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A synthesis of upper ocean carbon and dissolved iron budgets for Southern Ocean natural iron fertilisation studies

Paul J. Morris [a*]

Matthew A. Charette [a]

[a] Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, 02540, USA

[*] Corresponding author

Email: pmorris@whoi.edu

Tel: +1 508 289 3823 Fax: +1 508 457 2193

New contact details starting 1st March 2013: School of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, UK. Email: p.j.morris@bristol.ac.uk

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Abstract

For over a decade the relationship between iron addition and carbon export has been an active topic of Southern Ocean biogeochemical investigation. To study the iron-carbon interaction, a number of natural iron sources within the Antarctic Circumpolar Current have been targeted to quantify the resultant particulate organic carbon (POC) export. Three studies in particular near the Crozet Islands, Kerguelen Plateau, and Antarctic Peninsula, have produced both estimates of dissolved iron (DFe) supply and POC export. For each area, we present a detailed synthesis of ^{234}Thorium-derived POC export and of the DFe budgets that fuel the substantial phytoplankton blooms observed in these areas. Furthermore, we discuss the nuances of calculating seasonal POC export, which is required to estimate the seasonal response of POC export to DFe fertilisation. To conclude, we review the relationship between DFe supply and POC export (C:Fe ratio) for these areas, which provides an estimate of POC export efficiency. Daily rates of POC export from the mixed layer of naturally Fe-enriched Southern Ocean blooms range from 15 to 32 mmol C m^{-2} d^{-1}, with associated control sites typically exporting ~3-times less POC, (5 to 12 mmol C m^{-2} d^{-1}). Within each project, the 3-fold trend is also observed in estimates of seasonal POC export; however, variation between study regions shows up to a 4-fold difference (range 1.4 – 5.0 mol m^{-2}). DFe supply is dominated by horizontal processes and spans an order of magnitude depending on the location (190 – 2700 nmol m^{-2} d^{-1}). Where the calculation of seasonal C:Fe ratios is possible, almost an order of magnitude variation (17,190 – 154,000) is observed between different Southern Ocean regions.

1 Introduction

Southern Ocean productivity is severely limited by a lack of iron; a hypothesis that has been repeatedly tested and verified by artificial iron enrichment experiments (Boyd *et al.*, 2007; de Baar *et al.*, 2005). To put the Southern Ocean's under-productivity into perspective, an initial estimate made during the advent of the '*Iron Hypothesis*', suggested that with complete utilisation of nitrate and phosphate, plentiful iron could increase new production by approximately 30-fold (Martin, 1990a). However, phytoplankton in the Southern Ocean fail to tap the nutrient rich water, and consequently the region remains persistently low in chlorophyll. This condition is known as high-nutrient low-chlorophyll (HNLC), of which the Southern Ocean is the largest example in the world (Watson, 2001).

The idea that iron (Fe) is the micro-nutrient that limits biological production in the Southern Ocean was reported in the scientific literature as early as the 1930s (Gran, 1931; Harvey, 1933; 1937; Ruud, 1930) and appears twice in the Discovery Reports from around the same time (Hart, 1934; 1942). However, the vanishingly low concentration of dissolved iron (DFe) in the surface water of the Southern Ocean was not fully recognized until the advent of trace-metal clean sampling techniques in the 1970s (review by Martin, 1991). This advance in understanding the distribution of DFe led to the formulation of the *Iron Hypothesis*, the idea that it may be possible to mitigate increasing atmospheric CO_2 by stimulating phytoplankton blooms, and thus fixing and transporting carbon (C) to the deep ocean (Martin, 1990a). This hypothesis was first tested by Martin & Fitzwater (1988), who concluded that Fe was in fact the limiting micro-nutrient for phytoplanktonic growth. That same year, John Martin passed a casual comment at an informal WHOI seminar: *"Give me half a tanker of iron, and I'll give you an ice age"*, which although was met with laughter at the time (Chisholm & Morel, 1991; Martin,

1990b), later become a serious research topic as a potential means to sequester CO_2 that is released by the burning of fossil fuels (Martin *et al.*, 1990).

Since the early 1990s there have been 13 artificial iron-addition experiments. Although all of these have demonstrated that biological productivity can be enhanced through the artificial addition of Fe, usually in the form of iron sulphate, only four of them produced multiple lines of evidence of enhanced C export (Boyd *et al.*, 2007; de Baar *et al.*, 2005). However, there is even less evidence to support enhanced C sequestration (Buesseler *et al.*, 2004), a depth at which C is isolated from atmospheric ventilation on a greater than seasonal time-scale. The finding of little or no significant C sequestration has led the scientific community to question the feasibility of using purposeful Fe fertilisation as a means to mitigate rising atmospheric CO_2 levels (Buesseler & Boyd, 2003; Buesseler *et al.*, 2008).

In parallel to the numerous artificial Fe fertilisation experiments in the early 2000s, several groups approached the topic of iron fertilisation from that of naturally iron fertilised systems. The two most prominent projects were the CROZet natural iron bloom and EXport experiment (CROZEX) (Pollard *et al.*, 2009), and the KErguelen Ocean and Plateau compared Study (KEOPS) (Blain *et al.*, 2007). In addition to these, there are four other noteworthy studies: the Blue Water Zone (BWZ) project (Zhou *et al.*, 2010; manuscripts within this issue), the Discovery 2010 cruises (Tarling *et al.*, 2012), the Dynamic Light on Fe limitation (DynaLiFe) program (Arrigo & Alderkamp, 2012), and most recently a return to the Kerguelen Plateau in late 2011 referred to as KEOPS 2 (Table 1). Productivity in these settings appears to be stimulated by Fe supplied from sources such as shelf and plateau sediments, glacial melting and, to a lesser extent, vertical mixing enhanced by ocean currents flowing over topographic features. These five projects represent the most thorough and integrative initiatives to investigate the

impact that natural Fe supply has on the ecology, productivity and geochemical cycles in these HNLC Southern Ocean systems.

INSERT TABLE 1

The aim of this synthesis is to focus on the current state of understanding of the C and iron budgets, and export efficiencies in naturally Fe fertilised Southern Ocean systems. Consequently, CROZEX, KEOPS and BWZ will be the focus of this synthesis as these three studies have the most comprehensive datasets of both DFe supply and POC export. Firstly, a brief description of each project will be presented, followed by a discussion of the rates of daily and seasonal POC export. Secondly, up to date DFe budgets will be presented so that the C:Fe ratio can be calculated; the molar ratio between DFe added and the response of C to this addition. Whilst presenting these geochemical budgets the nuances and limitations of the various approaches will be discussed, and the varying results will be compared. The motivation for this paper arose from a workshop at WHOI in July 2011 (Charette *et al.*, 2011) called *'Modeling and Synthesis of Southern Ocean Natural Iron Fertilzation'* (http://www.whoi.edu/sbl/liteSite.do?litesiteid=48732).

2 Description of natural Fe fertilisation studies

The underlying structure of a natural Fe fertilisation field campaign is to survey the Fe enriched bloom region, and compare it to a nearby Fe limited non-bloom, HNLC region. Then by comparing the Fe enriched and Fe depleted regions, it is possible to gauge the impact of Fe supply on the subject of interest; in this case POC export. To ensure successful field campaigns,

the chosen study site must support a reproducible bloom with a similar timing and magnitude each year. The first three projects listed in Table 1, which are the focus of this synthesis, are briefly described below, and further specifics on the details of the CROZEX and KEOPS blooms can be found in Supplementary Table 1 of Pollard *et al.* (2009).

2.1 CROZEX

Sampling for CROZEX took place in Nov 2004 – Jan 2005 on two cruises onboard the RRS *Discovery*, cruises D285 and D286, which are later referred to as leg 1 and leg 2 respectively (Pollard *et al.*, 2007a; Pollard & Sanders, 2006). The Crozet islands lie just south of the SubAntarctic Front (SAF), within the eastward flowing Antarctic Circumpolar Current (ACC) (Pollard *et al.*, 2007b). As the ACC encounters the Del Caño Rise and the Crozet Plateau, it is forced to fragment with one filament pushed northwards and another filament skirting south of the Crozet Plateau (Figure 1). The northern filament flows north between the Del Caño Rise and the Crozet Plateau, turns west following constant depth topography, resulting in an anticyclonic flow, before finally turning east as part of the Crozet Front (Pollard & Read, 2001). It is believed that the northern branch of the ACC is a physical constraint on the spatial distribution of the Crozet bloom (Pollard *et al.*, 2002). For a complete overview of the circulation around the Crozet archipelago see (Pollard *et al.*, 2007b).

The Crozet archipelago consists of 5 islands, with a plateau that covers an area of approximately 1200×600 km. The plateau rises from a surrounding abyssal depth of ~3800 m to form a subsurface plateau ~1000 m deep. The two major islands, Île de l'Est and Île de la Possession, are centred around 52°E and 46.4°S, approximately 2500 km southeast of Durban, South Africa. Île de l'Est and Île de la Possession reach maximum heights of 1090 m and 934 m

and cover areas of 130 km^2 and 150 km^2 respectively. The seasonally consistent bloom begins in late September, peaks in late October and decays away to a smaller bloom close to the islands in December. The main bloom covers an area of about 90,000 km^2, with chlorophyll-*a* (chl-*a*) concentrations peaking at about 6 $\mu g\ L^{-1}$ (Figure 1).

INSERT FIGURE 1

2.2 KEOPS

Sampling for KEOPS took place in Jan-Feb 2005 (Blain *et al*., 2008a), the same austral summer as CROZEX, on board the RV *Marion Dufresne* (cruise MD145). The Kerguelen Islands lie just north of the Polar Front (PF) and represent the northern emerged part of the Kerguelen Plateau (KP). The plateau, which is centered around 72°E and 51°S emerges a second time about 500 km to the southeast, this time just south of the PF, to form the Heard and McDonald Islands (Figure 2). Together they cover areas of 7215 km^2 and 368 km^2, and reach heights of 1850 m and 2745 m respectively. It has been shown that about three quarters of the flow of the ACC passes to the north of the Kerguelen Plateau, with the reminder passing between the Kerguelen Islands and Antarctica. The southern branch of the ACC that encounters the KP is channeled through the Fawn Trough as the Fawn Trough Current (FTC) in a northeasterly direction. The FTC is predominantly redirected east again to rejoin the ACC core that passed to the north of the KP. However a small branch of the FTC splits away northwestward and heads up the eastern side of the KP (Park *et al.*, 2008b). As a result this creates an isolated area of relatively quiescent water over the shallow part of the KP (<1000 m) and constrains the site of

the main bloom. A second, smaller chlorophyll patch is also observed to the northeast of the Kerguelen Islands and is pinched in between the PF and the ACC core (Blain *et al.*, 2008a).

INSERT FIGURE 2

The field study focused on the bloom present over the relatively shallow (*ca.* 500 m) plateau between the Kerguelen Islands and the smaller Heard and McDonald Island to the southeast. The bloom, which is less intense than CROZEX, reaches a maximum chl-*a* concentration of about 3 μg L^{-1}. It also appears to be roughly constrained by the seabed topography, is about 45,000 km^2, and is present between mid November to late February (Blain *et al.*, 2007; Blain *et al.*, 2008a).

2.3 Blue Water Zone (BWZ)

The BWZ project was carried out in two phases: austral summertime cruises in 2004 and 2006 and an austral winter study in 2006 (Zhou *et al.*, 2012; Zhou *et al.*, 2010; Table 1). The study site was located in the region of the western Antarctic Peninsula, southern Drake Passage and southern Scotia Sea (Figure 3), which is among the most productive areas in the Southern Ocean from primary producers and krill to higher trophic level predators (Ducklow *et al.*, 2007; Hofmann *et al.*, 2004; Holm-Hansen *et al.*, 1994; Hopkinson *et al.*, 2007; Huntley *et al.*, 1991; Martin, 1990a; Nowacek *et al.*, 2011). The Circumpolar Deep Water (CDW) is the primary source water for the ACC, which in turn is the main source water for the shelves of the western Antarctic Peninsula (WAP) (Hofmann *et al.*, 1996; Nowlin & Klinck, 1986; Orsi *et al.*, 1995). As such, the low Fe concentrations in the CDW become a critical factor in limiting primary production in the upper water column of this region (Ardelan *et al.*, 2010; Hopkinson *et al.*,

2007; Measures *et al.*, 2012). Aside from dust, Fe delivery processes to the euphotic zone include vertical mixing of DFe-rich deep waters and lateral transport and mixing of DFe-rich shelf waters (Dulaiova *et al.*, 2009; Frants *et al.*, 2012; Zhou *et al.*, 2010). In addition to driving high rates of productivity along the WAP, the DFe plume and associated productivity extends from the shelf area between Livingston Island (LI) and Elephant Island (EI) and into the southern Scotia Sea at a spatial scale of ~1000 km (Hopkinson *et al.*, 2007; Kahru *et al.*, 2007). The peak chl-*a* associated with the spring phytoplankton bloom typically occurs in October; enhanced productivity is often associated with eddies formed in the wake of the Shackleton Transverse Ridge (Kahru *et al.*, 2007). The bloom be divided into two regions: the area to the north of EI, and the area to the north of LI and KGI. The EI bloom depicted by the red box (Figure 3) is 62,500 km^2 and was previously described by Dulaiova *et al.* (2009). The bloom to the north of LI and KGI has not been previously constrained, so here we use a satellite image to define two regions of this bloom (Figure 3). The solid-lined black box is 50 × 120 km (6000 km^2) and is assumed to be the area fertilised by 50 km of LI shoreline, in line with DFe supply constrained by Dulaiova *et al.* (2009) (Section 4). The dashed-lined black box is a 200 × 120 km (24,000 km^2) extension that encompasses the remainder of the bloom seen to the north of both LI and KGI for a total area of 30,000 km^2 (Figure 3). For the BWZ study, POC export data (available from the ALMR 2006 austral summer cruise; Table 1) derived from the $^{234}Th/^{238}U$ disequilibrium method have not been previously published, but are discussed here and are available online via the Biological & Chemical Oceanography Data Management Office (BCO-DMO) (data.bco-dmo.org/jg/serv/BCO/Unaffiliated/Charette/Antarctic2006/Thorium_Summary.html0).

INSERT FIGURE 3

3 POC export

The most common approach for measuring upper ocean POC export is the $^{234}Th/^{238}U$ technique, an approach that measures the disequilibrium between particle reactive ^{234}Th and its conservative parent ^{238}U (Rutgers van der Loeff *et al.*, 2006). The measured ^{234}Th flux ($t_{½}$ = 24.1 d) is then converted to a POC flux using a POC:^{234}Th ratio measured on the >~50 µm particulate material (Buesseler *et al.*, 2006). This larger size fraction typically represents the sinking component of the particulate pool (Fowler & Knauer, 1986). The ^{234}Th approach provides a means to estimate POC export without the need for deploying sediment traps, and thus offers the opportunity to compile relatively high resolution maps of POC export. However, one source of uncertainty is natural variability in the POC:Th ratio, which tends to decrease with increasing depth due to preferential remineralisation of POC as particles sink (Buesseler *et al.*, 2006). Consequently, the depth at which *in situ* pumps are used to collect sinking particles should ideally match the depth at which POC export efficiency is required for a given C mass balance (e.g. euphotic zone, winter mixed layer). Additional consideration must also be given to the integrative trait of the ^{234}Th tracer, typically 31 days (mean life-time) (Buesseler, 1998). Related to this is the frequent assumption of steady state to ^{234}Th flux models, which may over or under estimate POC export depending on the stage of the phytoplankton bloom (Savoye *et al.*, 2006).

3.1 Daily rates

For leg 1 of CROZEX the mean POC export in the bloom was 15 mmol C m^{-2} d^{-1} compared to 5 mmol C m^{-2} d^{-1} at the control site. However, the 3-fold difference between the

bloom and control site was not present during leg 2, which showed mean POC exports of 15 and 17 mmol C m^{-2} d^{-1} at the bloom and control sites respectively (Morris *et al.*, 2007). The reason for the unexpectedly high POC export at the control site during leg 2 was attributed to a small, but significant increase in surface chl-*a* in the 2-3 weeks before the control site was sampled during leg 2 (Morris, 2008; Morris & Sanders, 2011; Morris *et al.*, 2007; Venables *et al.*, 2007). This highlights the quasi-integrative nature of the ^{234}Th tracer, and also suggests that a significant amount of POC can be exported even at relatively low chlorophyll concentrations. KEOPS observed slightly higher POC export rates as CROZEX, with 23 mmol C m^{-2} d^{-1} in the bloom and 12 mmol C m^{-2} d^{-1} at the control site (Savoye *et al.*, 2008). However, the 2-fold difference between bloom and control sites is broadly consistent with the trend of POC export on leg 1 of CROZEX. Summertime BWZ ^{234}Th-derived POC export measurements for the region to the north of LI are presented in Figure 3. The two easterly stations agree closely and have a mean POC export of 32.3 mmol C m^{-2} d^{-1}, whereas the westerly station is ~3 times lower at 11.5 mmol C m^{-2} d^{-1}. The two easterly stations are certainly within waters of elevated chl-*a*, but are not in the core of the bloom (Figure 3). Conversely, the westerly station is in a transition zone from low to high chl-*a*, but is not in the extremely low chlorophyll waters that are observed substantially upstream (westward) of the Antarctic Peninsula (Figure 3). However, the westward station agrees well with the KEOPS control site, but is higher than the CROZEX control site (5 and 12 mmol C m^{-2} d^{-1} respectively). Given these comparisons, the westerly station is probably an upper limit on non-bloom POC export in this region.

3.2 Seasonal export

Daily rates of POC export provide an incomplete picture of a bloom's capacity to transfer C from the surface ocean to deeper depths. A more meaningful measure of POC export is the amount of export that happens over the duration of the bloom. By estimating the seasonal export of POC, it follows that seasonal geochemical budgets can be constructed, which allows for equitable cross comparison between different bloom settings. Without seasonal geochemical estimates, daily rate comparisons may be misleading; for example, growth-phase estimates of POC export are not comparable to the declining-phase estimates of POC export from another bloom. By estimating POC export over the full growth season, short-term temporal variations are smoothed out and it becomes possible to compare like-for-like. However, in attempting to calculate seasonal POC export, new uncertainties may be introduced. The remainder of this section will explore the nuances of daily and seasonal estimates of POC export and discuss the caveats associated with these calculations.

Direct measurements of seasonal POC export out of the euphotic zone are not possible using traditional methods in the systems we are discussing. For example, bottom tethered sediment traps deployed within the upper several hundred meters tend to result in substantial under sampling (Baker *et al.*, 1988; Buesseler *et al.*, 2007a), and it is impractical to deploy drifting sediment traps for periods of weeks to months at a time. Consequently, it is necessary to approach the calculation of seasonal POC export using a geochemical budget. The most widely used technique approaches the calculation by assuming that the DIC deficit (ΔDIC) observed over the course of the bloom is equivalent to the amount of C removed by downwards POC export. Over the course of the season, ΔDIC must also be refined to accommodate vertical supply, air-sea exchange, and accumulation of DOC and POC in the euphotic zone.

Seasonal POC export for KEOPS measured using the ΔDIC approach was calculated as follows: ΔDIC + DIC vertical supply + DIC air-sea supply – POC accumulation – DOC accumulation (Blain *et al.*, 2007). Using this approach it was estimated that the KEOPS bloom exported 5047 mmol C m^{-2} compared with 1730 mmol C m^{-2} at the control HNLC site (Blain *et al.*, 2007). This approach was taken further by Jouandet *et al.* (2008) to also include a horizontal supply of DIC, thus adding the term "+ DIC horizontal supply" to the seasonal POC export equation. Factoring in horizontal supply, the bloom POC export increases to 5400 mmol C m^{-2}. This small increase reinforces the robustness of the Blain *et al.* (2007) estimate, which remains the commonly cited value in the literature. In the same way as ^{234}Th-derived POC export (Savoye *et al.*, 2008), it was also assumed that POC export was roughly the same at just below the mixed layer as at 200 m. For a detailed discussion of the DIC approach to estimating POC export for KEOPS see Jouandet *et al.* (2008).

The CROZEX project took a different approach to estimate seasonal POC export; a temporal scaling method based on the silicon cycle was used instead. The *silicon-scaling* technique asks the question: "How many days does the observed export of biogenic silica need to persist in order to close the Si budget?" (Morris, 2008; Morris & Sanders, 2011; Pollard *et al.*, 2009). During the CROZEX study, the silicon budget was relatively well constrained in terms of stocks and fluxes. Combining this information into a silicon budget was more straightforward than for either carbon or nitrogen as there is no gaseous silicon phase, and silicon does not progress beyond the trophic level of the primary producers, a consequence of the insolubility of silica in the gut of zooplankton (Brzezinski & Nelson, 1989; Dagg *et al.*, 2003; Dugdale *et al.*, 1995; Tande, 1985). These factors lend themselves to developing a simple silicon budget, which can be used to derive a quantitative scaling factor that can be applied to daily rates of POC

export to hence estimate seasonal POC export. The details of the silicon-scaling model, including the assumptions and caveats surrounding the C:Si ratio, which is implicit to the calculation of the scaling factor, are described in Morris & Sanders (2011). This approach concluded that at 100 m the CROZEX bloom exported 1437 mmol C m^{-2} compared with 396 mmol C m^{-2} at the HNLC control site. Following Pollard *et al.* (2009), POC export at 100 m can be extrapolated to 200 m using the canonical Martin curve (Martin *et al.*, 1987) with a *b*-value of -0.99 [$F = F_{100}(z/100)^{-0.99}$]. Applying this to POC export at 100 m, POC export extrapolated to 200 m is 723 and 199 mmol C m^{-2} at the bloom and control sites respectively.

The CROZEX estimates of seasonal POC export are about 3.5 and 4.4 times lower than the KEOPS POC export in the bloom and non-bloom regions respectively. Together, these studies' estimates of seasonal POC export represent the extent of such data in naturally Fe fertilised blooms in the Southern Ocean. Although both these estimates are derived using different approaches and exhibit about a 4-fold difference between the two, the results are internally consistent, demonstrating that about 3.3-times more POC is exported in the bloom region when compared to the HNLC control site.

INSERT TABLE 2

3.3 The caveats of calculating seasonal POC export

Aside from the major methodological differences used to estimate seasonal POC export (ΔDIC *vs.* silicon-scaling), there are several nuances that further differentiate CROZEX and KEOPS, which may have a significant bearing on the final estimate of seasonal POC export. For KEOPS, the ΔDIC budget outlined in Section 3.2 was calculated using a mixed layer depth of 70

m and 68 m at the bloom and HNLC sites respectively. POC export out of the mixed layer (*ca.* 70 m) was then assumed to be roughly the same as POC export at 200 m (Blain *et al.*, 2007). POC export was extrapolated to 200 m (temperature minimum) as this was the depth at which it was assumed that C had been isolated from atmospheric ventilation on a greater than seasonal time-scale (sequestered). The assumption that POC export at the mixed layer is roughly equal to POC export at 200 m was founded on the ^{234}Th-derived POC export, which showed consistent levels of POC export through 100 m and 200 m at both the bloom and HNLC regions (Savoye *et al.*, 2008). Based on this assumption, no Martin-style correction was made when translating POC export from 70 m to 200 m, which has an inherent assumption that little or no remineralisation occurred over the intervening 130 m. In contrast to the ^{234}Th results, Jacquet *et al.* (2008) did detect a small amount of POC remineralisation between 125-450 m using the barium-excess proxy technique, and estimated that in the bloom region 9-13% of POC export was remineralised before it reached 450 m. The HNLC region showed 18-39% remineralisation over the same depth range and suggests that POC export was more efficient under the bloom.

For CROZEX, the silicon-scaling budget outlined in Section 3.2 was calculated using an integration depth of 100 m, and was chosen based on the nitrate and DIC fields, which displayed more consistent vertical and horizontal homogeneity once this depth was reached (Bakker *et al.*, 2007; Sanders *et al.*, 2007). Furthermore, an integration depth of 100 m included the deepest mixed layers observed during the study, which based on 5-years worth of Argo float data, are reported to be about 60 m in the bloom region and 40-100 m in the HNLC region (Venables *et al.*, 2007). To make the comparison with KEOPS, seasonal POC export at 100 m was extrapolated to 200 m using Martin curve with a *b*-value of -0.99. The value for *b* was derived by fitting a Martin curve between 100 m POC export and POC export measured at 3000 m with

bottom tethered sediment traps (Pollard *et al.*, 2009). Performing this calculation with the derived *b*-value for extrapolation assumes that the shape of the Martin curve can be fixed by two data points, one at each extreme, and is applicable to the intervening 2900 m. Although the derived *b*-value is realistic when comparing it to the canonical Martin b-value of -0.86, the CROZEX *b*-value of -0.99 does imply greater POC flux attenuation and has the effect of predicting a POC flux that is about 10% lower at 200 m, than if a *b*-value of -0.86 was used. Furthermore, caution should be used when deriving a *b*-value with so little data and over such a large depth range.

To summarise, both CROZEX and KEOPS approached the calculation of seasonal POC export from two different approaches. Furthermore, the methods of manipulating the data were different in two major ways. Firstly, the integration depths picked for each study were different, about 70 m for KEOPS and 100 m for CROZEX. Secondly, and probably most importantly, the KEOPS approach for extrapolating POC export to a sequestration depth (200 m) was made with no adjustment. In an attempt to compare seasonal POC export for CROZEX with the KEOPS 200 m POC export estimate, a Martin-style extrapolation was made. When comparing the seasonal POC export estimates from both these projects, these major differences should be considered. Consequently, the 200 m comparison between CROZEX and KEOPS may not be the best approach for comparison. In light of this discussion, the best like-for-like comparison should probably stop at upper-ocean (<100 m) integrations without further manipulation (Table 2).

4 Supply of Dissolved Iron

An underlying hypothesis of studies that investigate the effects of natural Fe fertilisation is that where Fe enrichment is observed there will be increased POC export. Consequently, considerable effort was made to measure DFe distributions and fluxes into the study systems. For CROZEX, Planquette *et al.* (2007) constructed a DFe budget in the bloom and HNLC regions so that the upper ocean, pre-bloom DFe inventory could be estimated. The DFe budget was comprised of vertical mixing, atmospheric deposition, and lateral advection to estimate the upper ocean DFe inventory that built up during winter mixing, and is thus available for phytoplankton growth when the bloom initiates. Atmospheric deposition and vertical mixing were considered to be the same in the bloom and HNLC regions and were estimated to supply 100 nmol Fe m^{-2} d^{-1} and 34 nmol Fe m^{-2} d^{-1} respectively (Charette *et al.*, 2007; Planquette, 2008; Planquette *et al.*, 2011; Planquette *et al.*, 2007). Consequently, horizontal supply was deemed to be the dominant source of additional DFe to the bloom area. The rate of horizontal supply was measured using mixing rates derived from ^{224}Ra and resulted in a flux of 390 nmol Fe m^{-2} d^{-1} (Charette *et al.*, 2007; Planquette *et al.*, 2007). Over a winter period of 100 days and an integration depth of 100 m, the Fe available for the initiation of the bloom is 0.039 mmol Fe m^{-2}. Morris & Sanders (2011) took this calculation further to include continued supply of Fe during the bloom period (58 days), which was estimated to supply an additional 0.023 mmol Fe m^{-2} to the bloom, resulting in a total Fe supply of 0.062 mmol Fe m^{-2} (Table 3).

For KEOPS, DFe supply was determined using the following approach: ΔDFe + DFe vertical supply (Blain *et al.*, 2007; Blain *et al.*, 2008b; Park *et al.*, 2008a). ΔDFe was calculated as the difference between winter and summer profiles of DFe, and vertical supply was calculated by multiplying the vertical diffusivity with the DFe concentration gradient. This approach yields a DFe supply of 0.006 mmol Fe m^{-2} and 0.001 mmol Fe m^{-2} in the bloom and HNLC regions

respectively, or a DFe excess of 0.005 mmol Fe m^{-2} to the bloom region, which is about 12-times less DFe than that estimated for CROZEX. However, this estimate may be on the low side, as a modeling study of the KEOPS bloom suggest that vertical mixing may supply as much as one to two orders of magnitude more DFe than is observed (Mongin *et al.*, 2008). The KEOPS DFe budget was later updated by Chever *et al.* (2010) to include a horizontal supply term, which increased the DFe supply by 0.017 mmol Fe m^{-2} to 0.022 mmol Fe m^{-2} (Table 3). The addition of a lateral supply term results in a greatly reduced (3-fold) difference between of DFe supply when comparing CROZEX and KEOPS. The inclusion of a lateral supply term clearly has a large impact on the DFe budget, however, this should not be unexpected considering that lateral mixing rates are typically many orders of magnitude greater than vertical advection. These subtle differences between seasonal DFe and POC budgets can manifest in a broad range of C:Fe ratios.

The DFe supply to surface waters of the BWZ bloom region has been estimated using several approaches. Dulaiova *et al.* (2009) used short-lived ^{224}Ra to make two estimates of lateral offshore DFe supply to the upper 50 m of the southern Drake Passage. The area to the north of EI had a DFe flux of 114,000 mol Fe d^{-1}, and the area to the north of LI had a DFe flux of 16,000 mol Fe d^{-1}, and. The DFe supply to the area north of EI fertilises a patch of ocean about (62,500 km^2; Figure 3), resulting in an apparent DFe supply of 1,800 nmol Fe m^{-2} d^{-1} (Table 3). The survey of the bloom to the north LI was considered to represent the DFe released from 50 km of shoreline (Dulaiova *et al.*, 2009). Using the satellite image of this region (Figure 3), it can be estimated that high chl-*a* extends approximately 120 km away from the Island resulting in a bloom area of ~6000 km. This results in 2,700 nmol Fe m^{-2} d^{-1}, the highest supply of DFe m^{-2} in any of the study regions discussed here (Table 3).

During a winter time cruise in the EI region, Hatta *et al.* (2012) calculated a DFe flux using a mass-transport approach. By assuming a DFe end-member of 2 nmol Fe L^{-1}, and a geostrophic transport of 0.8 Sv (1 Sv = 10^6 m^3 s^{-1}), an estimated 136,900 mol Fe d^{-1} was released into the upper 100 m of the water column. Scaled to represent only the top 50 m, this equates to 68,450 mol Fe d^{-1}, which is about half the ^{224}Ra-derived flux estimate. In contrast, using the same approach as Hatta *et al.* (2012), two years earlier during the austral summer Measures *et al.* (2012) estimated the DFe flux to be 7,666 mol Fe d^{-1} in the upper 100 m, or 3,833 mol Fe d^{-1} in the upper 50 m. This estimate is about 20-times lower than the estimate of Hatta *et al.* (2012) and is due to a lower DFe end member concentration and a lower geostrophic transport rate largely driven by winter-summer differences in off-shelf mixing (Zhou *et al.*, 2012). Vertical supply of DFe in the Ona Basin is thought to be driven by two processes: vertical mixing and entrainment through deepening mixed layer depths. Individually, these processes are thought to deliver 64 nmol Fe m^{-2} d^{-1} and 5-25 nmol Fe m^{-2} d^{-1} respectively (Frants *et al.*, 2012).

INSERT TABLE 3

4.1 Efficiency of POC Export When Iron is Added

There is now little debate in the scientific community that when HNLC waters are supplied with Fe, naturally or artificially, biological production will increase. This is not to say that Fe can be added at infinitum, as some other nutrient will become limiting as is dictated by Liebig's law of the minimum (de Baar, 1994; Liebig, 1847; Martin, 1991). However, while Fe is the limiting micro-nutrient for biological metabolic function, then the amount of function that the additional Fe causes (beyond the normal control conditions) can be parameterized by the molar

ratio between C and Fe (C:Fe ratio, de Baar *et al.*, 2008). Mathematically it is computed as $C_{bloom} - C_{control} / Fe_{bloom} - Fe_{control} = C_{xs}/Fe_{xs}$. The C:Fe ratio can be calculated to determine the enhancement of C at any stage in the marine C cycle, from initial DIC drawdown, to benthic C export.

The C:Fe ratio for POC exiting the mixed layer has often been referred to as the sequestration efficiency (SE). However, the term 'SE' has almost become synonymous with the amount of C that can be removed through geo-engineering means. Considering that natural Fe fertilisation experiments are not attempts at geo-engineering, we will refrain from using the term SE to express the efficiency that Fe addition has on POC export. Instead, we will simply express the export efficiency in terms of the 'C:Fe ratio' – the extra POC exported for the extra Fe added (C_{xs}/Fe_{xs}) on a mole per mole basis.

The motivation for calculating seasonal budgets for DFe input and POC export is that these numbers can be used to calculate an integrated seasonal C:Fe ratio. For CROZEX, Pollard *et al.* (2009) estimated the C:Fe ratio to be 17,190 at 100 m; however this decreases to 8640 at 200 m after POC export is extrapolated to 200 m using the Martin curve correction discussed in Section 3.2. Following Pollard *et al.* (2009) the CROZEX C:Fe ratio was re-evaluated by Morris & Sanders (2011) but did not significantly change (16790 at 100 m; 8450 at 200 m). The *b*-value of -0.99 has the effect of halving POC export, with which the C:Fe ratio scales linearly, and thus plays a large role in determining the final C:Fe ratio. On the other hand, the KEOPS C:Fe ratio was estimated to be 668,000 (Blain *et al.*, 2007) at 100 m and 200 m. At 200 m, CROZEX and KEOPS C:Fe ratios differ by a factor of nearly 80 (8,450 *vs.* 668,000). This is primarily due to a significantly lower DFe supply for KEOPS, but is further compounded by the

application (or not) of depth-adjusted POC export when normalising to a common depth horizon (Section 3.3).

The re-evaluation of the KEOPS iron budget to include lateral supply of DFe by Chever *et al.*, (2010) increased the total DFe supply by 4.4-times the previous estimate of Blain *et al.* (2007). The increased estimate of DFe supply decreases the C:Fe ratio from 668,000 to 154,000. There is evidence from radium isotopes (van Beek *et al.*, 2008) and other rare earth elements (Zhang *et al.*, 2008) that nearby Heard and McDonald Islands are major sources of DFe and soluble Fe-bearing lithogenic particles. This lateral supply of DFe over the Kerguelen Plateau was a key area of investigation during the recent KEOPS 2 field study (Blain & Queguiner, 2011), which will hopefully help to better constrain the DFe budget in this region. Following the revision of the KEOPS DFe budget, and the discussion of Section 3.3, which suggests that the best like-for-like comparison will only directly compare upper-ocean C:Fe ratios, the ratios now only differ by a factor of about 9 (17,190 *vs.* 154,000) and thus begin to converge to within an order of magnitude. Consequently, depth manipulation of the POC fluxes, whether it is the assumption of no remineralisation between 70-200 m (KEOPS) or the application of a Martin curve (CROZEX), may prove to be less informative for cross comparison than just comparing the upper-ocean mixed layer inventories.

Before CROZEX and KEOPS, the extent of knowledge on Southern Ocean C:Fe ratios was mainly derived from artificial Fe fertilisation experiments. The average C:Fe ratio of all artificial experiments is ~4,300 (de Baar *et al.*, 2005), which is 4-times less than CROZEX and 35-times less than KEOPS. Although there is significant variation in these values, there appears to be a tendency for natural systems to export POC more efficiently. However, there is no

reason to expect the same C:Fe ratio from natural or artificial systems given the difference in the form and delivery of Fe to the system.

Insufficient data prevents the calculation of a seasonal C:Fe ratio for the BWZ bloom. However, enough information does exist to determine an instantaneous C:Fe for the area to the north of LI and KGI, if some assumptions are made about the DFe supply and the POC export in the non-DFe impacted areas for this region. The bloom north of LI is part of a bigger bloom that also extends past KGI (Figure 3). Assuming that DFe is released at the same rate along LI and KGI (~250 km of shoreline), and the bloom area is 30,000 km^2 (Figure 3), then DFe supply is 2,700 nmol Fe m^{-2} d^{-1}. This DFe supply fuels a summer time mean ^{234}Th-derived POC export of 32.3 mmol C m^{-2} d^{-1} (Figure 3). Assuming that the westerly station can be used as a control station, the POC_{xs} for the area is 20.8 mmol C m^{-2} d^{-1} and the C:Fe ratio is 7,700. However, this is likely to represent a lower limit on the C:Fe ratio because the westerly control station is probably an over estimate of true HNLC POC export. If the CROZEX control POC export estimate is used (5 mmol C m^{-2} d^{-1}), a realistic upper limit of 10,200 is calculated for the C:Fe ratio. For comparison, the equivalent instantaneous C:Fe ratio is 25,400 for CROZEX, and 45,000 for KEOPS, which appear to be operating approximately 3-5 times more efficiently than the BWZ region. There are several possibilities for the relatively low BWZ C:Fe ratio. Firstly, it appears that the Antarctic Peninsula is seeding the surrounding waters with much higher concentrations of DFe when compared to CROZEX and KEOPS, a hypothesis that is supported by the observations of horizontal supply (Table 3). Given such high concentrations, one possible explanation is that a significant account of DFe is lost via inorganic scavenging onto particle surfaces. Alternatively, our estimate of summer time POC export (given the relatively small number of stations) may under estimate the export that is typical for this region. The ^{234}Th POC

export measurements were made on the periphery of the bloom core (Figure 3), and may thus under represent the true extent of POC export. Consequently, the BWZ C:Fe ratio (7,700-10,200) should be viewed with caution.

5 Summary & Recommendations

The budgeting exercises presented here aim to highlight the strengths and weaknesses of the various approaches used, and attempt to shed light on the inherent nuances when comparing natural Fe fertilisation studies. Any budgeting exercise will benefit from complete quantification of the inventories involved, and where applicable, the fluxes in and out of these inventories. In the case of a C budget that uses the ΔDIC approach, it is essential to make sure that adequate quantification of the upper-ocean POC and DOC inventories are also made in conjunction with DIC measurements. Furthermore, sufficient data should be collected to adequately estimate air-sea supply of CO_2 and vertical mixing of DIC, which usually require wind speeds and mixing rates respectively. The quantification of a silicon budget can be a more straightforward as there is no gaseous air-sea supply term. However, all the other major stocks (dissolved silicate and biogenic silica) need to be well quantified, in addition to vertical supply of silicate. Lithogenic particles can be a potential source of silicon to the silicon budget. For CROZEX lithogenic supply of silicon was deemed to be negligible (Morris, 2008); however, in other regions such as where the ACC brushes against a continental landmass like the Antarctic Peninsula, the assumption of insignificant lithogenic supply should be tested, and if necessary be taken into account.

Determining the supply of Fe to the mixed layer of a bloom region should be a top priority. Supply terms include atmospheric deposition, and vertical and horizontal supply. Of

these terms, atmospheric deposition is usually determined to be the same across the whole study site and is typically quantified using aerosol and rain samplers. Horizontal supply can be determined by combining an end member concentration of DFe with a geostrophic transport rate, or by combining the concentration gradient with a mixing rate. The latter approach can also be applied to vertical supply. An area that has received little attention in previous studies is the bioavailability of particulate Fe and how this can impact the Fe budget (Boyd & Ellwood, 2010).

A common parameter for determining flux measurements, whether it is DFe, DIC or nutrients, is the determination of vertical and horizontal mixing rates. Mixing rates can be estimated by approaches such as observing the temperature and salinity structure of the water column (e.g. Leach *et al.*, 2011), or through using acoustic Doppler current profilers (e.g. Garabato *et al.*, 2004). However, there is increasingly more interest in using conservative tracers that originate from seabed sediments or the coastline of land masses, which are often the sources of nutrients such Fe. For example, radium isotopes were successfully used to quantify mixing rates in the CROZEX, KEOPS and BWZ studies (Charette *et al.*, 2007; Dulaiova *et al.*, 2009; van Beek *et al.*, 2008), and is currently contributing to trace metal flux calculations for the GEOTRACES program (Morris *et al.*, 2012a; Morris *et al.*, 2012b). Sampling for radium in the open-ocean requires hundreds to thousands of litres of seawater, which has limited sample resolution and hence its usefulness in the past. However, recent methodological advances in extracting radium from seawater, coupled with improved *in situ* sampling technology, are making this tracer ever more accessible and useful (Henderson *et al.*, 2012; Morris *et al.*, 2011).

A major goal of large-scale Fe fertilisation studies is to generate a seasonal estimate of both Fe supply and POC export. Furthermore, there is a need to be able to make like-for-like comparisons between different studies if meaningful conclusions are to be made. Consequently,

great care and consideration needs to be given to the integration depth at which this done and how POC export is normalised to a particular depth. For example, one should be very clear about the goal of any study comparison. If the query is difference in POC export efficiency between studies, in the form of a C:Fe ratio, then estimating this at the base of the mixed layer is probably most appropriate. However, if the question is of sequestering POC on a longer than seasonal time-scale, which is typically below the deep winter mixed layer, then extrapolating the C:Fe ratio to this depth can give rise to increased uncertainty in any conclusions and cross comparisons. Given that the twilight zone is the depth zone of greatest variability in POC export (Buesseler & Boyd, 2009), future studies should make this an area of intense scrutiny. Things to consider include, thorough depth resolution of the C:Th ratio (Buesseler *et al.*, 2006), and where possible an assessment of the rate of remineralisation in this zone, for example from neutrally buoyant sediment traps or by a proxy such as Ba_{xs}. (Buesseler *et al.*, 2007b; Jacquet *et al.*, 2008; Salter *et al.*, 2007)

Natural Fe fertilisation experiments have proven to be an immensely powerful approach for investigating the interaction between Fe and C. Natural systems deliver Fe slowly and chronically to a relatively large patch of ocean, which offers several advantages over artificial experiments. First and foremost, natural systems remove the necessity, and associated logistics, of dumping Fe into the ocean. In 2009, the most recent artificial Fe fertilisation experiment, LOHAFEX, was delayed for two weeks while a dispute was settled between environmentalists, politicians, and scientists over the legitimacy of the experiment. The row was sparked by a 2008 United Nations moratorium that decided to limit Fe fertilisation to small-scale scientific research studies within coastal waters (Editorial, 2009). Given the difficulties encountered by LOHAFEX, it is easy to see the benefits of using naturally Fe fertilised systems to investigate Fe

and C biogeochemistry. From a scientific perspective, natural systems can remove some of the problems that have been encountered during artificial experiments, for example one fertilised patch during Southern Ocean Iron Experiment (SOFeX) was eventually subducted deeper into the water column, which was an unintended consequence that limited scientific interpretation (e.g. Bishop *et al.*, 2004; Buesseler *et al.*, 2005; Hales & Takahashi, 2012). Even with all the research to date, and the leaps forward in understanding the role that iron has on the marine carbon cycle, there is still a need for further research to help reduce uncertainty and increase our understanding. In some cases this may even warrant further Fe enrichment studies, if only to eliminate it as a viable geo-engineering strategy. In the spirit of advancing scientific understanding, the ISIS (In-Situ Iron Studies) Consortium was established in 2010, which aims to promote the use of well-designed experiments and modelling studies to resolve the impact of Fe fertilisation on marine ecosystems (isis-consortium.org). Additionally, to ensure that the maximal benefits of observational data-sets are realised, there should be continuous discussion and collaboration between modellers and observational oceanographers at all stages of any project. Modelling approaches can offer critical insights into how the system is functioning and can offer direction on how to improve and focus sampling strategies for future field studies.

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Figure 1. Satellite image of the CROZEX study region with major hydrographical features (Modified from Pollard *et al.*, 2009). Abbreviations: Agulhas Return Current (ARC), SubAntarctic Front (SAF).

Figure 2. Satellite image of the KEOPS study region with major hydrographical features. (Modified from Park *et al.*, 2008b)

Figure 3. Satellite image of chl-*a* (μg L^{-1}) for the BWZ study region during the time of the 2006 ALMR cruise Modified from Dulaiova *et al.*, 2009. Values are ^{234}Th-derived POC export (mmol m^{-2} d^{-1}) integrated to 100 m, and the thick black lines mark the sampling locations. The red box defines the EI bloom area discussed by Dulaiova *et al.* (2009). The solid-lined black box defines a bloom area of 50 × 120 km and is assumed to be the area fertilised by the 50 km of LI shoreline that Dulaiova *et al.* (2009) surveyed. The dashed-lined black box defines an additional 200 × 120 km, which is assumed to be fertilised from the remainder of LI and KGI. Abbreviations: Livingston Island (LI), King George Island (KGI), Elephant Island (EI).

Table 1. Projects that have targeted naturally iron fertilised regions in the Southern Ocean

Project	Region	Lat, Long (°)	Cruise number & Date	Primary sources
CROZEX	Crozet Plateau	44°S, 50°E	D285: Nov-Dec 04 D286: Dec 04-Jan 05	(Pollard *et al.*, 2009); DSRII 54(18-20)
KEOPS	Kerguelen Plateau	50°S, 73°E	MD145: Jan-Feb 05	(Blain *et al.*, 2007); DSRII 55(5-7)
BWZ	Antarctic Peninsula, Southern Drake Passage	61°S, 57°W	LMG0402: Feb-Mar 04 AMLR: Jan-Feb 06 NBP0606: Jul-Aug 06	This issue
Discovery 2010	South Georgia Islands	56°S, 42°W	JCR161: Oct-Dec 06 JCR177: Dec 07-Feb 08 JCR200: Mar-Apr 09	DSRII 59-60
DynaLiFe	Pine Island Polynya, Amundsen Polynya	74°S, 105°W 73°S, 118°W	NBP0901: Jan-Feb 09	DSRII 71-76
KEOPS 2	Kerguelen Plateau	50°S, 73°E	MD188: Oct-Nov 11	(Blain & Queguiner, 2011)

Table 2. Summary of seasonally integrated POC export for KEOPS and CROZEX

	KEOPS	CROZEX
Approach	ΔDIC+DICvert-DOC-POC	Silicon-scaling
Upper ocean integration depth	70 m (+Fe); 68 m (-Fe)	100 m (+Fe & -Fe)
Upper ocean POC export (mmol m^{-2})	5047 (+Fe); 1730 (-Fe)	1437 (+Fe); 396 (-Fe)
Martin-style correction	No	Yes (*b*-value = -0.99)[a]
200 m POC export (mmol m^{-2})	5047 (+Fe); 1730 (-Fe)	723 (+Fe); 199 (-Fe)
POCxs (mmol m^{-2})	3317 (70 m & 200 m)	1041 (100 m); 524 (200 m)

[a] See Pollard *et al.* (2009) for details on how the *b*-value was calculated

Table 3. Summary of DFe budgets for CROZEX, KEOPS and BWZ

	CROZEX[a]	KEOPS[b]	BWZ (EI)[c]	BWZ (LI)[d]
Bloom area (km^2)	90,000	45,000	62,500	6,000
Integration depth (m)	100 (+Fe & -Fe)	70 (+Fe); 68 (-Fe)	50	50
Period of winter mixing (days)	100 (+Fe & -Fe)	90 (+Fe & -Fe)	ND	ND
Bloom duration (days)	58 days (+Fe & -Fe)	75-105 (+Fe & -Fe)	ND	ND
Atmos. DFe supply (nmol m^{-2} d^{-1})	100 (+Fe & -Fe)	2 (+Fe & -Fe)	ND	ND
Vertical DFe supply (nmol m^{-2} d^{-1})	34 (+Fe & -Fe)	31 (+Fe); 4 (-Fe)	69-89 (+Fe)	ND
Horizontal DFe supply (nmol m^{-2} d^{-1})	390 (+Fe); 0 (-Fe)	189 (+Fe); 0 (-Fe)	1800 (+Fe); 0 (-Fe)	2700 (+Fe); 0 (-Fe)
Total DFe supply (mmol m^{-2})	0.083 (+Fe); 0.021 (-Fe)	0.023 (+Fe); 0.001 (-Fe)	ND	ND
DFe_{xs} supplied to bloom (mmol m^{-2})	0.062	0.022	ND	ND

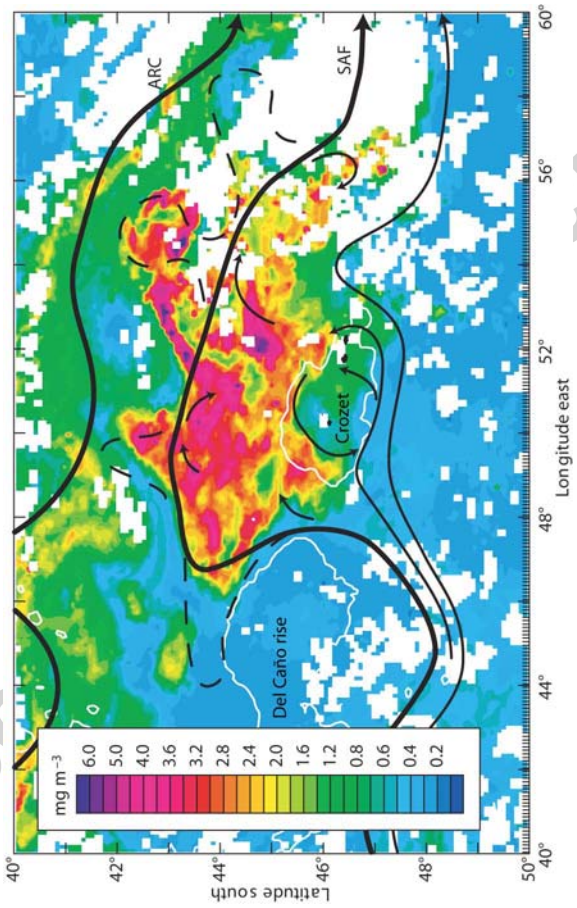
ND means 'not determined'

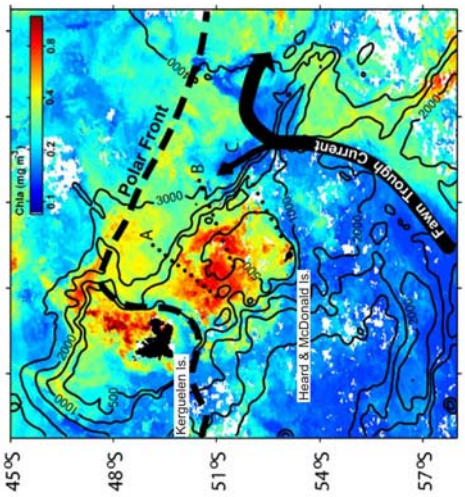
[a] Summary of DFe budget presented in Morris & Sanders (2011) with primary sources being Planquette *et al.* (2007), Charette *et al.* (2007), Pollard *et al.* (2009), and Planquette *et al.* (2011)

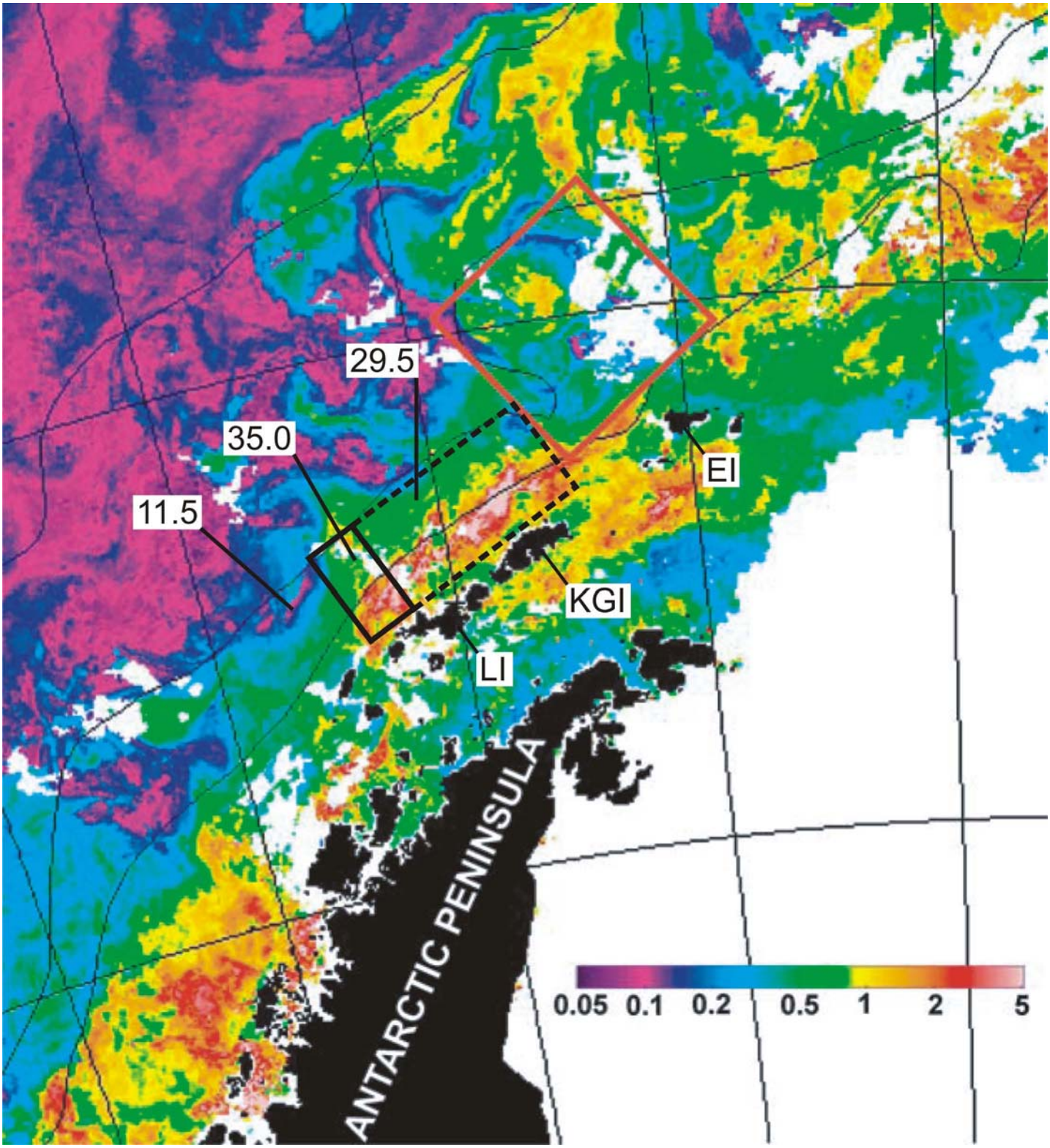
[b] Summary of DFe budget used in Chever *et al.* (2010) with primary sources being Blain *et al.* (2007; 2008b), and Park *et al.* (2008a)

[c] Horizontal supply DFe of and bloom area is taken from Dulaiova *et al.* (2009), and vertical supply is from Frants *et al.* (2012).

[d] Horizontal supply of DFe and bloom area is taken from Dulaiova *et al.* (2009). Bloom area is the solid-lined black box in Figure 3.



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