Reviewer 1:

We would like to thank the reviewer for their positive and constructive comments on this manuscript. Their time invested is greatly appreciated and certainly improved this manuscript.

Please find below point by point responses to the reviewers comments.

I found this to be an excellent paper which is certainly publishable, given that minor changes and some cuts are made. The study compares the particulate chemistry at a series of sites on the well-fertilised Kerguelen plateau with more remote sites that are poorly fertilised. The particulate chemistry is able to show that the Fe used for fertilisation originates from the re-suspension of shelf sediments and from fluvial and glacial sources derived from the Kerguelen Archipelago. This is an important finding some aspects of which need to be emerge more clearly. My main criticism is that the calculation in section 3.7 rests on the assumption that all particulate P is biogenic and this needs to be supported. What are the compositions of the rocks of Heard and Kerguelen Island- basalts can be high in P and may be an important source to the sediments? There may also be other non-biogenic sources. This calculation would require chemical and mineralogical data for the island rocks and the sediments for publication. In the absence of this data I would omit this section. The paper also tends to lose focus towards the end and removal of section 3.7, and also 3.9, would help to retain focus.

We considered the reviewers comments together with the second reviewers comments also regarding section 3.7 and rewrote this section and bolstered the calculation of biogenic Fe with correlations between biogenic Fe and fluorescence and dissolved oxygen. We have also listed the elemental molar ratios of Fe:P in Kerguelen Basalt and upper crust to show the factor of 1000 increase in pP within the suspended particles compared to these potential sources. We have cut section 3.9, together with figure 9 as these were minor parts of the paper and as the reviewer points out, their removal helps maintain focus. The new text regarding the biogenic Fe calculation in section 3.7 is as follows:

"If we assume that all particulate phosphorus (pP) is of biogenic origin, we can calculate the biogenic Fe fraction of the total Fe concentration by normalising to pP and comparing with published elemental ratios of Southern Ocean diatoms (Planquette et al., 2013). For the calculations we used the upper limit of Fe:P (1.93 mmol mol $^{-1}$) reported by Twinning et al. (2004) for Southern Ocean diatom assemblages. Given that pP and POC are remineralised throughout the water column and are generated within the surface mixed layer, calculations of biogenic trace metals will only be valid within the surface mixed layer, as the concentration of pP and POC decreases strongly with depth. It should also be noted that Kerguelen Island basalts and upper continental crust can contribute particulate phosphorus concomitantly with pFe to the particulate pool. However the Fe:P ratio found within Kerguelen Island basalts and the continental crust is 12.8 and 25.8 (mol:mol) respectively (Gautier et al., 1990; Wedepohl, 1995). Thus, the factor of 1000 increase in pP within suspended particles compared to these rock sources indicates that this pP is likely produced *insitu* within the mixed layer from dissolved PO_4^- rather than supplied from rock weathering. Furthermore, within the upper 200 m of the water column, biogenic Fe correlates significantly with both fluorescence (Spearmans RHO R = 0.518, $P < 0.05$, n = 30) and dissolved oxygen (Spearmans RHO R = 0.507, $P < 0.05$, n = 30) confirming the autotrophic composition of the particles identified as high in biogenic Fe."

Additional Comments below keyed to page and line numbers.

13392 line 14. What sedimentary records?

Thank you for noticing this, it is a mistake, I have changed the wording from "sedimentary records", to "Antarctic continental ice records".

The new test within the introduction is as follows:

"This limitation on the biological pump means that the Southern Ocean does not realise its full potential in transferring atmospheric CO2 into the ocean interior; a result illustrated in Antarctic continental ice records over geological timescales and supported by modelling studies (Barnola et al., 1987; Bopp et al., 2003; Martin, 1990; Watson et al., 2000)."

13393 line 7. Needs dFe inside the bracket. Also important here to point out that deFe includes colloidal and nanoparticulate Fe (which may be only partially bioavailable) as well as aqueous Fe (which is probably all bioavailable).

Changed to include these suggestions

The new text within the introduction is as follows:

“Dissolved Fe (dFe < 0.2 µm) includes colloidal and nanoparticulate Fe, which may only be partially bioavailable, as well as soluble Fe (sFe < 0.02 µm) which is highly bioavailable (de Baar and de Jong, 2001).As a result, the larger particulate fraction (> 0.2 µm) is often less studied due to the perception that it has low bioavailability.”

Line 16. Better to write inside the bracket as follows (e.g. weathering products delivered by fluvial and glacial processes, resuspension of sediments and porewaters, : : :).

It is likely that the porewaters contain reduced Fe which is oxidised to nanoparticulate Fe (oxyhydr)oxides on entering seawater. This is the main source of potentially bioavailable Fe from re-suspension.

The MS was changed to include these suggestions

13394 line 5. Unclear, re-write this sentence.

Sentence has been reworded to:

“Blain et al., (2007) and Chever et al.,(2009) demonstrated that dFe fertilisation from the plateau increased primary production in the area.”

13395 line 11. I am not familiar with this methodology but would not expect that you could combust nylon and polyester. Is this correct as written?

No it is not correct, this was a typographical error which has been changed to show that only the QMA filters were combusted.

The methods section has been changed as follows:

“The ISPs were fitted with 142 mm quartz micro fibre (QMA) (Sartorius) filters with 53 µm Petex pre-filters and 350 µm polyester supports. QMA filters were pre-combusted to remove particulate organic carbon and then acid-washed with Seastar Baseline™ HCl and rinsed with copious amounts of ultra-pure water according to the methods outlined in the GEOTRACES sample handling protocols handbook (Cutter et al., 2010). The pre-filters and supports were carefully acid washed and rinsed with copious amounts of ultra-pure water before use.”

13399 line 5. Fig. 2 seems to show that the southern waters are colder but less salty. Check this.

While it is true that there is some localised salinity variability in Figure 2, particularly near the Le Claire rise, the overall surface salinity north of the polar front is illustrated in blue (~33.7) and south of the polar front is green (33.9). In a small area downstream of the Le Claire rise this trend seems to be reversed, however this could be either bad data or inter-annual variability in the position of the polar front.

line 25. Write ‘contain recycled Fe’. Delete a form of.

Done

13400 line 7. Clarify that these are molar ratios here and in the Tables.

Thankyou for noticing this. All ratios are molar ratios except for the Kerguelen Archipelago Basalts listed in Table 2 from the Doucet et al 2005 reference. We have updated this table with the molar ratios of Kerguelen Island basalts from Gautier et al 1990 and also included the upper continental crust ratios of Wedepohl 1995. On reviewing the reference used as an end-member for Kerguelen Island Basalts we decided that the work of Gautier et al 1990 was more appropriate as the work of Doucet et al 2005 focuses on a less common subset of Kerguelen island high MgO basalts and Picrites.

13401 lines 8-14. Start with R2 and move these lines to the end of the paragraph – a more logical order to fit the following discussion.

Done, text changed as follows:

“The reference station (R-2) has a bottom depth of 2528 m and is characterised by low surface Chl a concentrations (Lasbleiz et al., 2014) and nutrient concentrations characteristic of HNLC waters (Blain et al., 2014). Station F-L is approximately 313 km northeast of Kerguelen Island with a bottom depth of 2690 m and represents the northern PF. Station F-L is downstream of Kerguelen Island, with the PF delivering waters that originated near station R-2. In this case, the waters crossing Station F-L have interacted with both the plateau and shallow coastal waters of Kerguelen Island. In contrast, station A3 is located over the Kerguelen Plateau and has a bottom depth of 527 m, making it the shallowest station sampled for trace metal analysis of suspended particles and one of the most likely to be influenced by resuspension of shelf sediments (Fig. 1). The proximity of the station to Heard and Kerguelen Island (roughly half way between the two) means that fluvial and glacial runoff may also drive fertilisation at this site. However, the hydrography of the area dictates that waters which previously interacted with upstream Heard Island are a more likely source to A3 than downstream Kerguelen Island (Park et al., 2008).”

13404 line 22. Briefly explain how Al was lost preferentially and why you think processes involved occurred here.

We are unclear on what is needed here as we go on to discuss this in detail in the following paragraph, citing Shigemitsu et al. (2013).

13406 line 5. The Scroth paper found that 2-3% of the total Fe (not of all the rock flour) could be leached by distilled water. This is a dFe measurement and may not all be bioavailable (see above).

We agree that clarity is needed on this point. We have changed the text to the following:

“Furthermore, it has been shown that 2 – 3 % of the Fe within glacial rock flour can be leached into the dissolved size fraction (< 0.2 µm) with ultrapure water, a large proportion of which should be bioavailable (Schroth et al., 2009).”

Line 7. Not quite correct. Write as follows- ‘: : :: : :this dFe is leached from nanoparticulate Fe (oxyhydr)oxides in glacial rock flour (Raiswell et al., 2010, Raiswell 2011)’ The 2011 reference is DSR v.58, p.1364.

Done, text changed to:

“It is thought that this dFe is leached from nanoparticulate Fe (oxyhydr)oxides in glacial rock over time (Raiswell, 2011; Raiswell et al., 2010) following an exponential decay, so it is possible that this source could be excluded from the < 0.2 µm dissolved fraction, but included in the 1-53 µm particulate fraction presented here.”

Line 20. See above. The assumption that all P is biogenic needs to be thoroughly justified or else this section should be left out. Even if you can justify this assumption the paper is starting to lose focus here and would be improved by leaving out this section.

See previous comment, we have now redrafted this section with justification and supporting correlations.

13408 line 19. Delete et al. This is the DSR 2011 reference.

Done

Section 3.9. I cannot see that you need this section and the paper would keep its focus better without this section. The relevant sentences from this section could be put elsewhere.

Agreed, we have now removed section 3.9 and figure 9 to maintain focus.

Reviewer 2:

We would like to thank the reviewer for their positive and constructive comments on this manuscript. Their time invested is greatly appreciated and certainly improved this manuscript.

Please find below point by point responses to the reviewers comments.

The authors present data on particulate Fe (pFe), Mn (pMn), Ba (pBa) and Al (pAl) in seawater, sediments and sinking particles, and then try to clarify possible transport routes of pFe in seawater around the Kerguelen Plateau. Through their careful evaluation of the data, they conclude that there are the several transport routes including sediment resuspension, glacial/fluvial inputs etc.. The paper is well written and the arguments made are well thought out. I have only a few suggestions.

I recommend publication with minor revision. The authors digested filter samples using only HNO3. On the other hand, they use HF in addition to HNO3 to decompose sediment samples. If HF is not used even in decomposition of filter samples, lithogenic fraction seems not to be completely digested. That is seemingly true for the measurements of the certified reference material, BCR-414, and the analytical precision for Al is extremely poor. When the authors aim to identify the possible transport routes of pFe in seawater, they rely on the elemental ratios of filter, sediment and sediment trap samples. Thus, I think that they should discuss the influence of the difference in digestion method between filter, sediment and sediment trap samples on their interpretation about the sources of pFe in seawater.

Yes, we agree with the reviewer that more clarity is needed with respect to the various digestion protocols used and how the protocols affect the results presented. Suspended particles and sediment trap samples were digested with HNO3 only due to the fact that QMA filters were not compatible with a full HF digestion as this increases the analytical blanks dramatically, while the sediment samples were digested with a mixture of strong acids including HF acid. This means that the recovery of lithogenic particles will be high in the sediment samples (near 100%), while only a fraction of the lithogenics will be completely digested and measured in the suspended particles and sediment trap samples. It should be noted that the recovery of elements within biogenic particles (as evidenced by analysis of the certified reference material BCR414) was close to 100%, although Al did indeed have high analytical variability in this case.

Our decision to use QMA filters was necessary to minimise “wash off” of sample from the surface of the filter during recovery of the in-situ pumps. We reasoned that the error associated with wash-off would likely be much larger than the error associated with low recoveries of lithogenic particles. Wash-off can introduce large errors when membrane filters are used due to the design of the current generation of filter heads (on both McLane and Challenger pumps used for this study) which allow seawater to become turbulent over the surface of the filter during retrieval. If a (HF-compatible) membrane filter is used, the filtered material can easily wash off the surface of the filter, in comparison a “depth filter” such as glass fibre or quartz micro fibre will significantly limit this wash-off effect because the particulate material becomes impregnated within the filter material and is not easily washed off. Of the available depth filters on the market, only quartz micro fibre filters can be cleaned sufficiently for trace metal analysis and digested with HNO3 to obtain suitable blank levels. The QMA filters were also combustible, and therefore subsamples were suitable for POC/PON elemental analysis.

We have added a short discussion on this in the methods section (section 2.4.1) to inform readers and aid interpretation:

“QMA filters were chosen as they could be acid cleaned to a trace-metal-clean level and the filter material allowed high particle loading and low wash-off upon pump retrieval. Furthermore, the filters were compatible for use with both Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and elemental (CHN) analysis due to their ability to be combusted. It should be noted that a compromise was made here by using QMA filters on the ISPs. The compromise is that HF acid cannot be used with QMA filters as it digests the filter material completely and leads to unacceptably high analytical blanks. Therefore, we used HNO_3 for the digestions of the QMAs and for consistency regarding the suspended particles, we also digested the pre-filter with the same acid. On the other hand, we used a full HF acid digestion for the underlying sediment analysis (Section 2.4.2). Therefore, recoveries of lithogenic trace elements will be close to 100% for the sediment analysis, but somewhat lower for the lithogenic suspended particles. However, a HNO_3 only digestion will recover effectively 100% of the trace elements of biogenic suspended particles (Table A1). For further information see Bowie et al., (2010)."

[Specific comments]

(1) Line 19 on page 13400: The reference of upper crustal ratio of Fe to Al is needed here.

Reference added.

(2) Lines 27-28 on page 13403, Lines 1-2 on page 13404: Which sample ratios do "the unique ratios" indicate? The ratios at station R-2? If so, I couldn't understand the part regarding "a combination of extremely high pFe and pAl supply over the Kerguelen Plateau.." because the R-2 station is located hydrographical upstream of the Kerguelen Plateau.

We agree with the reviewer that this section was not clear. We have changed the MS as follows:

"Figure 5 illustrates the full water column elemental ratios at the reference station (R-2) in comparison to the Kerguelen Plateau stations (A3-1 and A3-2) and reveals that Mn:Fe as well as Ba:Al are strikingly unique. At station R-2, below 500 m, we see Mn:Fe 2x higher than A3, Mn:Al 4.5x higher and Ba:Al ratios 10x higher than at A3, making this source signature relatively clear (Table 4). The unique ratios below 500 m at R-2, may arise from a source of dissolved or particulate Mn, uncoupled from pFe and pAl from the Leclaire Rise. Furthermore, the elemental ratios over station A3 are generally much lower due to high pFe and pAl supply over the Kerguelen Plateau that is relatively deficient in pMn such as would be found in glacial runoff that has a signature which reflects fresh weathering of basaltic rocks (Doucet et al., 2005)."

(3) Lines 15-16 on page 13405: I recommend the authors to show each metal ratio of upper crust and basalt.

Thank you, we have now included the elemental ratios of upper continental crust as well as the ratio of Kerguelen basalts in table 2. We have also combined tables 2, 3 and 4 into one table which simplifies the layout and makes it easier to compare values.

(4) Lines 23-25 on page 13406: Do the authors measure particulate phosphorus of their samples for the calculation written here?

Yes, particulate phosphorus was measured together with a suite of other elements on the ICPMS.

We have modified the text in the methods section (2.4.1) as follows:

"Samples were analyzed by Sector Field ICP-MS (Finnigan Element II, Thermo Scientific) (Cullen and Sherrell, 1999; Townsend, 2000). A full suite of trace elements was measured including Fe, Al, Mn, Ba, and P."

(5) Lines 19-21 on page 13407: How can the author calculate the fraction of authigenic sediment within each sample by the calculation method written here? I think that the amounts of Mn and Al of sediments added to suspended particles are mixed with other components Mn and Al, which seems not to allow the authors to use the method.

If sediments were a major source of trace metals to the overlying waters we would expect to see similar elemental ratios when comparing the sediments to suspended particles. Likewise if weathering of basaltic or crustal material was a major source. To address the reviewers concerns, we have rewritten this section in a simplified and more qualitative sense using Figure 6 to highlight the sources to each region as follows:

"Alternatively, the relative importance of sedimentary input at each of the stations can be gauged by observing the pMn:pAl molar ratio within suspended particles and comparing these to known molar ratios of pMn:pAl within Kerguelen Island basalts, A3 authigenic sediments and R-2 authigenic sediments (Fig. 6). At station A3 we see that almost all the suspended particles lie within the ratio of plateau sediments and Kerguelen Island basalts with the remaining suspended particles associated with the development of a bloom in surface waters at A3-2, which is also where we see an increase in biogenic Fe. Mid-depth suspended particles at E4-W (red dots) also lie between Kerguelen Island basalts and plateau sediments, indicating a similar source to station A3. The reference station exhibits highly modified pMn:pAl molar ratios within the suspended particles and its underlying sediment. This modification is most likely due to biogenic incorporation of bioessential elements such as Mn into particles. The remaining stations are intermediate between A-3 and R-2."

(6) Lines 14-18 on page 13410: Before this part, the authors state that pAl is stripped out preferentially with settling lithogenics (Lines 16-17 on page 13408), but here that kind of thing is not referred to. Why?

We agree that this is also a possibility that cannot be excluded, although the surface freshening that corresponds to the surface enrichment suggests that a glacial/fluvial source may well be driving this enrichment. We have modified the text accordingly:

"The observation of pFe enrichment in surface waters of the recirculation structure without proportional concentrations of pAl may be due to biological uptake and conversion from a bioavailable pool into the biogenic particulate pool. Settling of refractory lithogenics that are high in Al may also partially explain the observation. Alternatively or in combination, a high pFe, low pAl source such as nanoparticulate Fe characteristic of glacial/fluvial runoff (Hawkings et al., 2014; Raiswell et al., 2008a, 2006a) on Kerguelen Island could explain this observation. Indeed, temperature and salinity profiles within the recirculation structure reveal fresher and warmer water within the upper 110 m than either R-2 or A3 stations suggesting that glacial/fluvial runoff from Kerguelen Island may well be delivering this high pFe, low pAl surface enrichment."

Marked-up version of MS:

Sourcing the iron in the naturally-fertilised bloom around the Kerguelen Plateau: particulate trace metal dynamics

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Abstract

The KEOPS2 project aims to elucidate the role of natural Fe fertilisation on biogeochemical cycles and ecosystem functioning, including quantifying the sources and processes by which iron is delivered in the vicinity of the Kerguelen Archipelago, Southern Ocean. The KEOPS2 process study used an upstream HNLC, deep water (2500 m), reference station to compare with a shallow (500 m), strongly fertilised plateau station and continued the observations to a downstream, bathymetrically trapped recirculation of the Polar Front where eddies commonly form and persist for hundreds of kilometres into the Southern Ocean. Over the Kerguelen Plateau, mean particulate (1-53 µm) Fe and Al concentrations (pFe = 13.4nM, pAl = 25.2 nM) were more than 20-fold higher than at an offshore (lower-productivity) reference station (pFe = 0.53 nM, pAl = 0.83 nM). In comparison, over the plateau dissolved Fe levels were only elevated by a factor of ~2. Over the Kerguelen Plateau, ratios of pMn/pAl and pFe/pAl resemble basalt, likely originating from glacial/fluvial inputs into shallow coastal waters. In downstream, offshore deep-waters, higher pFe/pAl, and pMn/pAl ratios were observed, suggesting loss of lithogenic material accompanied by retention of pFe and pMn. Biological uptake of dissolved Fe and Mn and conversion into the biogenic particulate fraction or

aggregation of particulate metals onto bioaggregates also increased these ratios further in surface waters as the bloom developed within the recirculation structure. While resuspension of shelf sediments is likely to be one of the important mechanisms of Fe fertilisation over the plateau, fluvial and glacial sources appear to be important to areas downstream of the island. Vertical profiles within an offshore recirculation feature associated with the Polar Front show pFe and pMn levels that were 6-fold and 3.5-fold lower respectively than over the plateau in surface waters, though still 3.6-fold and 1.7-fold higher respectively than the reference station. Within the recirculation feature, strong depletions of pFe and pMn were observed in the remnant winter water (temperature-minimum) layer near 175 m, with higher values above and below this depth. The correspondence between the pFe minima and the winter water temperature minima implies a seasonal cycle is involved in the supply of pFe into the fertilized region. This observed association is indicative of reduced supply in winter, which is counterintuitive if sediment resuspension and entrainment within the mixed layer is the primary fertilising mechanism to the downstream recirculation structure. Therefore, we hypothesise that lateral transport of pFe from shallow coastal waters is strong in spring, associated with snow melt and increased runoff due to rainfall, drawdown through summer and reduced supply in winter when snowfall and freezing conditions predominate in the Kerguelen region.

~~1 Introduction~~

~~Small scale fertilisation experiments have now clearly established that Southern Ocean primary production is limited by the availability of the micronutrient iron (Fe) (Boyd et al., 2007; de Baar, 2005). This limitation on the biological pump means that the Southern Ocean does not realise its full potential in transferring atmospheric CO_2 into the ocean interior; a result illustrated in sedimentary records over geological timescales and supported by modelling studies (Bopp et al., 2003; Martin, 1990; Watson et al., 2000). Less well understood is the overall system response to the addition of Fe as efficiency estimates (defined here as the amount of carbon exported relative to Fe added above baseline conditions) can vary by an order of magnitude (Blain et al., 2007; Pollard et al., 2009; Savoye et al., 2008). Both the original and subsequent KEOPS missions aimed to resolve not only the efficiency estimate, but also the response of the ecosystem and the overall effect on biogeochemical cycles due to natural Fe fertilisation in the vicinity of the Kerguelen plateau. The KEOPS natural fertilisation experiment is complementary to artificial Fe enrichment~~

~~experiments due to the fact that its scale is much larger and timeframe longer than what is currently feasible in artificial fertilisation experiments. Furthermore, due to the sustained release of Fe into the fertilised region, as opposed to a sudden pulse artificial experiment, the technical challenges of monitoring carbon export are reduced. Furthermore, there is growing evidence that sustained Fe fertilisation favours large, highly silicified, slow growing diatoms that are efficient at exporting carbon into the ocean interior (Quéguiner, 2013). When the results of process studies such as KEOPS are extrapolated over the whole Southern Ocean, a small change in the efficiency estimate could result in different conclusions as to the efficacy, for instance, of artificial Fe fertilisation as a means of mitigating rising atmospheric concentrations of anthropogenic~~ ~~CO_2.~~

~~Dissolved Fe (< 0.2 µm) is traditionally identified as the size fraction that is available for biological uptake (de Baar and de Jong, 2001), and as such, the larger particulate fraction (> 0.2 µm) is often less studied. However, the particulate fraction can yield important information for several reasons; firstly the dissolved fraction is constantly in a state of change with uptake, particle scavenging and remineralisation occurring simultaneously and at varying rates depending on many factors including complexation with organic ligands (Johnson et al., 1997) and the biological community present (Sunda, 2001). Thus, interpretation of dFe data is difficult without a rarely-obtained perspective on the time varying aspects of the dFe distribution. Secondly, as a fraction of the total Fe, the major sources of Fe into fertilised regions (e.g. continental bed rock weathering, resuspension of authigenic sediments, atmospheric and extra-terrestrial dust) are small particles (> 0.2 µm), with the concentration being more stable over weeks to months, due to its abundance and relatively slow biological uptake. The particulate fraction is primarily lost from surface waters through sinking, either directly or via adhesion to bioaggregates (Frew et al., 2006). However, there is a constant transfer of dissolved Fe to particulate Fe, either via biological uptake or precipitation and, particulate Fe to dissolved Fe, via dissolution and biologically mediated processes (Moffett, 2001). Thus, the particulate fraction that is small enough to avoid sinking out of the water column rapidly (0.2 - 5 µm) can be considered as a significant source of dissolved Fe, with the rate of supply into surrounding waters dependent on the dissolution and leaching rate. Furthermore, there is growing evidence that particles in this size fraction are readily produced by mechanical erosion of bedrock due to glacial processes at high latitudes and that this large~~

~~source may be partially bioavailable (Hawkings et al., 2014; Poulton and Raiswell, 2005; Raiswell et al., 2008a, 2008c, 2006a).~~

~~The first KEOPS process study was conducted in 2005 and specifically focused on processes affecting the demise of the Spring bloom over the Kerguelen Plateau (Blain et al., 2007). The findings included determining Fe principally activated increased primary production in the area (Blain et al., 2007; Chever et al., 2009). From the data gathered it was proposed that resuspension of plateau-derived sediments and entrainment into the mixed layer during increased wind mixing that deepened the mixed layer, was the primary source of particulate and subsequently, dissolved Fe to the downstream blooms. Resolution of the Fe budget (accounting for all sources and sinks of Fe in the system), from observations made during the first mission, found that the vertical supply of dissolved Fe was not sufficient to supply phytoplankton demand. Blain et al, (2007) closed the KEOPS Fe budget by assuming that dissolution of a small fraction of the unconstrained particulate Fe pool must occur. The KEOPS2 mission aimed to improve on the successes of the first process study by accounting for the missing Fe in the budget, namely particulate Fe (pFe). Thus, we aim to test the KEOPS1 hypothesis that unconstrained particulate Fe is the missing Fe of the KEOPS Fe budget by documenting the particulate metal enrichment around the Kerguelen plateau. Our goal is to determine the sources of Fe enrichment within areas of interest (i.e. reference, plateau and the recirculation structure, see Fig. 1). Together with trace metal analysis of suspended particles, underlying sediment and settling particulate material will be analysed to elucidate the source to sink progression of Fe pools. Following on from this work, and together with dissolved Fe measurements (Quéroué et al., this issue), a focused Fe budget will be constructed (Bowie et al., this issue).~~

1 Introduction

Small scale fertilisation experiments have now clearly established that Southern Ocean primary production is limited by the availability of the micronutrient iron (Fe) (Boyd et al., 2007; de Baar, 2005). This limitation on the biological pump means that the Southern Ocean does not realise its full potential in transferring atmospheric CO_2 into the ocean interior; a result illustrated in Antarctic continental ice records over geological timescales and supported by modelling studies (Barnola et al., 1987; Bopp et al., 2003; Martin, 1990; Watson et al., 2000). Less well understood is the overall system response to the addition of Fe as efficiency estimates (defined here as the amount of carbon exported relative to Fe added above baseline conditions) can vary by an order of magnitude (Blain et al., 2007; Pollard et al., 2009; Savoye et al., 2008). Both the original and subsequent KEOPS missions aimed to resolve not only the efficiency estimate, but also the response of the ecosystem and the overall effect on biogeochemical cycles due to natural Fe fertilisation in the vicinity of the Kerguelen plateau. The KEOPS natural fertilisation experiment is complementary to artificial Fe enrichment experiments due to the fact that its scale is much larger and timeframe longer than what is currently feasible in artificial fertilisation experiments. Furthermore, due to the sustained release of Fe into the fertilised region, as opposed to a sudden pulse artificial experiment, the technical challenges of monitoring carbon export are reduced. Furthermore, there is growing evidence that sustained Fe fertilisation favours large, highly silicified, slow growing diatoms that are efficient at exporting carbon into the ocean interior (Quéguiner, 2013). When the results of process studies such as KEOPS are extrapolated over the whole Southern Ocean, a small change in the efficiency estimate could result in different conclusions as to the efficacy, for instance, of artificial Fe fertilisation as a means of mitigating rising atmospheric concentrations of anthropogenic CO_2.

Dissolved Fe (dFe < 0.2 µm) includes colloidal and nanoparticulate Fe, which may only be partially bioavailable, as well as soluble Fe (sFe < 0.02 µm) which is highly bioavailable (de Baar and de Jong, 2001). As a result, the larger particulate fraction (> 0.2 µm) is often less studied due to the perception that it has low bioavailability. However, the particulate fraction can yield important information for several reasons; firstly the dissolved fraction is constantly in a state of change with uptake, particle scavenging and remineralisation occurring simultaneously and at varying rates depending on many factors including complexation with organic ligands (Johnson et al., 1997) and the biological community present (Sunda, 2001). Thus, interpretation of dFe data is difficult without a rarely-obtained perspective on the time varying aspects of the dFe distribution. Secondly, as a fraction of the total Fe, the major sources of Fe into fertilised regions (e.g. weathering products delivered by fluvial and glacial processes, resuspension of sediments and porewaters, atmospheric and extra-terrestrial dust) are small particles (> 0.2 µm), with the concentration being more stable over weeks to months, due to its abundance and relatively slow biological uptake. The particulate fraction is primarily lost from surface waters through sinking, either directly or via adhesion to bioaggregates (Frew et al., 2006). However, there is a constant transfer of dissolved Fe to particulate Fe, either via biological uptake or precipitation and, particulate Fe to dissolved Fe, via dissolution and biologically mediated processes (Moffett, 2001). Thus, the particulate fraction that is small enough to avoid sinking out of the water column rapidly (0.2 - 5 µm) can be considered as a significant source of dissolved Fe, with the rate of supply into surrounding waters dependent on the dissolution and leaching rate. Furthermore, there is growing evidence that particles in this size fraction are readily produced by mechanical erosion of bedrock due to glacial processes at high latitudes and that this large source may be partially bioavailable (Hawkings et al., 2014; Poulton and Raiswell, 2005; Raiswell et al., 2008a, 2008c, 2006a).

The first KEOPS process study was conducted in 2005 and specifically focused on processes affecting the demise of the Spring bloom over the Kerguelen Plateau (Blain et al., 2007). Blain et al., (2007) and Chever et al.,(2009) demonstrated that dFe fertilisation from the plateau increased primary production in the area. From the data gathered it was proposed that resuspension of plateau-derived sediments and entrainment into the mixed layer during increased wind mixing that deepened the mixed layer, was the primary source of particulate and subsequently, dissolved Fe to the downstream blooms. Resolution of the Fe budget (accounting for all sources and sinks of Fe in the system), from observations made during the first mission, found that the vertical supply of dissolved Fe was not sufficient to supply phytoplankton demand. Blain et al, (2007) closed the KEOPS Fe budget by assuming that dissolution of a small fraction of the unconstrained particulate Fe pool must occur. The KEOPS2 mission aimed to improve on the successes of the first process study by accounting for the missing Fe in the budget, namely particulate Fe (pFe). Thus, we aim to test the KEOPS1 hypothesis that unconstrained particulate Fe is the missing Fe of the KEOPS Fe budget by documenting the particulate metal enrichment around the Kerguelen plateau. Our goal is to determine the sources of Fe enrichment within areas of interest (i.e. reference, plateau and the recirculation structure, see Fig. 1). Trace metal analysis of suspended particles, underlying sediment and settling particulate material will elucidate the source to sink progression of the particulate Fe pool. Following on from this work, and together with dissolved Fe measurements (Quéroué et al., 2014), a focused Fe budget will be constructed (Bowie et al., 2014).

2 Methods

2.1 In situ pumps (ISP)

All sample handling, processing and preparation was performed in accordance with general GEOTRACES protocols (http://www.geotraces.org/) and specific methodologies outlined in Bowie et al. ~~(2010)~~(2010). Briefly, suspended particles were collected using up to 11 *in situ* pumps (ISPs) (McLane WTS and Challenger) suspended simultaneously at varying depths throughout the water column. Depths were chosen after viewing conductivity, temperature and depth (CTD) data to sample within oceanographic features of interest as well as obtaining a representative full water column profile. The ISPs were fitted with~~,~~ 142 mm quartz micro fibre (QMA) (Sartorius) filters with 53 µm ~~nylon~~Petex pre-filters and 350 µm polyester supports~~ (all~~. QMA filters~~ and supports~~ were pre-combusted to remove particulate organic carbon and then acid-washed with Seastar Baseline™ HCl and rinsed with copious amounts of ultra-pure water~~). Both the nylon prefilter~~ according to the methods outlined in the GEOTRACES sample handling protocols handbook (Cutter et al., 2010). The pre-filters and supports were carefully acid washed and rinsed with copious amounts of ultra-pure water before use. Both the Petex pre-filter and QMA filter were analysed for every pump giving two size fractions at each sampling location. Therefore, all particles greater than 53 µm were collected on the ~~prefilter~~pre-filter and all particles within the 1 – 53 µm size range were collected on the underlying QMA filter. Lithogenics sourced from bedrock or sediments in the larger size range (>53 µm) would have a high sinking velocity (> 500 m day^{-1}) according to Stokes law and as such would be expected to make up a relatively small fraction of the total particles in this size range. In comparison, the 1-53 µm size class can potentially capture both small biogenic and lithogenic particles. This is due to the prediction that small lithogenic particles (1 – 5 µm) have significantly slower sinking rates (0.1 – 10 m day^{-1}) than large lithogenic particles according to Stokes law.

The ISPs were programmed to pump for up to four hours, allowing up to 2000 L of seawater to be filtered. After retrieval, the filters were bagged and processed within an ISO class 5, containerised clean room. Replicate 14 mm punches were taken using an acid-washed polycarbonate punch and stored frozen at -18 °C until analysis at the home laboratory. The 14 mm punches were then used for particulate metal analysis, particulate organic carbon and particulate organic nitrogen analysis.

2.2 Sediment traps (Technicap PPS3~~/3~~)

For a full description of the sediment trap data during KEOPS2 see Laurenceau et al. ~~(this issue) and Bowie et al.~~(2014) and Bowie et al. ~~(this issue).~~(2014). Two Technicap PPS3 free-floating sediment traps were deployed below the mixed layer at a depth of 200 m. The two sediment traps were deployed twice, giving a total of 4 deployments. The traps were prepared with acid-cleaned sampling cups containing low-trace-metal brine solution (salinity ~ 60). The trap was programmed to sample for 1.5 to 5.5 days, whilst the 12 individual sampling containers were open for an equal portion of the total deployment. Upon retrieval, the sampling containers were removed from the carousel, sealed and processed within an ISO class 5, containerised clean room. The samples were filtered onto acid-washed, 2 µm polycarbonate membrane ~~filter~~filters via a 350 µm~~ nylon~~ pre-filter using a Sartorius™ PTFE filtration unit. The 350 µm pre-filter was selected to exclude large copepods and other large plankton that would lead to unrealistic sample variability.

2.3 Sediment coring

An Oktopus Multicorer (www.oktopus-mari-tech.de) was used to collect 8 replicate, 610 x 95 mm sediment cores, simultaneously within a 1 m^2 area at each station. The uppermost 5mm of surface sediment was subsampled according to Armand et al. (2008) representing an approximate sedimentation period of < 1000 years.

Field Code Changed

~~2.4 Analysis~~

~~2.4.1 ISP filters for particulate metals~~

~~All digestions and evaporations were carried out within a digestion hood (SCP Science), where air was HEPA filtered during intake and subsequently extracted through a fume hood. Filter blanks and sample filters were digested in 15 mL acid cleaned, Teflon perfluoroalkoxy (PFA) screw cap vials (Savillex™) using ultra-pure nitric acid (1 mL 16 M HNO_3) (Seastar Baseline™) heated to 120 °C for 12 hours on a Teflon coated hotplate (SCP Science~~

~~DigiPREP™), following the method outlined in Bowie et al. (2010). Blanks containing only HNO_3 were also analysed to determine the contribution of the digestion acid without filter material. No hydrofluoric acid (HF) was used during the digestion as it was incompatible with the QMA filters used by the ISPs. QMA filters were chosen as they could be acid cleaned to a trace-metal-clean level and the filter material allowed high particle loading and low wash-off upon collection. Furthermore, the filters were compatible for use with both Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and elemental (CHN) analysis. The digest solution was diluted with 10 mL of ultra-high purity water and spiked with 10 ppb indium as an internal standard. Samples were analyzed by Sector Field ICP-MS (Finnigan Element II, Thermo Scientific) (Cullen and Sherrell, 1999; Townsend, 2000). The data were quality controlled by comparison with a certified reference material with a similar composition to the material collected (BCR-414 trace metals in phytoplankton, European Commission).~~

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The digest solution was diluted with 10 mL of ultra-high purity water and spiked with 10 ppb indium as an internal standard. Samples were analysed by Sector Field ICP-MS (Finnigan Element II, Thermo Scientific) (Cullen and Sherrell, 1999; Townsend, 2000). A full suite of trace elements was measured including Fe, Al, Mn, Ba, and P. The data were quality controlled by comparison with a certified reference material with a similar composition to the material collected (BCR-414 trace metals in phytoplankton, European Commission) (Table A1).

Quartz micro-fibre (QMA) filters were chosen as they could be acid cleaned to a trace-metal-clean level and the filter material allowed high particle loading and low wash-off upon pump retrieval. Furthermore, the filters were compatible for use with both Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and elemental (CHN) analysis due to their ability to be combusted. It should be noted that a compromise was made here by using QMA filters on the ISPs. The compromise is that HF acid cannot be used with QMA filters as it digests the filter material completely and leads to unacceptably high analytical blanks. Therefore, we used HNO_3 for the digestions of the QMAs and for consistency regarding the suspended particles we also digested the pre-filter with the same acid. On the other hand, we used a full HF acid digestion for the underlying sediment analysis (Section 2.4.2). Therefore, recoveries of lithogenic trace elements will be close to 100% for the sediment analysis, but somewhat lower for the lithogenic suspended particles. However, a HNO_3 only digestion will recover effectively 100% of the trace elements of biogenic suspended particles (Table A1). For further information see Bowie et al., (2010).

2.4.2 Sediment analysis for particulate metals

Digestions and analysis were performed as per the ISP filters except that HF acid was used to digest these highly refractory samples. The HNO_3 digest used for the ISP filters is relatively weak but digests the biogenic fraction completely as evidenced by the excellent recoveries on the BCR414 certified reference material (trace metals in phytoplankton) (Table A1) but has limited recoveries of the lithogenic fraction as evidenced by the low recoveries of pAl and pTi in MESS-3 and PACS-2 sediment certified reference material ~~(Bowie et al., 2010)~~(Bowie et al., 2010).

During the HF digest, a mixture of strong acids (250 µL HNO_3, 250 µL HF and 500 µL HCl) were used as per Bowie et al. ~~(2010).~~(2010). After 12 hours at 95° C the digest PFA vials were uncapped and evaporated to dryness under HEPA filtered air at 60° C for 4 hours. The digest was then resuspended in 10% HNO_3 with 10 ppb indium added as internal standard. A 100x dilution factor (v:v) was considered sufficient to place the ~20 mg sediment samples within the calibration range of the SF-ICP-MS.

2.4.3 Particulate organic carbon (POC) and nitrogen (PN)

All glassware in contact with POC samples was pre-combusted prior to field work (450 °C for 12 h). Total nitrogen, carbon and hydrogen were determined at the Central Science Laboratory, University of Tasmania, using a Thermo Finnigan EA 1112 Series Flash Elemental Analyzer (estimated precision ~1%).

3 Results and Discussion

3.1 *Station-types*

The sampling locations of KEOPS2 (Fig. 1) were designed to capture the key regime types of the Kerguelen Archipelago ~~(Blain et al., submitted) ~~including the high nutrient, low chlorophyll (HNLC) reference waters (station R-2), the high-trace-metal plateau waters (station A3), the northern Polar Front (station F-L) and a quasi-stationary, bathymetrically trapped recirculation structure (E-1, E-3 and E-5) to the east of Kerguelen Island (Table 1). Stations E-1, E-3 and E-5 can be thought of as a pseudo-Lagrangian time series. In addition, two stations were sampled at the eastern and western extremes of the recirculation structure (E-4W and E-4E) which proved to contrast in absolute concentrations as well as elemental ratios of particulate trace metals.

3.2 Surface water flow around the Kerguelen Plateau

During KEOPS1, van Beek et al. ~~(2008)~~(2008), Zhang et al. ~~(2008) and Chever et al.~~(2008) and Chever et al. ~~(2009)~~(2009) revealed that the water column southeast of Kerguelen Island was modified by passing over the Heard Island Plateau. Park et al. ~~(2008)~~(2008) demonstrated that the interaction of the water masses over the Kerguelen Plateau could be divided into the southern and northern water masses separated by the Polar Front (PF) (Fig. 1). The southern water mass has source waters being derived from the Antarctic surface waters (AASW), southwest of Kerguelen which is bound to the north by the shallow bathymetry of the Leclaire Rise. These surface waters are generally colder and saltier than to the north (Fig. 2). The AASW also flows around Heard Island and a weaker surface current flows northwest over the Kerguelen Plateau towards the north east of Kerguelen Island where it is bound to the north by the PF. This cold surface current can be seen during winter in Figure 2. The northern water mass has a source of easterly flowing Sub Antarctic Surface

Waters (SASW). The portion of the SASW that interacts with Kerguelen Island is termed Kerguelen Island source waters and is bound to the south by the PF (Fig. 2). A broad and poorly defined mixing zone to the east of Kerguelen Island has been identified at the junction of these southern and northern water masses. As a result of the mixing, eddies commonly form in this region. Also within this mixing zone, surface filaments, identified by elevated Chlorophyll *a*, can be seen in SeaWiFS images diverging from the PF and entering the eastern boundary of the recirculation structure (see supplementary material in Trull et al., ~~(this issue)).~~(2014)).

The Kerguelen Archipelago is isolated, being a relatively small and localised source of Fe fertilisation surrounded by the large and deep, HNLC, low Fe, Southern Ocean. Therefore, when identifying an Fe source to the region, our focus is on the plateau and the two islands, Kerguelen and Heard. Over geological timescales, all pFe distributed throughout the water column within this region must be derived from all forms of weathering of bed rock including, fluvial and glacial outflow as well as dust from the islands, hydrothermal and extra-terrestrial input. Over shorter time frames, shelf sediments in the region ~~are a form of~~contain recycled Fe as the vast majority of these sediments are a combination of siliceous ooze ~~(Armand et al., 2008)~~(Armand et al., 2008) and glacio-marine sediments; the exported product of the highly productive overlying waters together with some lithogenics (sourced from bed-rock) that were unutilised or non-bioavailable and fast-sinking. Therefore, understanding the pathways of supply of this new Fe is important to understanding the processes controlling the long term productivity and therefore, carbon sequestration, in the area.

3.3 Underlying sediment analysis

Analysis of sediments sourced from cores taken at each station revealed a distinctly different sediment signature at station R-2 compared with any other station (Table 2). The reference station signature was approximately six times enriched in Mn relative to Al (Mn:Al 0.063) in comparison to the plateau station (A3) (Mn:Al 0.011). The Mn:Al sedimentary signature at A3 was almost identical to authigenic sediments previously reported from the Amundsen Sea ~~(Angino, 1966).~~(Angino, 1966). We consider the enriched Mn at R-2 could be due to either MnO_2 enrichment in the surface sediments during redox cycling of early diagenesis ~~(Planquette et al., 2013)~~(Planquette et al., 2013), or supplied via a Mn enriched source such as hydrothermal venting near the Leclaire Rise. The extremely low carbon content of the sediment at station R-2, as evidenced by its near white colour, low diatom content (L. Armand, pers. obs.) and low carbon export flux (Laurenceau et al., ~~this issue~~2014; Planchon et al., ~~this issue~~2014), suggests that MnO_2 enrichment in the surface sediments during redox cycling is more likely at R-2.

Field Code Changed

The authigenic sediment ratio of Fe:Al was also lower at station R-2 (Fe:Al = 0.73) in comparison to any other station (Fe:Al range 0.81 – 1.1). However, all of our observed pFe:pAl ~~ratios were higher than upper crustal ratios (Fe:Al 0.2)~~molar ratios were higher than upper crustal molar ratios (Fe:Al 0.19) (Wedepohl, 1995) or Amundsen Sea surface sediments (Fe:Al 0.26) ~~(Angino, 1966).~~(Angino, 1966). Interestingly, our observed pFe:pAl sedimentary ratios were similar to the ratio found in phytoplankton such as the BCR-414 certified reference material (freshwater phytoplankton) (Fe:Al = 1.01) used in this study (Table A1). Furthermore, the pFe:pAl ratio of sinking particles captured by the free floating PPS3 sediment traps (marine snow) had similar ratios of pFe:pAl of 1.02, 1.05, 0.91 and 0.70 for stations E-1, E-3, E-5 and A3-2, respectively (Table ~~3~~2). These observations highlight the major contribution of sinking biogenic material to the authigenic sediments in the area around the Kerguelen Plateau which was in contrast to the signature at station R-2 due to its low productivity. The pFe in the sediments at all stations and primarily at station R-2 (as a fraction of its total weight) were similar to Weddell Sea surface sediments ~~(Angino and Andrews, 1968) which ranged from 0.9 – 3.2%.~~(Angino and Andrews, 1968) which ranged from 0.9 – 3.2%. In comparison, station R-2 has a mean value of 0.1 % Fe while station E-3, A3, F-L and E-4W had mean values of 0.3, 0.8, 1.5 and 2.5% respectively. The low fraction of Fe within the authigenic sediment at R-2 indicates limited pFe supply at this station in comparison to either the Weddell Sea or the Kerguelen Plateau presented here.

3.4 Plateau, reference and polar front stations

~~Station A3, located over the Kerguelen Plateau,~~The~~ has a bottom depth of 527 m, making it the shallowest station sampled for trace metal analysis of suspended particles and one of the most likely to be influenced by resuspension of shelf sediments (Fig. 1). The proximity of the station to Heard and Kerguelen Island (roughly half way between the two) means that fluvial and glacial runoff may also drive fertilisation at this site. However, the hydrography of the area dictates that Heard Island is upstream of A3 and Kerguelen Island is downstream (Zhou et al., 2014). In contrast, the~~ reference station (R-2) has a bottom depth of 2528 m and is characterised by low surface Chl *a* concentrations ~~(Lasbleiz et al., 2014)~~(Lasbleiz et al., 2014) and nutrient concentrations characteristic of HNLC waters ~~(Blain et al., 2014)~~(Blain et al., 2014). Station F-L is approximately 313 km northeast of Kerguelen Island with a bottom depth of 2690 m and represents the northern PF. Station F-L is downstream of Kerguelen Island, with the PF delivering waters that originated near station R-2. In this case, the waters crossing Station F-L have interacted with both the plateau and shallow coastal waters of Kerguelen Island. In contrast, station A3 is located over the Kerguelen Plateau and has a bottom depth of 527 m, making it the shallowest station sampled for trace metal analysis of suspended particles and one of the most likely to be influenced by resuspension of shelf sediments (Fig. 1). The proximity of the station to Heard and Kerguelen Island (roughly half way between the two) means that fluvial and glacial runoff may also drive fertilisation at this site. However, the hydrography of the area dictates that waters which previously interacted with upstream Heard Island are a more likely source to A3 than downstream Kerguelen Island (Park et al., 2008).

The pFe, pAl and pMn concentrations at the reference station (R-2) only increase slightly towards the sea floor; however, enrichment in pFe, pAl and primarily pMn is evident at 500 m likely due to proximity to the Leclaire Rise (Fig. 3) (discussed in detail below). The northern PF station (F-L) exhibits moderate concentrations of pFe, pAl and pMn throughout the water column, somewhat higher than the reference station, and much higher concentrations are observed in close proximity to the sea floor. It should be noted that the deepest sample at R-2 was 148 m above the seafloor, while at F-L it was only 90 m above the sea floor and this could well explain the observed difference, given the strong decrease of nepheloid layers away from the seabed ~~(Blain et al., 2007; Jouandet et al., 2014)~~(Blain et al., 2007; Jouandet et al., 2014).

Profiles of pFe and pAl in the 1 - 53 um size range from station R-2, A3 and F-L are shown in Figure 3. The plateau station (A3) was sampled twice during the study (A3-1 and A3-2), separated by 20 days. Surface chlorophyll images revealed that between visits to the site, a large bloom developed in the vicinity and extended over the site, and was beginning to fade again by the time of the second sampling ~~(Trull et al., this issue).~~(Trull et al., 2014). Thus, station A3-1 can be thought of as pre-bloom and A3-2 as post-bloom conditions. Particulate Fe, Al and Mn generally increased towards the sea floor at station A3, with the exception of a slight enrichment below the mixed layer during the second visit (A3-2) to the station in the > 53 μm size fraction (Fig. 4). To investigate the progression of pFe through time, we integrated the pFe throughout the full water column, and observed a decrease in the pFe stock from 9.1 to 4.5 mmol m^{-2} between the first and second visit to station A3. This translates to a 51% reduction in pFe for all size classes combined (i.e. >1 µm). However, if we look closer at the pFe distribution only within the surface mixed layer (165 m) between A3-1 and A3-2, we observe a loss of 70% of the integrated total pFe (>1um) (Fig. 4). Concurrently, using an Underwater Vision Profiler to track particle size distribution, Jouandet et al., ~~(2014)~~(2014) noted a 4 fold increase in particle numerical abundance through the full water column. Their one dimensional particle dynamic model supported the hypothesis that the increase in biogenic particles, due to blooming conditions, resulted in the rapid formation of large particles due to coagulation and subsequent vertical transport to the base of the mixed layer. This result is supported in the current data set, in that we see a large decrease in small pFe particles within the mixed layer and a moderate increase in large pFe particles at the base of the mixed layer when comparing pre (A3-1) to post (A3-2) bloom conditions (Fig. 4). Furthermore, we observed an increase in biogenic pFe within the surface mixed layer between A3-1 and A3-2 (Section 3.7).

Thus, it appears that physical aggregation within the mixed layer of the particles onto biogenic phyto-aggregates during the bloom development and export to the base of the mixed layer, combined with significantly lower concentrations above the seafloor resulted in the observed 51% reduction in pFe (>1 µm) between A3-1 and A3-2. The significantly lower concentration at 440m during the post-bloom conditions of A3-2 may be due to increased small particle scavenging resulting from sinking phyto-aggregates or alternatively, small-scale variation in the thickness of the nepheloid layer.

3.5 Elemental ratios at stations R-2, F-L and A3

As station A3 is located over the Kerguelen Plateau and also is in close proximity to fluvial and glacial runoff from Heard Island, we would expect the trace metal source signature of suspended particles to be unique here in comparison to our reference (R-2) and PF (F-L) stations. The particles over the Kerguelen Plateau were characterised by very high pFe (0.94 – 30.4 nM) and pAl (1.5 – 58.6 nM) with concentrations an order of magnitude higher than R-2 (<DL-1.35 nM Fe and <DL – 2.08 nM Al). The reference station was characterised by low surface Chl *a* concentrations characteristic of HNLC waters ~~(Lasbleiz et al., 2014)~~(Lasbleiz et al., 2014), however, it is relatively close to the Leclaire Rise; a seamount with its shallowest point 135 km west northwest of station R-2 rising up to approximately 395 m. The Leclaire

Rise extends to 70km northwest of station R-2 where it reaches a depth of approximately 550 m. It is important to recall in this context that the PF divides the northeast flowing AASW from the eastward flowing SASW to the north ~~(Park et al., 2008)~~(Park et al., 2008). Classical theory suggests that this oceanographic feature should block much of the enrichment from the Leclaire Rise to station R-2. However, enrichment was evident in the vertical profiles of pFe, pMn and pAl at station R-2 at 500 m depth (Fig. 3).

Figure 5 illustrates the full water column elemental ratios at the reference station (R-2) in comparison to the Kerguelen Plateau stations (A3-1 and A3-2) and reveals that Mn:Fe as well as Ba:Al are strikingly unique. At station R-2, below 500 m, we see Mn:Fe 2x higher than A3, Mn:Al 4.5x higher and Ba:Al ratios 10x higher than at A3, making this source signature relatively clear (Table ~~4). The unique ratios are considered a combination of extremely~~2). The unique ratios below 500 m at R-2, may arise from a source of dissolved or particulate Mn (uncoupled from pFe and pAl) from the Leclaire Rise. Furthermore, the elemental ratios over station A3 are generally much lower (Fig. 5) due to high pFe and pAl supply over the Kerguelen Plateau that is relatively deficient in pMn such as would be found in glacial runoff that has a signature which reflects fresh weathering of basaltic rocks ~~(Doucet et al., 2005). Furthermore, a source of dissolved or particulate Mn, uncoupled from pFe and pAl from the Leclaire Rise could alter the elemental ratios as observed.~~(Doucet et al., 2005). This source theory is supported by the observation of high dissolved Mn (dMn) near the Leclaire Rise ~~(Quéroué et al., this issue) and uniquely high pMn:pFe in sediments found below station R-2 (Table 2).~~(Quéroué et al., 2014) and uniquely high pMn:pFe in sediments found below station R-2 (Table 2). Surface water particulate trace metals also reveal distinct differences. The ratios of pFe:pAl, pMn:pAl and pMn:pFe all increase from the bottom of the mixed layer to the surface at stations R-2 and F-L (Fig. 5). This profile characteristic is in contrast to stations A3-1. The observed modification of the elemental ratios in the surface mixed layer at R-2 and F-L is most likely due to biological uptake of dissolved trace elements and conversion into the biogenic particulate fraction.

Particulate Al and pFe were closely coupled across all stations (Spearmans RHO R=0.91 P<0.01 n=70). However, pAl and pMn, although still strongly correlated (P=0.80 P<0.01 n=70), appeared more variable than pFe versus pAl. Figure 6 illustrates this variability in the pMn in comparison to pAl as a function of its location within the study area. The observed variability in pMn but not pFe relative to pAl highlights the uncoupling between some of the sources of pMn and pFe. Specifically, the observed variability points to a uniquely high Mn:Fe source either in the authigenic sediments of the Leclaire Rise and/or a hydrothermal source ~~(German et al., 1991)~~(German et al., 1991), or a process whereby pAl is preferentially stripped out with distance from the source. A study by Shigemitsu et al. ~~(2013)~~(2013) showed that the concentration of pAl in suspended particulate material in the Intermediate Water of the Sea of Okhotsk (western Pacific Ocean), decreased with distance from the shelf source preferentially in relation to pFe and pMn. They concluded that increasing pFe:pAl and pMn:pAl ratios occurred with distance from the source and suggested that the denser, lithogenic particles settled out preferentially, stripping out pAl. Furthermore, they found pFe~~,~~ became associated with organic matter more readily than pAl and therefore, remained suspended in the water column more readily than pAl. These processes could explain the observed modification of the elemental ratios between stations R-2, A3 and possibly F-L. The stations that were in close proximity to the shelf source such as A3-1 and A3-2 were indeed enriched in lithogenic pAl and as such pFe:pAl was relatively low (Fig. 5). In contrast, F-L was at the greatest distance from a sedimentary source and displayed the highest pFe:pAl ratio, whereas station R-2, being relatively close to the Leclaire rise, had an intermediate ratio.

3.6 What are the sources of particulate trace metals over the plateau and downstream?

The high particulate trace metal concentrations found at 440 m, at A3-1 and A3-2, near the sea floor, most likely originated from resuspension of deep (~500 m) shelf sediments. The cause of the variability between A3-1 and A3-2 at this depth remains unclear, but could reflect small scale variability in the depth of the nepheloid layer or be the result of temporal variability due to the action of tides and internal waves ~~(McCave, 1986).~~(McCave, 1986). The pMn:pAl, pMn:pFe and pBa:pAl ratios for A3-1 and A3-2 are similar from the sea floor to the approximate base of the surface mixed layer, with values higher than the mean crustal ratios ~~(Taylor and McLennan, 1985)~~(Taylor and McLennan, 1985), but lower than either basalt ~~(Doucet et al., 2005)~~(Doucet et al., 2005) or the underlying sediment ratios (Table 2). Within the surface mixed layer, A3-1 maintains similar ratios to the deep water column, while at A3-2 the ratios diverge towards the surface. The particulate trace metal signature within the mixed layer at A3-2 increases in pMn and pBa relative to pAl, which is most likely ~~results from particle scavenging and settling~~driven by biogenic conversion of ~~Al-rich, refractory~~

~~lithogenics as outlined above~~dissolved bioessential elements into biogenic particles (section 3.~~4~~7).

Glacial flour is the result of mechanical erosion of bed rock by glaciers. Typical particle sizes are within the silt size range but can overlap with clays (0.002 - 0.063 mm). Recent research suggests that Fe sourced from glacial erosion can be a major source of bioavailable Fe to the Southern Ocean ~~(Poulton and Raiswell, 2005; Raiswell et al., 2008b, 2008c, 2006b)~~(Poulton and Raiswell, 2005; Raiswell et al., 2008b, 2008c, 2006b). Assuming no mixing and a dilute suspension, Stoke's law predicts that the small grain size of glacial flour allows it to remain suspended within a 500 m water column for between 2 and 2500 days or within a 165m mixed layer for 1 to 831 days depending on particle size. Certainly, mixing within the surface mixed layer would increase this duration significantly, meaning that glacial and fluvial input from both Heard and Kerguelen Island could remain suspended in the mixed layer for long enough to travel well past any of the stations in the present study~~.~~, excluding the reference station (R-2). Furthermore, it has been shown that 2 – 3 % of the Fe within glacial rock flour ~~is directly soluble and therefore~~can be leached into the dissolved size fraction (< 0.2 µm) with ultrapure water; a large proportion of which should be bioavailable ~~(Schroth et al., 2009).~~(Schroth et al., 2009). It is thought that this ~~soluble fraction~~ dFe is leached from nanoparticulate Fe (oxyhydr)oxides in glacial rock flour over time ~~(Raiswell et al., 2010)~~(Raiswell, 2011; Raiswell et al., 2010) following an exponential decay~~ (Raiswell, 2011), so it is possible that this source could be excluded from the < 0.2 µm dissolved fraction, but included in the 1-53 µm particulate fraction presented here.~~, so it is possible that this source could be excluded from the < 0.2 µm dissolved fraction, but included in the 1-53 µm particulate fraction presented here. This is especially true of nanoparticulate Fe that is attached to the surface of larger sediment grains as has been observed previously in glacial sediments (Shaw et al., 2011). Given that the particulate fraction is generally an order of magnitude higher in concentration than the dissolved fraction, this source may well be more significant in stimulating phytoplankton blooms than previously estimated. Overall, station A3 appeared to be directly fertilised by resuspension of shelf sediments at depth, and entrainment of this pFe-rich water occurred during events that deepen the mixed layer periodically. However, lateral supply above the mixed layer of small particles from shallow coastal sources around Heard Island, including glacial melt waters, cannot be ruled out.

Field Code Changed

3.7 Biogenic and sedimentary particulate trace metals

If we assume that all particulate phosphorus (pP) is of biogenic origin, we can calculate the biogenic Fe ~~and Mn~~ fraction of the total Fe ~~and Mn~~ concentration by normalising to pP and comparing with published elemental ratios of Southern Ocean diatoms ~~(Planquette et al., 2013).~~(Planquette et al., 2013). For the calculations we used the upper limit of Fe:P (1.93 mmol mol $^{-1}$) ~~and Mn:P (0.42 mmol mol^{-1})~~ reported by Twinning et al. ~~(2004)~~(2004) for Southern Ocean diatom assemblages. Given that pP and POC are remineralised throughout the water column and are generated within the surface mixed layer, calculations of biogenic trace metals will only be valid within the surface mixed layer, as the concentration of pP and POC decreases strongly with depth. It should also be noted that Kerguelen Island basalts and upper continental crust can contribute particulate phosphorus concomitantly with pFe to the particulate pool. However the Fe:P ratio found within Kerguelen Island basalts and the continental crust is 12.8 and 25.8 (mol:mol) respectively (Gautier et al., 1990; Wedepohl, 1995). Thus, the factor of 1000 increase in pP observed within suspended particles compared to these rock sources indicates that this pP is likely produced *insitu* within the mixed layer from dissolved PO_4^- rather than supplied from rock weathering together with Fe. Furthermore, within the upper 200 m of the water column, biogenic Fe correlates significantly with both fluorescence (Spearmans RHO R = 0.518, P < 0.05, n = 30) and dissolved oxygen (Spearmans RHO R = 0.507, P < 0.05, n = 30) confirming the autotrophic composition of the particles identified as high in biogenic Fe. Figure 3 illustrates the contribution of biogenic Fe in surface waters at stations R-2, A3 and F-L. ~~The biogenic Fe and Mn (data not shown) fractions within the surface mixed layer correlate with POC (Spearmans RHO, R = 0.75 P<0.01 and R = 0.85 P<0.01, respectively).~~ Station R-2 and F-L have biogenic Fe fractions that are higher near the surface than at depth (Fig. 3). In contrast, at stations A3-1 and A3-2, biogenic Fe and Mn only make up a relatively small fraction of the total pFe throughout the water column although at station A3-2 we see a slight increase in biogenic pFe towards the surface, corresponding with the development of a bloom. Biogenic Fe at stations A3-1 and A3-2 constitutes less than 1 and 5% respectively of the total Fe. The low biogenic fraction at station A3-1 most likely results from an excess of lithogenic Fe, Al and Mn to the water column from the shelf sediments as well as fluvial/glacial runoff from nearby Islands of the Kerguelen Archipelago, which are ~~in~~ excess to demand. A similar pattern was observed during a study located in the Amundsen Sea ~~(Planquette et al., 2013)~~(Planquette et al., 2013) where the percentage of biogenic Fe ~~and Mn~~ (full water column mean) reduced with proximity to the trace metal source.

~~Alternatively, the relative importance of sedimentary input at each of the stations can be gauged by comparing the Mn:Al ratios observed throughout the water column with mean ratios of Mn:Al in crustal rocks (0.0034 mol mol^{-1}) (Taylor and McLennan, 1985) and Kerguelen Plateau (A3) authigenic sediments (0.011 mol mol^{-1}) (Table 2). If we divide our measured Kerguelen Plateau sediment ratio by the ratio observed at each site we obtain the fraction of authigenic sediment within each sample (Planquette et al., 2013). The sedimentary Mn:Al ratio is quite consistent between all sites (0.011 –~~ Alternatively, the relative importance of sedimentary input at each of the stations can be gauged by observing the pMn:pAl molar ratio within suspended particles and comparing these to known molar ratios of pMn:pAl within Kerguelen Island basalts, A3 authigenic sediments and R-2 authigenic sediments (Fig. 6). At station A3 we see that almost all the suspended particles lie within the ratio of plateau sediments and Kerguelen Island basalts with the remaining suspended particles associated with the development of a bloom in surface waters at A3-2, which is also where we see an increase in biogenic Fe. Mid-depth suspended particles at E4-W (red dots) also lie between Kerguelen Island basalts and plateau sediments, indicating a similar source to station A3. The reference station exhibits highly modified pMn:pAl molar ratios within the suspended particles and its underlying sediment. This modification is most likely due to biogenic incorporation of bioessential elements such as Mn into particles. The remaining stations are intermediate between A-3 and R-2.

~~0.016) except station R-2 (0.063) (Table 2), therefore we used the sedimentary ratio at station A3 as the source signature. Chever et al. (2009) suggested that lateral transport from the northern and southern Kerguelen Plateau is a strong source to downstream stations. The mean sedimentary contribution to the Mn inventory is >100% at station A3 (Fig. 3), implying some degree of freshly weathered (low Mn:Al) crustal or basaltic input, in combination with sedimentary resuspension. This result supports a glacial/fluvial input or other form of bed rock weathering from Heard Island in combination with sedimentary resuspension as a source to station A3. Station R-2 had the lowest recorded mean sedimentary Mn contribution of 30%. The recirculation-structure stations displayed mean sedimentary contributions from 40 -~~

~~88 %. The full water column mean sedimentary Mn contribution at station E-4E was 41%, whereas at station E-4W (at close proximity to the Kerguelen Plateau) the observed value was 88%.~~

3.8 Pseudo-Lagrangian, recirculation-structure

~~Station E-4W has trace metal concentrations and elemental ratios similar to A3 and will be discussed separately. However, the~~ Station E-4W has trace metal concentrations, elemental ratios and community size structure (Trull et al., 2014) similar to A3 and as such, will be excluded from the discussion in this section. The remaining recirculation structure stations exhibit profiles of pFe and pMn which show a minimum at approximately 150 - 175 m (Fig. 7). Our detailed depth profile indicates that the pFe and pMn minima coincide with the remnant winter water temperature minimum~~.~~ (Fig. 8). Interestingly, Blain et al. ~~(2014)~~(2014) also estimated a winter water depth of approximately 150 m. They observed at 150m, that nitrate and phosphate profiles within the recirculation feature, from multiple years and seasons, converged with striking consistency. Particulate Fe and pMn, concentrations increase above and below the temperature minimum, however, pAl only increases below 175 m. Particulate Al is stripped out preferentially with settling lithogenics while pFe and pMn are retained either through conversion to the biogenic particulate fraction (uptake) or adsorbed onto organic particles. It should be noted here that the work of Raiswell~~ et al.~~ (2011) indicates that iceberg and glacially derived Fe nanoparticulate material is typically high in Fe and low in Al. Thus, supply of glacially derived nanoparticulate Fe from Kerguelen Island, via the north east of the recirculation structure could also cause the observed high Fe, low Al surface enrichment within the recirculation structure.

Given that the pFe and pMn minima coincides with the remnant-winter-water temperature minimum, the total amount of particulate trace metals distributed throughout the winter mixed layer must be lower than during summer. This is counterintuitive if sediment resuspension is the primary source of particulate trace metals into the recirculation feature. During winter we would expect increased wind mixing, leading to more entrainment of pFe over the plateau and more supply into the recirculation feature leading to a maximum at the temperature minimum. Given that we observe the inverse situation, supply into the recirculation structure must be low during winter. Thus, we suggest that the lateral supply of fluvial and glacial derived particulate trace metals must be an important source. This source would be expected to reduce in winter when precipitation as snow and glacial freezing is at a maximum and conversely, during spring, snow and ice melt and rainfall increases runoff into the coastal areas and induces a fertilisation event downstream of Heard and Kerguelen Islands. Kerguelen Island is a subantarctic island, and its climatology is cold and wet, with the Port-aux-Francais weather station recording mean daily temperatures of 2.1° C in winter and 8.2° C in summer and year round consistent precipitation (730 mm annually) (Meteo France). It should be noted that due to its sheltered location and sea level altitude, the Port-aux-Francais location is relatively mild compared to the west coast and interior of the island which is estimated to receive 3 times the rainfall of the east coast, or 2124 mm annually. Therefore, having a climate of high precipitation and seasonal thawing, increased seasonal runoff can be expected in spring and summer from Kerguelen Island.

~~The importance of fluvial sources in supplying dissolved Fe and Mn into coastal waters to the north east of Kerguelen, north of the PF, has been shown previously by Bucciarelli et al., (2001). The authors found a linear relationship between dissolved Fe and lithogenic silica and suggested that this was indicative of weathering of silicate rich minerals that characterise the Kerguelen Islands with a concomitant release of dissolved Fe and Mn. Indeed in the present study, using the lithogenic and biogenic silica data presented in Closset et al., (2014), total particulate Fe correlated significantly with total lithogenic silica (R=0.76, P<0.01) but not with biogenic silica. However, this significant correlation was not limited to the coastal regions in the present study and instead was observed for all stations and depths combined. Bucciarelli et al., (2001) found an exponential decrease in dissolved Fe with distance from the coast, further supporting their theory of a dominant coastal source in this region. This exponential decrease would be expected to apply to the particulate fraction also, however, it appears that even with an exponential decrease in pFe with distance from the coast, particulate Fe enrichment, sourced from fluvial runoff, is evident on the southern side of the PF within the recirculation feature.~~

~~The hypothesis of pFe supply from north of the PF into the eastern side of the recirculation feature via the mixing zone is supported by radium isotope data (Sanial et al., this issue) collected during the KEOPS2 mission.~~The importance of glacial/fluvial sources in supplying dissolved Fe and Mn into coastal waters to the north east of Kerguelen, north of the PF, has been shown previously by Bucciarelli et al., (2001). The authors found a linear relationship between dissolved Fe and lithogenic silica and suggested that this was indicative of weathering of silicate rich minerals that characterise the Kerguelen Islands with a concomitant release of dissolved Fe and Mn. Indeed in the present study, using the lithogenic and biogenic silica data presented in Closset et al., (2014), total particulate Fe correlated significantly with total lithogenic silica (R=0.76, P<0.01) but not with biogenic silica. However, this significant correlation was not limited to the coastal regions in the present study and instead was observed for all stations and depths combined. Bucciarelli et al., (2001) found an exponential decrease in dissolved Fe with distance from the coast, further supporting their theory of a dominant coastal source in this region. This exponential decrease would be expected to apply to the particulate fraction also; however, it appears that even with an exponential decrease in pFe with distance from the coast, particulate Fe enrichment, sourced from fluvial runoff, is evident on the southern side of the PF within the recirculation feature.

The hypothesis of pFe supply from north of the PF into the eastern side of the recirculation feature via the mixing zone is supported by radium isotope data (Sanial et al., 2014) collected during the KEOPS2 mission. Apparent radium ages derived from the ratio of ^{224}Ra/^{223}Ra (and using the ratio observed within the Baie des Baleiniers as the starting time) suggest that the age of water since fertilisation within the recirculation feature was only 5-8 days. This indicates that there is likely rapid transfer across the PF of fertilised waters which were sourced from nearby shallow coastal areas such as the Baie des Baleiniers, Kerguelen Island. The authors go on to highlight that the heterogeneous distribution of ^{224}Ra and ^{223}Ra indicates that transfer across the polar front is sporadic in nature.

The observation of pFe enrichment in surface waters of the recirculation structure without proportional concentrations of pAl may be due to biological uptake and conversion from a bioavailable pool into the biogenic particulate pool. Settling of refractory lithogenics that are high in Al may also partially explain the observation. Alternatively or in combination, a high pFe, low pAl source such as nanoparticulate Fe characteristic of glacial/fluvial runoff ~~(Hawkings et al., 2014; Raiswell et al., 2008a, 2006a) on Kerguelen Island could explain this observation. Indeed, temperature and salinity profiles within the recirculation structure reveal fresher and warmer water within the upper 110 m than either R-2 or A3 stations suggesting that glacial/fluvial runoff from Kerguelen Island may well be delivering this high pFe, low pAl surface enrichment.~~

~~*3.9 Elemental ratios at stations E-1, E-3, E-5, E-4E and E-4W*~~

~~Vertical changes in the observed elemental ratios during the pseudo-Lagrangian recirculation-structure study (Fig. 9) highlighted the influence of proximity to the fast flowing PF on E-4W, which contrasts with the other stations during the recirculation-structure study. The particles captured from the water column near station A3 have a characteristically low Mn:Fe and Ba:Al ratio in comparison to station R-2. Station E-4W was the closest recirculation-structure station to the Kerguelen Plateau and appeared to be influenced by sedimentary sources having Mn:Fe and Ba:Al ratios much closer to A3 than any other recirculation-structure station. The profiles of trace metals within the recirculation structure (Fig. 7) also highlighted unusually high pFe and pAl at station E4-W, which further supports the hypothesis that E-4W was very similar to A3 in its trace metal inventory and most likely had a similar source. Trull et al., (this issue) analysed surface water community size structure based on chemical and isotopic measurements and also revealed many similarities between stations A3 and E-4W and resulted in the authors grouping these stations together and separate from the remaining recirculation structure stations.~~

~~Conversely, E-4E, which is the recirculation-structure station at the greatest distance from the Kerguelen Plateau, had elemental ratios below the mixed layer similar to station R-2 (Table 4). The particulate trace metal inventory observed at station E-4E we believe has originated from modified HNLC-type water in the vicinity of the Leclaire Rise. The remaining recirculation-structure stations (E-1, E-3, E-5) appear to have source signatures reflecting intermediate elemental ratios between the two unique end-member stations, E-4W and E-4E, and indicates a degree of mixing between these two unique sources. Interestingly, below the depth of the winter water temperature minimum of 150-175 m, we observe striking consistency in the elemental ratios of pFe:pAl and pMn:pAl. This suggests that the particles distributed throughout the water column below approximately 175 m have a similar composition and therefore source.~~ (Hawkings et al., 2014; Raiswell et al., 2008a, 2006a) on Kerguelen Island could explain this observation. Indeed, temperature and salinity profiles within the recirculation structure reveal fresher and warmer water within the upper 110 m than either R-2 or A3 stations suggesting that glacial/fluvial runoff from Kerguelen Island may well be delivering this high pFe, low pAl surface enrichment.

4 Conclusions

This study has identified two distinct areas of Fe fertilisation in the vicinity of Kerguelen Island. Firstly, the plateau itself is a major source of resuspended shelf sediments to station A3 especially below the mixed layer. Secondly, fluvial and glacial runoff into coastal waters in combination with resuspension of shallow coastal sediments fertilises areas to the north of the PF, east of Kerguelen Island, but also across the PF and into the recirculation feature from the north-east. Indications of particle transport across the PF were observed at station R-2 sourced from the Leclaire Rise to the north of the PF. Satellite imagery also revealed filaments clearly diverging from the main jet of the PF and into the north east of the recirculation structure. Within the recirculation structure, the correspondence of the winter water temperature minimum with the particulate trace metal minimum implies that a seasonal cycle is involved in the supply of trace elements. This is most likely driven by increased fluvial and glacial runoff in summer, associated with rainfall and basal melt and reduced supply in winter when snowfall and freezing conditions predominate. In this complex region, it appears that weathering of the islands themselves are direct sources of new Fe and help stimulate the seasonal bloom that is significant in terms of the regional carbon cycle.

Over the mesoscale, it appears that physical processes associated with settling of refractory lithogenic particles was an important process in modifying the particulate elemental ratios. However, on the individual profile scale, biological processes seem important in modifying the elemental ratios in surface waters through preferential uptake of bio-essential elements, even from the particulate fraction.

Repeat sampling over the plateau provided a perspective on the persistence of the particulate Fe availability. Small particles containing pFe were efficiently transported out of the mixed layer during a bloom event over stations A3. This resulted in a 70% reduction in the integrated pFe stock within the mixed layer as a result of physical aggregation of small particles onto phyto-aggregates, presumably decreasing particle buoyancy and increasing export out of the mixed layer. This is likely to be an important aspect of the complex interaction between iron supply and biological availability, capable of mediating bloom duration and thus the efficiency of carbon sequestration.

Appendix: Certified reference material analysis

Table A1: Percentage recoveries of BCR-414 certified reference material. Certified and single lab values taken from the final report of the Commission of the European Communities, Community Bureau of Reference for BCR-414, EUR14558.

mg/kg	Rep 1	Rep 2	Rep 3	Mean	SD	RSD (%)	Certified	% recovery	single lab analysis	% recovery
Ba	34	26	32	31	4.0	13.1			31	99
Al	2243	1349	1943	1845	454.6	24.6			1800	102
Mn	278	284	283	282	3.4	1.2	299	94		
Fe	1874	1850	1878	1867	15.0	0.8	1850	101		

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Table 1. KEOPS2 sampling locations and station types.

	A3-1	A3-2	R-2	F-L	E-1	E-3	E-5	E-4E	E-4W
Station type	Kerguelen Plateau 1st visit	Kerguelen Plateau 2nd visit	HNLC reference station	Northern Polar Front	recirculation structure	recirculation structure	recirculation structure	Eastern recirculation structure	Western recirculation structure
Sampling date	20/10/2011	16/11/2011	25/10/2011	6/11/2011	29/10/2011	3/11/2011	18/11/2011	13/11/2011	11/11/2011
Latitude (S)	50° 37.7574'	50° 37.4306'	50° 21.52'	48° 31.394'	48° 29.5728'	48° 42.1334'	48° 24.698'	48° 42.9218'	48° 45.927'
Longitude (E)	72° 4.8193'	72° 3.3366'	66° 43.00'	74° 40.036'	72° 14.1467'	71° 58.0027'	71° 53.7894'	72° 33.7792'	71° 25.51'
Bottom depth (m)	505	505	2528	2690	2050	1910	1920	2200	1400
Time series	Yes	Yes	No	No	Yes	Yes	Yes	No	No
Particulate Trace Metals	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
POC PON	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Sediment samples	Yes	Yes	Yes	Yes	No	Yes	No	Yes	Yes
Sediment trap samples	No	Yes	No	No	Yes	Yes	Yes	No	No

~~Table 2. Mean elemental ratios of authigenic sediments at each station.~~

Table 2. Mean elemental molar ratios of marine snow particles captured in free-floating sediment traps, particulate matter (<53 µm) below the mixed layer and authigenic sediments at each station. Note that station TEW1 is a near-coastal station located within Hillsborough Bay, Kerguelen Island. Station TEW-1 is not discussed in detail in the MS as no samples were collected for suspended particles; however, details are included here to show the influence of close proximity to the island and fluvial/glacial sources.

~~Station~~Sediment trap @ 210 m	**pFe:pAl**	**pMn:pAl**	**pMn:pFe**	**pBa:pAl**
~~TEW1~~A3-2	0.70~~1.10~~	0.~~013~~008	0.~~012~~011	0.~~003~~025
E-1	1.02	0.009	0.009	0.162
E-3	1.05	0.010	0.010	0.285
~~E3~~E-5	0.~~93~~91	0.~~015~~008	0.~~016~~009	0.~~125~~318
Suspended particles mean (> MLD)				
~~E4W~~A3-1	0.~~81~~53	0.~~013~~007	0.~~016~~013	0.~~013~~027
~~R2~~A3-2	0.~~73~~63	0.~~063~~009	0.~~086~~014	0.~~892~~034
R-2	0.65	0.036	0.059	0.322
F-L	0.77	0.020	0.027	0.190
E-4E	0.86	0.037	0.045	0.383
E-4W	0.63	0.014	0.021	0.078
E-1	0.68	0.023	0.034	0.185
E-3	0.71	0.024	0.033	0.258
E-5	0.68	0.020	0.030	0.260
Sediment analysis				
TEW-1	1.10	0.013	0.012	0.003
A3	0.87	0.011	0.013	0.026
R-2	0.73	0.063	0.086	0.892
~~FL~~F-L	0.82	0.016	0.019	0.040
E-4W	0.81	0.013	0.016	0.013
E-3	0.93	0.015	0.016	0.125
Kerguelen Archipelago ~~Basalts (Doucet~~Basalt mean (Gautier et al., ~~2005~~1990)	0.~~77 -~~ ~~1.4~~08 - 0.49	0.~~011~~004 - 0.~~045~~010	0.~~013~~021 - 0.~~014~~050	0.~~0014 -~~ 002- 0.~~0024~~004
Upper continental crust (Wedepohl, 1995)	0.19	0.003	0.017	0.002

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~~Table 3. Mean elemental ratios of marine snow particles captured in free-floating sediment traps.~~

~~Station~~	~~Fe:Al~~	~~Mn:Al~~	~~Fe:Mn~~	~~Ba:Al~~
~~E-1~~	~~1.02~~	~~0.009~~	~~113~~	~~0.16~~
~~E-3~~	~~1.05~~	~~0.010~~	~~105~~	~~0.28~~
~~E-5~~	~~0.91~~	~~0.008~~	~~112~~	~~0.32~~
~~A3-2~~	~~0.70~~	~~0.008~~	~~88~~	~~0.03~~

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~~Table 4. Mean elemental ratios of particulate matter (<53 µm) below the mixed layer at each station.~~

~~**Station**~~	~~pBa : pAl~~	~~pMn : pAl~~	~~pFe : pAl~~	~~pMn : pFe~~
~~**A3-1**~~	~~0.027~~	~~0.007~~	~~0.53~~	~~0.013~~
~~**A3-2**~~	~~0.034~~	~~0.009~~	~~0.63~~	~~0.014~~
~~**R-2**~~	~~0.322~~	~~0.036~~	~~0.65~~	~~0.059~~
~~**F-L**~~	~~0.190~~	~~0.020~~	~~0.77~~	~~0.027~~
~~**E-4E**~~	~~0.383~~	~~0.037~~	~~0.86~~	~~0.045~~
~~**E-4W**~~	~~0.078~~	~~0.014~~	~~0.63~~	~~0.021~~
~~**E-1**~~	~~0.185~~	~~0.023~~	~~0.68~~	~~0.034~~
~~**E-3**~~	~~0.258~~	~~0.024~~	~~0.71~~	~~0.033~~
~~**E-5**~~	~~0.260~~	~~0.020~~	~~0.68~~	~~0.030~~

Figure Captions:

Figure 1:

SeaWiFS surface chlorophyll on the 11th of November 2011, approximately half way through the KEOPS2 sampling program. Kerguelen and Heard Island are visible in grey. Stations that were sampled for suspended particles are indicated with black circles. Distinct regimes of interest for the KEOPS2 program are indicated in red.

Figure 2:

Surface (10 m) temperature in Spring-Summer (a) and Winter-Autumn (b) as well as surface salinity in Spring-Summer (c) and Winter-Autumn (d) within the study area from 1970 until 2013. The PF is identified as a solid black line. Kerguelen and Heard Island are visible in dark grey and black respectively and the Leclaire Rise can be identified as the shallow bathymetry, north of the PF, near the western boundary of the map. Data obtained from the World Ocean Database (http://www.nodc.noaa.gov).

Figure 3:

Profiles of particulate Fe (a), Al (b) and Mn (c) (1 - 53 µm) at the reference HNLC station (R-2), the northern PF station (F-L) and pre and post-bloom over the plateau station (A3-1 red circle, A3-2 green square), highlighting the contrasting particulate trace metal supply to these locations. ~~Profiles of biogenic Fe (d) and sedimentary Mn (e) are given to highlight the source to each station (see text for details). Biogenic Fe~~Biogenic Fe (d) (as a percentage of the total Fe) in surface waters shows a clear progression that can be explained by the location of each station within the study area whereby, biogenic Fe at R-2 >> F-L > A3-2 > A3-1. ~~Sedimentary Mn values greater than 100% indicate a source signature with low Mn:Al such as bedrock (0.0034).~~

Figure 4:

Particulate Fe at the plateau station (A3) by size class. The integrated full water column pFe (>1µm) reduced by 51% between A3-1 and A3-2 (9.1 – 4.5 mMol m^{-2} at A3-1 and A3-2 respectively). The integrated mixed layer pFe reduced by 70% between A3-1 and A3-2 (1.4 – 0.56 mMol m^{-2} at A3-1 and A3-2 respectively). The mixed layer shoaled between A3-1 and

A3-2 as illustrated by the dashed horizontal line. The calculation of integrated mixed layer pFe used a constant mixed layer depth of 165m for both A3-1 and A3-2 to allow comparison between these stations.

Figure 5:

Profiles of elemental ratios at the reference station (R-2), northern PF (F-L) and pre and post-bloom over the plateau station (A3-1, red circles; A3-2, green squares respectively). Note the increase in pMn and pBa relative to pAl at station R-2 below 500 m.

Figure 6:

~~Ratio of pMn:pAl versus depth, separated by station type. Vertical lines represent the mean crustal ratio (black), authigenic Kerguelen Plateau sediments (red) and station R-2 authigenic sediments (green).~~

Molar ratio of pMn:pAl versus depth, separated by station type. Vertical lines represent the median molar ratios within Kerguelen Island basalts (Gautier et al., 1990) (black), authigenic Kerguelen Plateau sediments (red) and station R-2 authigenic sediments (green).

Figure 7:

Profiles of particulate trace metals during the pseudo-lagrangian recirculation-structure study. Station E-4W (red circles) exhibits unique trace metal profiles in comparison to the remaining stations (see text for details). Note the distinct pFe and pMn minima at 150-175 m. Particulate Al exhibits a similar profile albeit without surface enrichment.

Figure 8:

a) Representative temperature profiles within the upper 500 m within the recirculation structure. b) Particulate Fe (1-53 µm) within the upper 500 m within the recirculation structure. Correspondence between the temperature minimum depth of winter water and pFe minimum is illustrated.

~~Figure 9:~~

~~Profiles of elemental ratios during the pseudo-lagrangian recirculation-structure study. Stations E-1, E-3 and E-5 can be considered a pseudo-lagrangian time series, while stations E-~~

~~4W and E-4E are situated at the western and eastern extremes of the recirculation structure. Note the relative consistency in various elemental ratios below the winter water temperature minimum depth of 150-175m.~~