.5670/oceanog.2012.104, 2012.

856 Boyd, P. W., Law, C. S., Wong, C. S., Nojiri, Y., Tsuda, A., Levasseur, M., 857 Takeda, S., Rivkin, R., Harrison, P. J., Strzepek, R., Gower, J., McKay, R. 858 M., Abraham, E., Arychuk, M., Barwell-Clarke, J., Crawford, W., Crawford, 859 D., Hale, M., Harada, K., Johnson, K., Kiyosawa, H., Kudo, I., Marchetti, 860 A., Miller, W., Needoba, J., Nishioka, J., Ogawa, H., Page, J., Robert, M., 861 Saito, H., Sastri, A., Sherry, N., Soutar, T., Sutherland, N., Taira, Y., 862 Whitney, F., Wong, S. K. E., and Yoshimura, T.: The decline and fate of an 863 iron-induced subarctic phytoplankton bloom, Nature, 428, 549-553, 2004.

864 Boyd, P. W., Watson, A. J., Law, C. S., Abraham, E. R., Trull, T., Murdoch, R., 865 Bakker, D. C. E., Bowie, A. R., Buesseler, K. O., Chang, H., Charette, M., 866 Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, 867 M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M. T., 868 McKay, R. M., Nobber, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., 869 Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., and 870 Zeldis, J.: Phytoplankton bloom upon mesoscale iron fertilization of polar 871 Southern Ocean water, Nature, 407, 695-702, 2000.

Bowie, A. R., van der Merwe, P., Quéroué, F., Trull, T., Fourquez, M.,
Planchon, F., Sarthou, G., Chever, F., Townsend, A. T., Obernosterer, I.,
Sallée, J.-B., and Blain, S.: Iron budgets for three distinct biogeochemical
sites around the Kerguelen archipelago (Southern Ocean) during the
natural fertilisation experiment KEOPS-2, Biogeosciences Discuss., 11,
17861-17923, doi:10.5194/bgd-11-17861-2014, 2014.

Broecker, W. S., Takahashi, T., Takahashi, T.: Sources and flow patterns of
deep-ocean waters as deduced from potential temperature, salinity and
initial phosphate concentration, J. Geophys. Res., 90, 6925-6939, 1985.

- Buesseler, K. O., Andrews, J.E., Pike, S.M., Charette, M.A.: The effect of iron
  fertilization on carbon sequestration in the Southern Ocean, Science, 304,
  414–417, 2004.
- Buesseler, K.O., Andrews, J.E., Pike, S.M., Charette, M.A., Goldson, L.E.,
  Brzezinski, M.A., Lance, V.P.: Particle export during the Southern Ocean
  Iron Experiment (SOFeX), Limnol. Oceanogr., 50 (1), 311– 327, 2005.
- Buesseler, K.O., Antia, A.N., Chen, M., Fowler, S.W., Gardner, W.D.,
  Gustaffson, Ö., Harada, K., Michaels, A.F., Rutgers van der Loeff, M.,
  Sarin, M., Steinberg, D.K., Trull, T.: An assessment of the use of sediment
  traps for estimating upper ocean particle fluxes. Journal of Marine
  Research, 65(3): 345-416, 2007a.
- 892 Buesseler, K.O., Lamborg, C.H., Boyd, P.W., Lam, P.J., Trull, T.W., Bidigare,
- R.R., Bishop, J. K. B., K.L., Casciotti, Dehairs, F., Elskens, M., Honda,
  M., Karl, D. M., Siegel, D. A., Silver, M. W., Steinberg, D.K., Valdes, J.,
  Van Mooy, B., Wilson, S.: Revisiting carbon flux through the ocean's
  twilight zone, Science, 316, 567–569, 2007b.
- Buesseler, K.O., and Boyd, P.W.: Shedding light on processes that control
  particle export and flux attenuation in the twilight zone. Limnol.
  Oceanogr., 54 (4), 1210-1232, 2009.
- Gardinal, D., Dehairs, F., Cattaldo, T., and André, L.: Constraints on export
   and advection in the Subantarctic and Polar Front Zones, south of
   Australia from the geochemistry of suspended particles, J. Geophys. Res.-

903 Oceans, 106, 31637-31656, doi : 10,1029/2000JC000251, 2001

904 Cardinal, D., Savoye, N., Trull., T.W., André, L., Kopczynska, E., Dehairs, F.,

- 905 2005. Particulate Ba distributions and fluxes suggest latitudinal variations
  906 of carbon mineralization in the Southern ocean, Deep-Sea Res. Pt. I, 52,
  907 355-370, 2005.
- 208 Carlotti, F., Jouandet, M.-P., Nowaczyk, A., Harmelin-Vivien, M., Lefèvre, D.,
  209 Guillou, G., Zhu, Y., Zhou, M. : Mesozooplankton structure and functioning

910 during the onset of the Kerguelen Bloom during Keops2 survey, this issue,911 in prep.

912 Cavagna, A. J., Fripiat, F., Elskens, M., Dehairs, F., Mangion, P., Chirurgien, L., Closset, I., Lasbleiz, M., Flores-Leiva, L., Cardinal, D., 913 914 Leblanc, K., Fernandez, C., Lefèvre, D., Oriol, L., Blain, S., and 915 Quéguiner, B.: Biological productivity regime and associated N cycling in 916 the vicinity of Kerguelen Island area, Southern Ocean, Biogeosciences 917 Discuss., 11, 18073-18104, doi:10.5194/bgd-11-18073-2014, 2014.

Closset, I., Lasbleiz, M., Leblanc, K., Quéguiner, B., Cavagna, A.-J., Elskens,
M., Navez, J., and Cardinal, D.: Seasonal evo- lution of net and
regenerated silica production around a natu- ral Fe-fertilized area in the
Southern Ocean estimated from Si isotopic approaches, Biogeosciences,
11, 5827-5846, doi: 10.5194/bg-11-5827-2014, 2014.

923 Christaki, U., Obernosterer, I., VanWambeke, F., Veldhuis, M., Garcia, N., and
924 Catala, P.: Microbial food web structure in a naturally iron fertilized area in
925 the southern ocean (Kerguelen plateau), Deep-Sea Res. Pt. II, 55, 706–
926 719, 2008.

927 Christaki, U., Lefèvre, D., Geoges, C., Colombet, J., catala, P., Courties, C.,
928 Sime-Ngando, T., Blain, S., and Obernosterer, I.: Microbial food web
929 dynamics during spring phytoplankton blooms in the naturally iron930 fertilized Kerguelen area (Southern Ocean), Biogeosciences, 11, 6739931 3753, doi:10.5194/bg-11-6739-2014, 2014.

932 Dehairs, F., Chesselet, R., Jedwab, J.: Discrete suspended particles of barite
933 and the barium cycle in the open ocean, Earth Planet. Sc. Lett., 49, 40-42,
934 1980.

Dehairs, F., Baeyens, W., Goeyens, L.: Accumulation of suspended barite at
mesopelagic depths and export production in the Southern Ocean, Science,
258, 1332–1335, 1992.

938 Dehairs, F., Shopova, D., Ober, S., Veth, C., Goeyens, L.: Particulate barium

stocks and oxygen consumption in the Southern Ocean mesopelagic water
column during spring and early summer: Relationship with export
production, Deep-Sea Res. Pt II, 44, 497-516, 1997.

Dehairs, F., Jacquet, S.H.M., Savoye, N., van Mooy, B., Buesseler, K., Bishop,
J., Lamborg, C., Elskens, M., Baeyens, W., Casciotti K., Monnin , C.:
Barium in twilight zone suspended matter as proxy for organic carbon
mineralization: results for the North Pacific, Deep-Sea Res. Pt. II, 55,
1673-1683, 2008.

947 Dehairs, F., Fripiat, F., Cavagna, A.-J., Trull, T. W., Fernandez, C., Davies, D.,
948 Roukaerts, A., Fonseca Batista, D., Planchon, F., and Elskens, M.: Nitrogen
949 cycling in the Southern Ocean Kerguelen Plateau area: evidence for
950 significant surface nitrification from nitrate isotopic compositions,
951 Biogeosciences Discuss., 11, 13905-13955, doi:10.5194/bgd-11-13905952 2014, 2014.

D'ovidio, F., Della Penna, A., Trull, T.W., Nencioli, F., Pujol, I., Rio, M.H., Park,
Y.H., Cotté, C., Zhou, M., Blain, S.: The biogeochemical structuring role of
horizontal stirring: Lagrangian perspectives on iron delivery downstream of
the Kerguelen plateau, in prep., this issue.

957 Dymond, J.R., Suess, E., Lyle, M.: Barium in deep-sea sediment: a
958 geochemical proxy for paleoproductivity, Paleoceanography, 7, 163–181,
959 1992.

Bellison, Eurachem/CITAC Guide CG4, Quantifying Uncertainty in Analytical
Measurement. Eds. S.L.R. Ellison, M. Rosslein and A. Williams. Second
edition ISBN 0948926 15 5, Pp 120, 2000.

François, R., Honjo, S., Krishfield, R., and Manganini, S.: Factors controlling
the flux of organic carbon to the bathypelagic zone of the ocean, Global
Biogeochem. Cy., 16(4), 1087 doi:10.1029/2001GB001722, 2002.

Gervais, F., Riebesell, U., Gorbunov, M. Y.: Changes in primary productivity
and chlorophyll a in response to iron fertilization in the southern Polar
Frontal Zone, Limnol. Oceanogr., 47, 1324–1335, 2002.

969 Henson, S. A., et al. (2011), A reduced estimate of the strength of the 970 ocean's biological carbon pump, Geophys. Res. Lett., 38(4), L04606.

Hoffmann, L., Peeken, I., Lochte, K., Assmy, P., Veldhuis, M.: Different
reactions of Southern Ocean phytoplankton size classes to iron
fertilization, Limnol. Oceanogr, 51, 1217–1229, 2006.

Jacquet, S.H.M., Dehairs, F., Cardinal, D., Navez, J., Delille, B.: Barium
distribution across the Southern Ocean Frontal system in the CrozetKerguelen Basin, Mar. Chem., 95(3-4), 149-162, 2005.

977 Jacquet, S.H.M., Dehairs, F., Elskens, M., Savoye, N., Cardinal, D.: Barium

978 cycling along WOCE SR3 line in the Southern Ocean, Mar. Chem., 106, 33-979 45, 2007.

Jacquet, S.H.M., Dehairs, F., Savoye, N., Obernosterer, I., Christaki, U.,
Monnin, C., Cardinal, D.: Mesopelagic organic carbon mineralization in the
Kerguelen Plateau region tracked by biogenic particulate Ba, Deep-Sea
Res. Pt. II, 55 (5-7), 868-879, 2008a.

Jacquet, S.H.M., Savoye, N Dehairs, F., Strass, V., Cardinal, D.: Mesopelagic
carbon mineralization during the European Iron Fertilization Experiment
(EIFEX), Glob. Biogeochem. Cy., 22, GB1023,
doi:10.1029/2006GB002902, 2008b.

Jacquet, S.H.M., Dehairs, F., Becquevort, S., Dumont, I., Cavagna, A.,
Cardinal, D.: Twilight zone organic carbon remineralization in the PFZ and
SAZ south of Tasmania (Southern Ocean), Deep-Sea Res. Pt. II, 58 (2221), 2222-2234 doi:10.1016/j.dsr2.2011.05.029, 2011a.

Jacquet, S.H.M., Lam, P., Trull ,T., Dehairs, F.: Carbon export production in
the Polar front zone and Subantarctic Zone south of Tasmania, Deep-Sea

994 Res. Pt. II, 58 (21-22), 2277-2292 doi:10.1016/j.dsr2.2011.05.035,
995 2011b.

- Jouandet, M.P., and others: Particles distribution in contrasted area of the ironfertilized region around Kerguenlen Islans, in prep., this issue.
- Lam, P. J., and Bishop, J. K. B.: High biomass, low export regimes in the
  Southern Ocean, Deep-Sea Research II, 54, 601-638, 2007.
- 1000 Lampitt, R. S., Achterberg, E.P., Anderson, T.R., Hughes, J.A., Iglesisas-
- 1001 Rodriguez, M.D., Kelly-Gerreyn, B.A., Lucas, M., Popova, E.E., Sanders,
- 1002 R., Shepherd, J.G., Smythe-Wright, D., Yool, A. : Ocean fertilization: A 1003 potential means of geoengineering?, Philos. Trans. R. Soc. A, 366, 3919–
- 1004 3945, doi:10.1098/rsta.2008.0139, 2008.
- Lampitt, R. S., Antia, A.N.: Particle flux in deep seas: regional characteristicsand temporal variability, Deep-Sea Res. Pt I, 44, 1377-1403, 1997.
- Lasbleiz, M., Leblanc, K., Blain, S., Ras, J., Cornet-Barthaux, V., Hélias
  Nunige, S., and Quéguiner, B.: Pigments, elemental composition (C, N, P,
  and Si), and stoichiometry of particulate matter in the naturally iron
  fertilized region of Kerguelen in the Southern Ocean, Biogeosciences, 11,
  5931–5955, doi::10.5194/bg-11- 5931-2014, 2014.
- 1012Laurenceau-Cornec, E. C., Trull, T. W., Davies, D. M., Bray, S. G., Doran, J., 1013 Planchon, F., Carlotti, F., Jouandet, M.-P., Cavagna, A.-J., Waite, A. M., 1014 and Blain, S.: The relative importance of phytoplankton aggregates and 1015zooplankton fecal pellets to carbon export: insights from free-drifting 1016 sediment trap deployments in naturally iron-fertilised waters near the 1017 Kerguelen plateau, Biogeosciences Discuss., 11, 13623-13673, 1018 doi:10.5194/bqd-11-13623-2014, 2014.
- 1019 Laws, E. A., et al. (2000), Temperature effects on export production the1020 ocean, Global Biogeochem. Cycles, 14(4), 1231–1246.
- 1021Lefèvre, D., Guigue, C., Obernosterer, I.: The metabolic balance at two1022contrasting sites in the Southern Ocean: the iron-fertilized Kerguelen area

and HNLC waters, Deep-Sea Res. Pt. II, 55, 766–776,
 doi:10.1016/j.dsr2.2007.12.006, 2008.

- Le Moigne, F. A. C., Moore, C. M., Sanders, R. J., Villa-Alfageme, M.,
  Steigenberger, S., and Achterberg, E. P.: Sequestration efficiency in the
  iron-limited North Atlantic: Implications for iron supply mode to fertilized
  blooms, Geophys. Res. Lett., 41, doi:10.1002/2014GL060308, 2014.
- 1029 Longhurst, A.R., Bedo, A.W., Harrison, W.G., Head, E.J.H., Sameoto, D.D. :
- 1030 Vertical flux of respiratory carbon by oceanic diel migrant biota, Deep-Sea1031 Res Pt, 37 (4), 685–694, 1990.
- Maiti, K., Charette, M., Buesseler, K., and Kahru, M.: An inverse relationship
  between production and export efficiency in the Southern Ocean, Geophys.
  Res. Lett., 40, 2013.
- 1035 Martin, J.H., Knauer, G.A., Karl, D.M., Broenkow, W.W.: VERTEX: carbon 1036 cycling in the NE Pacific, Deep-Sea Res., 34, 267–285, 1987.
- Monnin, C., Jeandel, C., Cattaldo, T., Dehairs, F.: The marine barite saturation
  state of the world's oceans, Mar. Chem., 65(3-4), 253-261, 1999.
- Morris, P.J, and Charette, M.A.: A synthesis of upper oceancarbon and
  dissolved iron budgets for Southern Ocean natural iron fertilization studies
  (2013), Deep-Sea Res., 90, 147-157, 2013.
- 1042 Passow, U., Carlson, C. A. : The biological pump in a high CO2 world, Mar.
  1043 Ecol. Prog. Ser., 470, 249–271, doi:10.3354/meps09985, 2012.
- Porris, P.J., Sanders, R., Turnewithsch, R., Thomalla, S., 234<sup>Th</sup>-derived
  particulate organic carbon export from an island-induced phytoplankton
  blomm in the Southern Ocean, Deep-Sea Res. Pt.II, 24, 2208-2232, 2007
- 1047 Mosseri, J., Quéguiner, B., Armand, L. K., and Cornet-Barthaux, V.: Impact of
- $1048\,$  iron on silicon utilization by diatoms in the Southern Ocean: a case study
- 1049 of Si/ N cycle decoupling in a naturally iron-enriched area, Deep-Sea Res.
- 1050 Pt. II, 55, 801-819, doi :10,1016/j.dsr2,2007,12,003, 2008.

Park, Y. H., Durand, I., Kestenare, E., Rougier, G., Zhou, M., d'Ovidio, F.,
Cotté, C., and Lee J. H.: Polar front around the Kerguelen islands: An upto-date determination and associated circulation of surface/subsurface
water. J. Geophys. Res. Oceans, 119, i10.1002/2014JC010061, 2014.

Park, Y.-H., Roquet, F., Durand, I., and Fuda, J.-L.: Large-scale circulation
over and around the Northern Kerguelen Plateau, Deep-Sea Res. Pt. II, 55,
566–581, doi:10.1016/j.dsr2.2007.12.030, 2008.

Planchon, F., Cavagna A.J., Cardinal, D., André, L., Dehairs, F. Late summer
particulate organic carbon export and twilight zone remineralisation in the
Atlantic sector of the Southern Ocean, Biogeosciences, 10, 803–820,
doi:10.5194/bg-10-803-2013, 2013.

Planchon, F., Ballas, D., Cavagna A. J., Van Der Merwe, P., Bowie, A., Trull,
T., Laurenceau, E., Davis, D., and Dehairs, F.: Carbon export in the
naturally iron fertilized Kerguelen area of the Southern Ocean using
234Th-based approach, in prep., 2014.

1066 Pollard, R. T., Salter, I., Sanders, R. J., Lucas, M. I., Moore, C. M., Mills, R. A., 1067 Statham, P. J., Allen, J. T., Baker, A. R., Bakker, D. C. E., Charette, M. A., 1068 Fielding, S., Fones, G. R., French, M., Hickman, A. E., Holland, R. J., 1069Hughes, J. A., Jickells, T. D., Lampitt, R. S., Morris, P. J., Nedelec, F. H., 1070 Nielsdottir, M., Planquette, H., Popova, E. E., Poulton, A. J., Read, J. F., 1071 Seeyave, S., Smith, T., Stinchcombe, M., Taylor, S., Thomalla, S., 1072Venables, H. J., Williamson, R., and Zubkov, M. V.: Southern Ocean deep-1073water carbon export enhanced by natural iron fertilization, Nature, 457, 1074 577-U581, Doi 10.1038/Nature07716, 2009.

1075 Quéroué, F., Sarthou, G., Planquette, H. F., Bucciarelli, E., Chever, F.,
1076 van der Merwe, P., Lannuzel, D., Townsend, A. T., Cheize, M., Blain, S.,
1077 d'Ovidio, F., and Bowie, A. R.: High variability of dissolved iron
1078 concentrations in the vicinity of Kerguelen Island (Southern Ocean),

1079 Biogeosciences Discuss., 12, 231-270, doi:10.5194/bgd-12-231-2015,
1080 2015.

Rembauville, M., Blain, S., Armand, L., Quéguiner, B., and Salter, I.: Export
fluxes in a naturally fertilized area of the Southern Ocean, the Kerguelen
Plateau: ecological vectors of carbon and biogenic silica to depth (Part 2),
Biogeosciences Discuss., 11, 17089-17150, doi:10.5194/bgd-11-170892014, 2014.

Robinson, J., Popova, E. E., Yool, A., Srokosz, M. A., Lampitt, R. S., and
Blundell, J. R.: How deep is deep enough? Ocean iron fertilization and
carbon sequestration in the Southern Ocean, Geophys. Res. Lett., 41,
2489-2495, 2014.

Salter, I., Lampitt, R.S., Sanders, R., Poulton, A., Kemp, A.E.S., Boorman, B.,
Saw, K., Pearce, R.: Estimating carbon, silica and diatom export from a
naturally fertilised phytoplankton bloom in the Southern Ocean using
PELAGRA: a novel drifting sediment trap, Deep-Sea Res. Pt. II, 54, 2233–
2259, 2007.

Sarmiento, J.L., Slater, R.D., Fasham, M.J.R., Ducklow, H.W., Toggweiler,
J.R.: A seasonal three-dimensional ecosystem model of nitrogen cycling in
the North Atlantic photic zone, Global Biogeochem. Cy., 7, 417–450, 1993.
Savoye, N., Trull, T., Jacquet, S.H.M., Navez, J., Dehairs, F.: <sup>234</sup>Th-derived

export fluxes during a natural iron fertilization experiment (KEOPS), DeepSea Res. Pt. II, 55 (5-7), 841-855, 2008.

Schlitzer, R., Ocean Data View, http://www.awi-bremerhaven.de/GEO/ODV,2002.

Schneider, B., Bopp, L., Gehlen, M.: Assessing the sensitivity of modeled
airsea CO2 exchange to the remineralization depth of particulate organic
and inorganic carbon, Global Biogeochem. Cy., 22, GB3021, doi:10.1029/
2007GB003100, 2008.

Shopova, D., Dehairs, F., Baeyens, W.: A simple model of biogeochemical
element distribution in the oceanic water column, J. Mar. Sy., 6, 331–344,
1109 1995.

1110 Smetacek, V., Klass, C., Strass, V.H., Assmy, P., %ontresor, M., Cisewki, B., 1111 Savoye, N., Webb, A., d'Ovidio, F., Arrieta, J.M., Bathmann, U., Bellerby, 1112R., Mine Berg, G., Croot, P., Gonzalez, S., Jenjes, J., Herndl, G.J., 1113 Hoffmann, L.J., Leach, H., Losh, M., Mills, M.M., Neill, C., Peeken, I., 1114Rottgers, R., Sachs, O., Sauter, E., Schmidt, M.M., Schwarz, J., 1115Terbruggen, A., Wolf-Gladrow, D. : Deep carbon export from a Southern 1116 Ocean iron-fertilized diatom bloom, Nature, 487, 313-319, 1117 doi:10.1038/nature11229, 2012.

Sternberg, E., Jeandel, C., Miquel, J.-C., Gasser, B., Souhaut, M., ArraesMescoff, R., Francois R. : Particulate barium fluxes and export production
in the northwestern Mediterranean. Mar. Chem. 105, 281–295, 2007.

Sternberg, E., Jeandel, C., Robin, E., Souhaut, M.: Seasonal cycle of
suspended barite in the Mediterranean Sea, Geochimica et Cosmochimica
Acta, 72, 4020-4034, 2008a.

Sternberg, E., Tang, D., Ho, T\_Y., Jeandel, C., Morel, M.M..: Barium uptake
and adsorption in diatoms, Geochimica et Cosmochimica Acta, 69, 11,
2745-2752, 2008b.

Strass, V., Cisewski, B., Gonzales, S., Leach, H., Loquay, K.-D., Prandke, H.,
Rohr, H., Thomas, M.: The physical setting of the European Iron
Fertilization Experiment 'EIFEX' in the Southern Ocean, Reports on Polar
and Marine Research, 500, 15–49, 2005.

Stroobants, N., Dehairs, F., Goeyens, L., Vanderheijden, N., Van Grieken, R.:
Barite formation in the Southern Ocean water column, Mar. Chem., 35,
411-422, 1991.

Taylor, S.R., McLennan, S.M.: The continental crust: its composition and
evolution, Blackwell Scientific Publications, 312pp, 1985.

1136 van der Merwe, P., Bowie, A. R., Quéroué, F., Armand, L., Blain, S., 1137 Chever, F., Davies, D., Dehairs, F., Planchon, F., Sarthou, G., 1138 Townsend, A. T., and Trull, T.: Sourcing the iron in the naturally-fertilised 1139bloom around the Kerguelen Plateau: particulate trace metal dynamics, 1140 Biogeosciences Discuss., 11, 13389-13432, doi:10.5194/bgd-11-13389-11412014, 2014.

Venchiarutti, C., Jeandel, C., Roy-Barman, M.: Particle dynamics study in the
wake of Kerguelen Island using thorium isotopes, Deep-Sea Res. Pt. I, 55,
1144 1343–1363, 2008.

Williams, P.J., Jenkinson, N.W. : A transportable microprocessor-controlled
precise Winkler titration suitable for field station and shipboard use.
Limnol. Oceanogr. 27, 576-585, 1982.

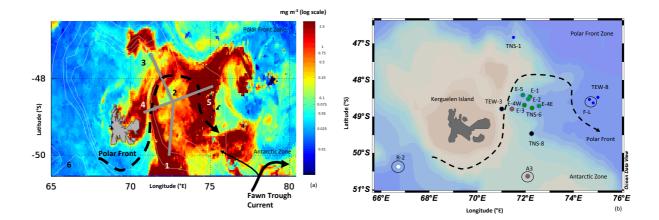
Zhou, M., Zhu, Y., Dorland, R.D., Measures, C.I.: Dynamics of the current
system in the southern Drake Passage, Deep-Sea Res. Pt I, 57, 1039–
1048, 2010.

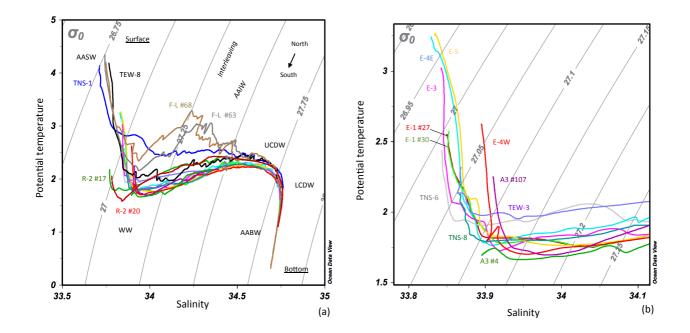
Zhou, M., Zhu, Y., Measures, C.I., Hatta, M., Charette, M.A., Gille, S.T.,
Frants, M., Jiang, M., Mitchell, B.G.: Winter mesoscale circulation on the
shelf slope region of the southern Drake Passage, Deep-Sea Res. Pt II, 90,
4–14, 2013.

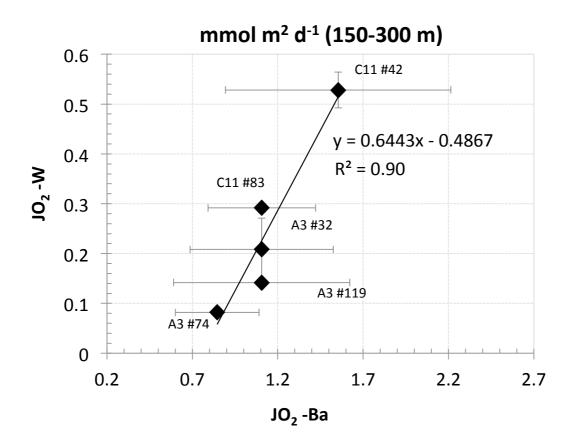
Zhou, M., and others: Estimates of particle settling and scavenging using
LISST-LOPC in Kergueln Plateau regions during the 2011 austral spring
KEOPS II cruise, in prep., this issue.

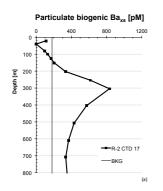
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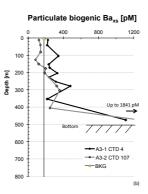
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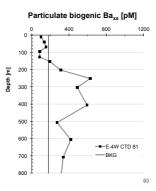






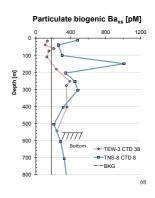




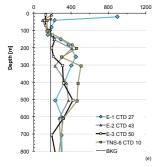


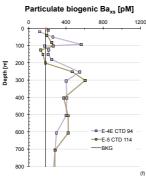
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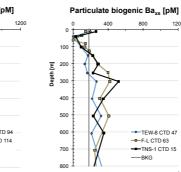
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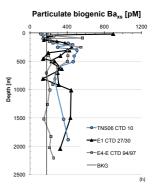


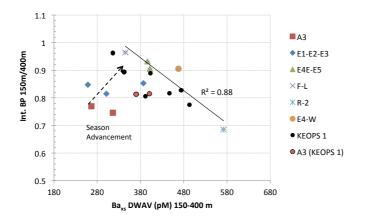
Particulate biogenic Ba<sub>xs</sub> [pM]





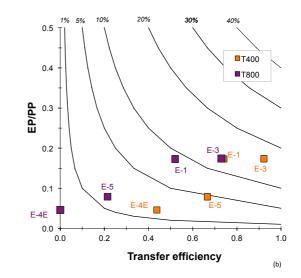


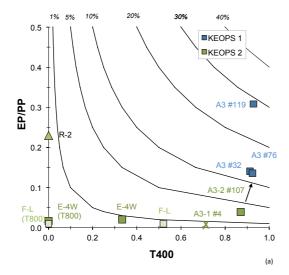


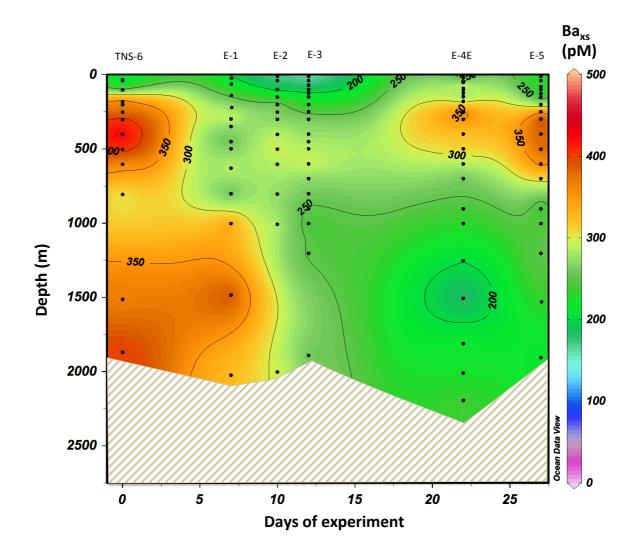


		OPS 2 pring 2011)	KEOPS 1 (Late summer 2005)				
	A3-1	A3-2	Mean of the 3 repeats				
PP	Not available	2172	864-1872				
	↓ -	4%	14 -31 %				
EP	47	85	250				
	- 🖌 29%	<1% 🖌 13%	1-2% <b>v 7</b> -9 %				
MR	14	11	17-23				

All fluxes in mgC m<sup>-2</sup> d<sup>-1</sup> 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 <sub>xs</sub> [pM] 150- 400 m	DWAv Ba <sub>xs</sub> [pM] 150- 800 m	MR°° 150- 400 m [mgC/m <sup>2</sup> /d]	MR Stnd Uncertainty %	MR 150- 800 m [mgC/m <sup>2</sup> /d]	MR Stnd Uncertaint %
teau											
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	/	/
ander 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
ar 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
ar Front											
E-4W	81/87	71.425	48.765	11,12/11	1384	468	411	36	8	76	18
arctic Zone											
-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  $\rm DWAV^o$  = Depht weighted average value  $\rm MR^{oo}$  = Mesopelagic C remineralization

Station	CTD	MLD [m]	Ez** [m]	PP° Ez [mgC/m²/d]	EP°° 150 m [mgC/m2/d]	MR 150-400 m [mgC/m <sup>2</sup> /d]	MR 150-800 m [mgC/m <sup>2</sup> /d]	EP/PP	r-ratio 150-400 m	r-ratio 150-800 m	T400	T800
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 si	te											
R-2	17/20	111	92	132	30	50	91	0.23	1.65	3.02	0	0
Meander tim	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	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 A3		Station RK2	
A3-1 CTD4 Niskin Depth [m] Ba <sub>xs</sub> [pM] AI [nM]	A3-2 CTD 107           Niskin         Depth [m]         Ba <sub>xs</sub> [pM]         Al [nM]	R-2 CTD17           Niskin         Depth [m]         Ba <sub>xs</sub> [pM]         AI [nM]	R-2 CTD 20 Niskin Depth [m] Ba <sub>xs</sub> [pM] AI [nM]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
<u>Station E</u> E-1 CTD 27	E-1 CTD 30	E-2 CTD 43	E-3 CTD 50
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Niskin         Depth (m)         Basic [pM]         AI         (nM]           24         11         129         45           23         42         117         93           22         71         130         28           20         102         160         22           18         125         201         11           16         133         252         23         3           13         252         233         3         1           12         304         309         6         10           10         404         316         7         9         505         419         64           7         606         320         14         5         707         193         12           1         912         265         5         5         5         5         5
Station E (continued) E-3 CTD 55	E-4W CTD 81	E-4W CTD 87	E-4E CTD 94
$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c } \hline Piskin & Depth [m] & Ba_{mc} [pM] & AI [nM] \\ \hline Piskin & Piskin &$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Niskin         Depth (m)         Ba.e. [pM]         AI (nM)           24         20         116         32           23         51         260         11           22         93         563         223           20         103         170         5           18         126         215         9           16         152         210         6           14         181         247         7           13         253         547         4           10         405         403         76           10         905         403         26           9         606         285         8           1         912         245         65
Station E (continued) E-4E CTD 97	E-5 CTD 113	E-5 CTD 114	
$\begin{array}{r                                    $	Niskin         Depth [m]         Bas_[[pM]         AI [nM]           10         911         111         3           8         1011         266         16           6         1214         256         15           1         1922         208         5	$\begin{tabular}{ c c c c c c } \hline Niskin & Depth [m] & Bas_m [pM] & AI [nM] \\ \hline 24 & 11 & 210 & 5 \\ 23 & 41 & 196 & 14 \\ 22 & 82 & 245 & 4 \\ 20 & 102 & 264 & 14 \\ 18 & 126 & 131 & 6 \\ 16 & 152 & 153 & 5 \\ 14 & 202 & 181 & 2 \\ 13 & 252 & 469 & 6 \\ 12 & 302 & 606 & 9 \\ 10 & 404 & 377 & 13 \\ 9 & 507 & 422 & 11 \\ 7 & 606 & 425 & 7 \\ 5 & 707 & 281 & 12 \\ 1 & 910 & 281 & 6 \\ \hline \end{tabular}$	
Transect West-East TEW-3 CTD38	TEW-8 CTD 47	Station F-L	F-L CTD 68
$\begin{array}{                                    $	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Niskin         Depth [m]         Base [pM]         AI [nM]           17         405         264         6           16         456         233         9           13         506         339         12           13         607         265         3           11         910         718         7           10         1013         257         5           8         1215         316         8           6         1772         225         7           1         2741         2999         131
Transect North-South TNS-1 CTD15 Nickle Death (and Death (and Death))	TNS-6 CTD 10	TNS-8 CTD8	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{tabular}{ c c c c c c c } \hline liskin & Depth [m] & Ba_{m}[pM] & AI [nM] \\ \hline 23 & 35 & 182 & 26 \\ \hline 21 & 42 & 141 & 12 \\ \hline 18 & 103 & 143 & 14 \\ \hline 16 & 184 & 413 & 11 \\ \hline 14 & 204 & 461 & 8 \\ \hline 12 & 205 & 556 & 57 \\ \hline 10 & 206 & 556 & 57 \\ \hline 10 & 206 & 556 & 57 \\ \hline 10 & 206 & 556 & 57 \\ \hline 10 & 206 & 556 & 57 \\ \hline 10 & 206 & 556 & 57 \\ \hline 10 & 206 & 556 & 57 \\ \hline 10 & 206 & 556 & 57 \\ \hline 10 & 206 & 556 & 57 \\ \hline 10 & 206 & 576 & 74 \\ \hline 11 & 206 & 576 & 74 \\ \hline 11 & 206 & 576 & 746 \\ \hline 11 & 206 & 576 & 746 \\ \hline 11 & 206 & 576 & 746 \\ \hline 11 & 206 & 576 & 746 \\ \hline 11 & 206 & 576 & 746 \\ \hline 11 & 206 & 576 & 746 \\ \hline 11 & 206 & 576 & 746 \\ \hline 11 & 206 & 576 & 746 \\ \hline 11 & 206 & 746 & 746 \\ \hline 12 & 20$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	