Fluxes of particulate iron from the upper ocean around the Crozet Islands, a naturally iron fertilized environment in the Southern Ocean

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Abstract

Despite a large macronutrient reservoir, the Southern Ocean has low levels of chlorophyll, primarily due to low iron availability. Exceptions to this situation are island systems where natural terrestrial iron inputs allow the development of large blooms. Particulate Organic Carbon (POC) and particulate (labile and refractory) iron analyses were performed on large (>53 µm) particles collected at the base of the mixed layer within such a system - the Crozet Islands - and in adjacent high nutrient low chlorophyll (HNLC) waters. Biogenic iron was obtained by removal of estimated lithogenic Fe from the total Fe present. We combine these data with ^{234}Th measurements to determine downward particulate Fe fluxes. Fluxes of Fe ranged from 4 to 301 nmol m^{-2} d^{-1} (labile), not detectable to 50 µmol m^{-2} d^{-1} (biogenic) and from 3 to 145 µmol m^{-2} d^{-1} (total) and on average were ~four times larger below the highly productive, naturally iron-fertilized region than below the adjacent HNLC area. Downward labile iron fluxes are close to the sum of dissolved terrestrial, atmospheric and upwelled iron calculated from the Planquette et al. (2007), model. Refractory iron fluxes are approximately two orders of magnitude larger and these can only have come from particles advected from the plateau itself. The "biogenic Fe", is a substantial fraction (0-76, mean 23 %) of the total particulate Fe to the north of the islands. The origin of this Fe pool must be dominantly biological conversion from the lithogenic fraction, as other supply terms including aeolian, deep mixing and lateral advection of dissolved Fe are inadequate to account for the magnitude of this Fe. Inclusion of the offshore biologically available fraction of the lithogenic iron flux is therefore required to calculate fully the yield of carbon exported per unit iron injected.

1. Introduction

The biological carbon pump in the ocean is a significant term in the global carbon cycle which transports approximately 10 GT C yr^{-1} (De La Rocha, 2003) from the surface waters to the ocean interior, mainly in the form of settling particles (Boyd and Trull, 2007). The organic material in these particles is ultimately derived from phytoplankton production in the sunlit upper ocean. For the majority of these surface waters phytoplankton production is limited by the macronutrients nitrate and phosphate, hence where these nutrient levels are elevated through seasonal mixing or upwelling and light levels are adequate, high production and associated increased carbon export are anticipated.

However in some regions this correlation breaks down and macronutrient levels are high in surface waters yet phytoplankton production is low. This HNLC (high nutrient, low chlorophyll) condition is most pronounced in the Southern Ocean (SO), the largest global repository of unused macronutrients. Despite this low production the SO has a potential role in regulating atmospheric carbon dioxide (Sigman and Boyle, 2000) as well as possibly contributing up to 30% of total ocean biological carbon flux (Schiltzer, 2002) and a more complete utilisation of the available macronutrient pool could increase this fraction.

A primary hypothesis to explain the HNLC condition of the SO has been iron limitation of primary production (e.g. Martin and Gordon, 1988; Martin, 1990; Martin et al., 1990, .de Baar et al., 1995; Fitzwater et al., 2000; Sedwick et al., 1999). Several artificial iron addition experiments have demonstrated enhanced biological activity (Boyd et al., 2007) and short term drawdown of CO_2 (Watson et al., 2000) upon addition of iron indicating a key role for this nutrient in regulating biological processes in this region. The present view is that iron is indeed the primary limiting nutrient (Boyd et al., 2007), and therefore understanding the supply to and cycling of this element in the upper ocean is fundamental to understanding the carbon pump in HNLC waters.

To date, this understanding is rather limited. The most complete iron budget available for HNLC waters, the Fe-Cycle study in the open Southern Ocean (Frew et al. 2006) indicates that Fe/C ratios increase with depth below the mixed layer. This suggests that Fe is preferentially retained within sinking particles compared to carbon, unlike the macronutrients N and P (Christian et al., 1997). This may result from either a preferential recycling of carbon relative to iron or to a preferential recycling of iron in the photic zone itself with any iron released from particles as the organic carrier phase is recycled then being rapidly taken up by the living organisms or particulate matter present. The preferential loss of carbon relative to iron from sinking matter means a need of external inputs of Fe for a sustained downward flux of carbon to occur.

External inputs of Fe are thought to be mainly atmospheric (Cassar et al., 2007; Jickells et al., 2005), or supplied through mixing with deeper Fe enriched waters (Elrod et al., 2004). An additional term is the offshore advection of dissolved iron rich water resulting from sediment water interactions in the nearshore zone (Lohan and Bruland, 2008). Within the Southern Ocean downstream of island systems are areas of seasonal high primary production within the otherwise HNLC waters. Here limitation of phytoplankton growth has been removed by natural Fe fertilisation through inputs from the islands and adjacent plateaux, as demonstrated for the Kerguelen (Blain et al., 2001, 2007, 2008) and Crozet (Pollard et al., 2009, Planquette et al., 2007) island systems.

The dissolved iron supply to the study area was calculated by Planquette et al. (2007) using a simple numerical model derived from bloom size, island/plateau dimension and morphology, observed gradients of dissolved iron and radium isotopes in the ocean, plus estimates of atmospheric and upwelling and horizontal fluxes. However, this analysis did not include lithogenic material transported horizontally.

Recently Lam et al. (2006) have suggested that the lateral transport of particulate iron may be a significant supply term over hundreds of kilometres, a surprising result given the inherently high density of mineral particles, and the expectation that they would be readily removed to deeper waters via gravitational sinking. Whether this transport mechanism is significant is a function of both the magnitude of this flux and of the bioavailability of Fe contained within it.

Additionally Frew et al. (2006) argued on the basis of changes in biogenic iron (BioFe) to total Fe between atmospherically introduced particles and those particles collected in the water column, that release of Fe from what have previously been regarded as refractory lithogenic phases, and the incorporation of this material into biogenic matter must occur. Southern Ocean island systems provide good models to test the significance of both the magnitude and bioavailability of lithogenic iron supply.

The focus of this study is on the removal processes of iron from the upper water column using sinking particles greater than 53 µm. Fractions less than 53 microns will play a crucial role in Fe recycling but they could not be investigated properly during the CROZEX project. CROZEX was conceived to test the hypothesis that when HNLC water moves

North across the shallow Crozet Plateau it picks up Fe en route and induces an increase in planktonic production and carbon export in the fertilised area.

In this paper we use data from this recent oceanographic campaign to address two key unknown terms: 1) the magnitude of vertical fluxes of lithogenic particles in the Crozet system in relation to horizontal dissolved Fe fluxes and other Fe inputs and 2) the potential for conversion of lithogenic Fe in the upper water column to biological Fe.

Thorium-234 depletions and Fe/Th ratios in sinking particles greater than 53 µm are used to evaluate the downward flux of lithogenic, BioFe and labile forms of iron, in order to investigate the magnitude of these fluxes, relative to the overall lateral advection of dissolved Fe from the island plateau to the surrounding Crozet region.
The comparison of fluxes and information on different Fe pools is then used to investigate the potential for biological uptake of Fe from lithogenic particles.

2. Methods

2.1 Regional setting, bloom characteristics and sampling sites

The volcanic archipelago of the Crozet Islands is located on a shallow Plateau on the eastern flank of the Southwest Indian Ridge in the high-nutrient low chlorophyll (HNLC) Southern Ocean. This archipelago (Figure 1) comprises two main islands, “Île de la Possession “and “Île de l’Est” in the east and three smaller islands on the plateau 100 km to the west.

Every year, a strong phytoplankton bloom occurs north of the Crozet Plateau due to natural iron fertilization processes (Pollard et al., 2007a). The bloom is located in the Polar

Frontal Zone with macronutrients present in non-limiting quantities at the end of the winter (Banse, 1996; Boyd et al., 2007). The Sub Antarctic Front (SAF) constrains the annual bloom to the west and north. The high chlorophyll zone is under the influence of a weak northerly surface flow that passes over and past the Crozet Plateau and Islands (Pollard et al., 2007b). Thus south of Crozet is "upstream", north of Crozet is "downstream" of the islands. Between mid November and early December 2004, the bloom in the northerly region had chlorophyll concentrations reaching up to 5 µg Chlorophyll L^{-1} (Seeyave et al., 2007) before collapsing. A secondary bloom developed in mid-January 2005 and was dominated by a microflagellate community. In the HNLC southern sites (M2 and M6 stations) a small bloom (0.7 µg Chla L^{-1}) occurred in late December, but chlorophyll levels were generally low (< 0.5 µg L^{-1}) and similar to background Southern Ocean levels.

<Figure 1>

Sampling sites (Figure 1) considered in this study were occupied during both legs of the CROZEX cruises D285 and D286 (Pollard et al., 2007a). Particulate samples were collected using high volume *in-situ* Stand Alone Pump Systems (SAPS, Challenger Oceanic Ltd.) deployed on plastic coated cables and mounted with cleaned 53 µm nylon filters. Two SAPS were deployed simultaneously; one for ^{234}Th and POC and one for trace metal measurements and each typically filtered ~2000 L. Details of each deployment can be found in Table 1 and in Morris et al. (2007).

2.2. Trace metal and POC analyses

Details of the trace metal procedures, including precision, blanks and accuracy can be found in Planquette et al. (2009). In brief, each sample collected from the SAPS dedicated to trace metal analysis was analyzed for the "labile" (HAc-Fe) fraction (extracted with 25%

acetic acid for 2 hours at room temperature; Hurst and Bruland; 2007) and then the more refractory fraction (PFe, fully digested with aqua-regia and hydrofluoric acid at 200°C). Digest solutions were analysed using an Agilent 7500ce ICP-MS with accuracy established using Certified Reference Materials (Planquette et al., 2009). Two fractions of Fe in the particles can therefore be determined: 1) the total Fe content, 2) the acetic acid labile leached fraction. Key analytical parameters (blanks, recovered, CRM results) are given in Table 1.

Sub-samples from the ^{234}Th SAPS were also taken for POC analysis. Particles were rinsed off the 53 µm nylon mesh and the bulk sample then split using a splitter. Individual splits were then filtered onto pre-weighed and pre-combusted 25 mm diameter GF/F filters and stored at -20 °C before analysis on a Carlo-Erba NA-1500 elemental analyzer, using standardization with acetanilide. The whole procedure is described in detail in Planquette et al. (2009) and Morris et al. (2007).

2.3. ^{234}Th analysis and export of POC and Fe

^{234}Th analysis – The radioactive element ^{234}Th is the daughter isotope of naturally occurring ^{238}U, which is conservative in seawater and proportional to salinity (Chen et al. 1986). ^{234}Th has been generally used to estimate the amount of photosynthetically fixed CO_2 exported to the deep ocean (Buesseler et al. 1992, 2006) as ^{234}Th tends to adhere to particles in the water column. In the particle rich mixed layer, ^{234}Th is scavenged onto particles, which can sink and exit the upper ocean. ^{234}Th removed by sinking particles results in a radioactive disequilibrium between ^{238}U and ^{234Th} that can be used to quantify

the rate of carbon export from the surface ocean, when combined with data on the ratio of POC to particulate ^{234}Th activity. Whilst previous studies (e.g. Savoye et al., 2008) reported some variations in the POC to Th ratio among different size fractions, the data presented here are internally consistent: ^{234}Th, POC and Fe were collected with the same pump types, on the same filter, at the same time and at the same depth so that the same particle size has been sampled. Furthermore, obvious swimmers have been removed right after recovery, minimizing any artifact on the ^{234}Th to POC ratio.

Total (dissolved and particulate) ^{234}Th activities in seawater were measured using the MnO_2 precipitation method described by Rutgers van der Loeff and Moore (1999), which is similar to the procedure used by Turnewitsch and Springer (2001) and Thomalla et al. (2006). Details of these measurements can be found in Morris et al. (2007).

POC and particulate iron export – Morris et al. (2007) used the ^{234}Th flux and C:Th ratio to derive the downward POC flux using the relationship:

$$POC_{flux} = (POC:Th) * P$$

where *POC flux* is the quantity of POC (μmol m^{-2} d^{-1}) falling out the surface ocean, *(POC:Th)* is the ratio of POC to ^{234}Th (μmol dpm^{-1}) on the large size class of particles (>50 μm), and *P* is the integrated ^{234}Th flux (dpm m^{-2} d^{-1}) calculated from the following equation (Buesseler et al., 1992; Cochran et al., 2000; Morris et al., 2007):

$$P = \int_0^z \lambda(Au - At)dz$$

where λ is the decay constant of ^{234}Th (d^{-1}), A_u is the ^{238}U activity (dpm m^{-3}), A_t is the total ^{234}Th activity (particulate and dissolved) and z is the depth of the overlying water column.

It is then possible to calculate the downward fluxes of particulate Fe (HAc-Fe_{flux} and PFe_{flux}) in both phases using the relationship:

$$PFe_{flux} = POC_{flux} * (PFe:POC)$$
$$HAc\text{-}Fe_{flux} = POC_{flux} * (HAc\text{-}Fe:POC)$$

where *(PFe:POC)* are the molar ratios of PFe/POC and HAc-Fe/POC respectively.

3. Results: Carbon and Particulate iron exports

3.1. Total particulate Fe export:

Total particulate Fe flux (PFe_{flux}) values are reported in Table 2 and shown in Figure 2. The largest particulate iron export was found at Station M3.5, reaching 145 μmol m^{-2} d^{-1}. The lowest value was obtained in the South at Station M2 (2.7 μmol m^{-2} d^{-1}). There is a clear meridional gradient in the data (Figure 2) with higher downward fluxes north of the islands. On average the PFe_{flux} was 40.5 μmol m^{-2} d^{-1} in the north and 7.3 μmol m^{-2} d^{-1} in the south.

The downward Fe fluxes calculated here for HNLC waters to the south of the Crozet Islands are of similar magnitude to the estimated total particulate iron fluxes given by Bowie et al. (2001) during the artificial iron addition experiment SOIREE (5.2 μmol m^{-2} d^{-1}), by Martin (1990) in the Drake Passage (2.4 μmol m^{-2} d^{-1}) and by

Martin and Gordon (1988) in the HNLC Subarctic Pacific (2.0 µmol m^{-2} d^{-1}). However, these PFe fluxes north of the Crozet plateau are up to 2 orders of magnitude higher than downward fluxes obtained by Frew et al. (2006) in sub-Antarctic waters southeast of New Zealand using sediment traps collecting particles greater than 0.4 µm at 80 and 120 m depth (range 0.22 – 0.55 µmol m^{-2} d^{-1}). Their POC export data ranged from 2.09 to 2.51 mmol m^{-2} d^{-1} which is about 10 times lower than the POC exports measured around Crozet. As organic C fluxes from the mixed layer to depth in the present study are generally higher, higher downward particulate Fe fluxes appear reasonable. In a subsequent section we compare our results with those of the FeCycle study (Boyd et al., 2005).

<Table1>

3.2. Labile and biogenic Fe export:

As pointed out by Wells et al. (1991, 2000) and others and as discussed in Berger et al. (2008), finding a leaching method that release the Fe in particulate matter which is associated with or available to the wide range of organisms in the ocean is a non-trivial problem. A variety of approaches have been taken ranging from the use of different acids, often in combination with reducing agents, to enzymatic dissolution. The approach instigated by Chester and Hughes (1967) for deep sea sediment of 25% acetic acid and 1M hydroxylamine hydrochloride has been used frequently, often in a simplified and less aggressive form for oceanic particles, in which the reducing agent is omitted. Until recently this acetic acid leach as applied here has been taken to provide an estimate of environmentally available metals (e.g. Landing and Bruland 1987, Statham et al.1993).

The recent work of Berger et al. (2008) has shown however that without the reducing agent and heating, only a limited release of iron from biological material will result. Additionally Hurst and Bruland (2007) showed that for biological material grown in Fe-57 amended incubation experiments, not all the isotope was recovered from the biological phase by use of the 25% acetic treatment alone. The 25% acetic acid method used here may therefore underestimate the total biogenic metal present in the samples analysed.

An alternative approach is to estimate Biogenic Fe (BioFe) by removing from a total Fe value the iron associated with lithogenic phases through use of the Al concentration in the sample and an appropriate value of Fe:Al for crustal materials. This approach was used in the FeCycle study of Frew at al. (2006), and has been used to calculate BioFe for the Crozet samples described here using an Fe:Al molar ratio of 0.51 mol.mol^{-1} (Gunn et al., 1970).

The Biogenic Fe approach is dependent on a range of factors including the chosen Fe:Al ratio, and the assumption that processes other than biological assimilation, such as adsorption, precipitation on the surface and the presence of other non biological Fe containing phases, are not significant. Both of the approaches described above therefore have limitations and a more appropriate estimate would be expected to lie between these two. The values found for HAcFe:C are low (0.08-62, mean 1.8 μmol.mol^{-1}) compared to the values given by Twining et al. (2004) for diatoms of circa 11-48 μmol.mol^{-1}, and are consistent with this leach removing only a fraction of the biologically associated Fe.

The best test for the ability of the biogenic iron calculation to produce reasonable results is to apply it in a region where the lithogenic fraction is large. The BioFe fraction in samples collected very close to the islands in the near shore lithogenically dominated Baie Americaine (Planquette et al., 2009) represents only about 2% of the total with a BioFe:C ratio of about 590 µmolFe/molC. This is close to BioFe:C ratios N and S of the islands. Thus the high lithogenic fraction does not seem to bias the BioFe fraction and we therefore conclude that the BioFe approach is a useful indicator of biological Fe plus other labile fractions associated with the particles.

The labile Fe fluxes (Figure 2) therefore may be considered as an estimate of the "potentially environmentally reactive" fraction (Landing and Bruland, 1987) of metals, whilst the BioFe fraction represents the maximum estimate of biologically associated Fe in the particles (Table 2).

< *Figure 2*>

The highest export of labile iron occurred at Stations M3.2 and M3.8 (November 2004 and January 2005 respectively) reaching ~301 nmol m^{-2} d^{-1}. Fluxes of labile iron show a similar latitudinal pattern to those of total Fe and were overall greater in the north than in the south by a factor of ~4. On average 97 nmol m^{-2} d^{-1} of labile iron were exported in the north, whereas only 26 nmol m^{-2} d^{-1} were exported in the south.

This downward labile Fe flux lies within the range of horizontal flux values for dissolved Fe obtained by Planquette et al. (2007), 66-390 nmol m^{-2} d^{-1}, although a direct comparison is not possible because of the varied mechanisms for organism acquisition of Fe and association with particles leaving the upper ocean. Labile particulate iron fluxes may be linked to the succession of phytoplankton communities during the survey documented by Poulton et al. (2007). For example, until the last occupations of Station M3 (M3.7 and M3.8), a mixed diatom community dominated the phytoplankton biomass (Poulton et al., 2007), reaching up to 80% of the biomass at the beginning of the survey. The diatom species *Thalassionema nitzchoides* dominated the bloom in the surface waters at all these stations with the noticeable exception of M3.3, M3.7, M3.8 where *Phaeocystis antarctica* dominated (Poulton et al., 2007).

During SOIREE, Bowie et al. (2001) reported biogenic iron fluxes ranging between 19 and 47 nmol m^{-2} d^{-1} derived from exported POC measured on 70 µm filters. Most of the values obtained in the present work fall within this range, except for a few occasions (Stations M3.2; M8E, M3.4, M3.7 and M3.8) where export was greater than 100 nmol m^{-2} d^{-1}. These higher values are consistent with an island source of Fe to the waters north of Crozet, fertilization of the phytoplankton there and subsequent export of Fe.

Biogenic Fe concentrations in particles exiting the upper ocean are higher by 1-2 orders of magnitude than the labile Fe fraction, and the downward fluxes also reflect these differences (Table 2). On average the downward fluxes of BioFe are 3.5 times greater to the north of the islands than to the South, inline with the other fractions of Fe determined. Given our present knowledge, this biogenic fraction represents our best estimate of Fe that has been accessed by biota.

4. Discussion

4.1. Evidence for release of Fe from lithogenic phases by biota

The ratio of BioFe to total Fe in particles is given in Table 2 and provides an indicator of non lithogenic Fe present in particles leaving the mixed layer. The very high values of BioFe:total Fe found at several locations around Crozet requires that the Fe in excess of lithogenic Fe be derived from either 1) dissolved Fe inputs that are taken up into particles from solution, and/or 2) from release of Fe from lithogenic phases by biota.

To test mechanism 1) the fluxes of Planquette et al (2007) derived from inputs of dissolved Fe to waters to the north of the Crozet Islands can be compared to fluxes of BioFe (i.e. non lithogenic Fe) leaving the water column determined here. Lateral dissolved, upwelling and atmospheric dissolved Fe fluxes to the north of Crozet sum to 362 (average) and 551 (maximum) nmol m^2 d^{-1}. This compares with the average BioFe flux of 12.4 μmol m^2 d^{-1}, and so these dissolved sources can only account for a maximum of 4.4% of the BioFe flux, with the highest BioFe fluxes being 2 orders of magnitude larger than the Planquette et al. (2007) flux.

To the south of the islands in HNLC waters, maximum atmospheric and upwelling sources of dissolved Fe (161 nmol m^2 d^{-1}) represents a contribution of 4.4% of the average BioFe flux (3.66 μmol m^2 d^{-1}). Thus the known fluxes of Fe into the mixed layer are ca. 20 times lower than the BioFe fluxes leaving this layer. The only significant source of Fe that can provide this extra BioFe flux from the upper ocean is the lithogenic pool i.e. source 2) above. Thus in waters both upstream and downstream of the islands the data argue for significant conversion of lithogenic to biogenic Fe.

The release of Fe to biota via conversion of litho to BioFe has been previously suggested by Lam et al. (2006, 2008), Frew et al. (2006), and more recently Cullen et al. (2009). The present work strongly supports this hypothesis and the data also suggests that the BioFe derived from lithogenic iron has a longer residence time in the upper ocean than does the lithogenic iron which is not accessed by biota. This can be demonstrated by considering a water parcel in the upper mixed layer containing lithogenic material and growing phytoplankton with transfer of Fe from lithogenic material to cells. If all this particulate material were to directly settle, the total amount of Fe and Al exported would be the same as in the original lithogenic material (although in different phases), and the use of Al/Fe ratios to estimate lithogenic iron would not allow the diagnosis of a biogenic fraction.

Therefore there must be some mechanism allowing build up of Fe within the mix of biogenic and lithogenic material. The most probable scenario is for pulses of lithogenic particles to be transported laterally to a zone with cells stressed by Fe depletion, with active uptake from lithogenic particles to biota occurring, followed by settling and loss of dense Fe depleted lithogenic particles from upper water column. Cells containing BioFe derived from lithogenic material remain in the mixed layer, and as the population grows, further Fe is needed and is obtained from a new lateral supply of lithogenic Fe.

Additionally Fe in phytoplankton that are recycled early in the plankton bloom will be recycled within the mixed layer as the plankton assemblage changes its dominant taxonomic group. When the bloom reaches a senescent stage, and large scale loss of biogenic material occurs from upper water column, BioFe removal within settling biomass and aggregates would be expected, as well as any Fe in lithogenic phases present at this time.

Lam et al. (2006) argue on the basis of observing enhanced phytoplankton biomass in association with high levels of small iron rich particles, that lithogenic particles must be bioavailable to some degree. Where significant aggregation occurs and lithogenic particles are present, Fe “hot spots” are seen (Lam et al., 2006) would be seen. In the above scenario, the fraction of BioFe relative to lithogenic iron found in sinking particles collected below mixed layer would depend on the stage of the bloom and the supply of particles. This will be variable and thus explains the wide range of BioFe:total Fe values observed here.

4.2 Impact of Fe sources on Fe:C ratios.

In this section we consider the relationship between BioFe and POC and the implications a source of Fe from lithogenic material has for Fe uptake by phytoplankton in the naturally fertilised zone to the North of the Crozet Islands, relative to HNLC waters to the south.

A comparison is made with reported BioFe and POC data with Fe:C molar ratios from the SOFEX and Fe Cycle studies and also with data derived from incubation studies during Crozex (Figure 3).

An intracellular ratio of ~11 μmol mol^{-1} before Fe addition and a ratio varying from 16 to 48 μmol mol^{-1} after iron addition were reported for diatoms collected in Antarctic waters during the SOFEX program (Twining et al., 2004).

<Fig. 3>

Most of the particulate material in the surface waters to the north of the islands are of biological origin (Planquette et al., 2009) and an estimate of BioFe: C in the mixed layer specific to the Crozet region of 249 Fe:C μmol mol^{-1} can be obtained (Table 3) from Moore et al. (2007). This value comes from onboard culture experiments designed to address biological responses to iron addition in which Fe is added and POC production is measured. The mean value obtained from the Moore et al. (2007) data is high relative to reported values for diatoms in the Southern Ocean (Twining et al., 2004, 11-48 μmol mol^{-1}) however potential unquantified adsorption of Fe to the bottle walls during incubation render these maximum values. Also, phytoplankton assemblages may differ from the two regions and this can also account for the difference observed.

The above values of BioFe:C, which are all lower than 250 μmol mol $^{-1}$ compare to average values around Crozet of 689 and 314 μmol mol^{-1} respectively north and south of the islands.

Within the Crozet system there is a meridional gradient: BioFe:C values to the north of the islands show extreme variability between 2260 and not detectable μmol mol^{-1} (Table 2). The station with the lowest BioFe: C ratio was M8E which had sharp contrasts in phytoplankton population relative to the adjacent M8W and most other stations sampled. The overall variability in BioFe:C reflects the combined effects of temporal and spatially variability in both transport of Fe from the islands, and removal of Fe from the upper water column with biological debris, in addition to there being secondary inputs from upwelling and atmospheric deposition (Planquette et al., 2007). However, it is evident that downstream of the islands (to the north) on average more Fe is available to biota on a per unit carbon basis (assuming most Fe is locked up in biota, or adsorbed onto it in the upper ocean), and this high BioFe:C ratio is reflected in the material exiting the upper ocean.

Frew et al. (2006) observed during FeCycle Fe:C ratios increasing with depth (in the range of 83-140 μmol mol^{-1} BioFe:C) due to C remineralisation and re-adsorption of the released Fe. However, the Fe Cycle study did not have data just below the mixed layer (~40m depth) but at the greater depths of 80 and 120m. In the present work, BioFe: C ratios are much greater at the base of the mixed layer than at any of the depths at the FeCycle site. This in part reflects the truly isolated nature of the FeCycle site and also the significant inputs of Fe to the north of the Crozex study area that stimulates primary production and increases the carbon flux. Even the stations to the south of the Crozet Islands in waters classified as HNLC have higher vertical fluxes of BioFe than at FeCycle suggesting either some leakage of Fe from the island system to the south or a regional difference in inputs of Fe from aeolian and upwelling sources. Despite caveats in comparing BioFe:C data with Twining et al. (2004) and Frew et al. (2006), the proposed recycling will explain the observed data and apparent behavior of iron, showing that there must be an input of Fe from the lithogenic fraction associated with a biological conversion.

4.3 The balance of iron input and removal fluxes

The objective of this section is to establish whether the offshore transfer of Fe in lithogenic particles is a significant source relative to other mechanisms by which Fe reaches the waters around the Crozet islands. The work of Lam et al. (2006) demonstrates that this delivery mechanism occurs, as does work by Cullen et al. (2009) and Johnson et al. (1997) in diverse ocean provinces, but the question of how significant it is relative to other pathways is unclear. Here we address this problem in the context of the Crozex study, for which a detailed iron budget is already available (Planquette et al., 2007).

As discussed in Planquette et al. (2009), the POC values are lower and Fe:C ratios very much higher (especially to the north of the islands) in Crozet relative to the FeCycle site (Frew et al. 2006). These observations are all consistent with the islands being a major source of lithogenic particulate Fe to the surrounding waters. This particulate material that is transported off-island is therefore an important, but previously unquantified, contribution to the downward flux of Fe exiting the upper ocean and measurements reported here (Table 2) allow this flux to be estimated and compared to other Fe fluxes in this system.

The downward fluxes diagnosed here are added to the Planquette et al. (2007) iron budget for this system in Figure 4. The 2007 budget comprises atmospheric sources (estimated to deliver 100 nmol m^{-2} d^{-1}), upwelling sources (estimated to total 34 nmol m^{-2} day^{-1}) and an offshore dissolved iron flux estimated as 228 nmol m^{-2} d^{-1} when normalised to bloom area. Labile downward particulate iron fluxes are estimated to be 97 nmol m^{-2} day^{-1}, which is of the same order as the total supply of dissolved Fe to the mixed layer. To a first order the budget therefore appears to be approximately balanced with known sources of iron accounting for the downward labile flux.

<Figure 4>

In addition to the downward flux of labile iron we estimate the refractory downward iron flux as 40 x 10^3 nmol m^{-2} day^{-1}, around 400 times larger than the downward labile flux (Table 2). The biogenic Fe flux represents about 31% on average of this refractory flux to the north of the islands. Thus the single largest term in the iron budget appears to be the downward flux of "refractory" particles. Figure 4b shows the biogenic Fe flux and Figure 4c both the biogenic flux and the total refractory fluxes.

The anticipated origin of these particles is the adjacent island system, hence we indirectly estimate the offshore transfer of terrestrial particles as being of approximately the same order as the downward refractory flux (Figure 4c). Overall the flux of iron from the terrestrial landmass is dominated by the small lithogenic particles with the dissolved phase being a minor component, and with some fractions of this lithogenic material being transformed to BioFe. Whilst the upper water column inventory of FeCycle shows the importance of the lithogenic component, to our knowledge this is one of the few systems where the relative sizes of these flux terms have been estimated.

An important point about these downward fluxes of total and biogenic Fe is their highly variable nature (Table 2). The variability will reflect both the magnitude of the source term (re-suspension, lateral advection) and the intensity of biological activity in converting lithogenic to biogenic Fe. The question of how far offshore the small particulate flux might be significant remains open. Lam et al. (2006), suggest that the offshore transfer of lithogenic iron is significant based on numerical modelling studies and observations over 700km from land of very small iron rich particles, less than 5 microns in diameter, captured by pumping systems collecting particles between 1 and 53 microns in size and greater than 53 microns in size (analogous to our observations here).

It is therefore plausible that a lithogenic iron plume from the Crozet islands could extend much further offshore than the many 10s of kilometres over which we have demonstrated it. As Pollard et al. (2007b) observed, the westerly winds that predominate in the area lead to Ekman flux across the Crozet Plateau, which allows sediments over the Plateau to be resuspended and brought from the south to the north, having the consequence to seed with particulate iron the waters north of the area. This Ekman transport certainly provide iron (particulate and dissolved) to the bloom area which is constrained to the North and West by the SAF and which spans approximately 2 degrees of latitude away from the island . It is also interesting to note the presence of refractory Fe to the south of the island albeit at lower concentrations than to the north. It is not known if this is leakage of particles from the north around the islands, although this seems unlikely given the circulation (Pollard et al., 2007b), or if they represent distal population of particles transferred over long distances to this site, or if there is a mixture of both sources.

5. Conclusions

Choosing an appropriate leaching technique is of paramount importance if useful downward flux estimates for Fe associated with biological material are to be obtained. Based on recent reports (Berger et al., 2008, Hurst and Bruland, 2007) a 25% acetic acid leach alone appears to underestimate the amount of Fe locked up within biogenic matter, although it should still provide an estimate of the most environmentally available Fe. The labile Fe:C ratio of the exported material observed during the Crozex study is smaller than that of biogenic particles estimated by Twining et al. (2004), in other Southern Ocean studies and of the biomass produced in bioassay experiments undertaken in the Crozex study. However, the BioFe approach for organism associated Fe in the system studied here appears more appropriate, although it may overestimate the Fe within organisms as it includes surface adsorbed and other inorganic associated forms of Fe.

The BioFe to C ratios to the north of Crozet are highly variable but on average are much higher than those found to the south which are in turn greater than those reported at depth by Frew et al.(2006). This observation reflects different Fe source strengths and processing in the water column for FeCycle samples. The extremely high BioFe:Total Fe ratios found to the north of Crozet in some samples cannot be explained solely through incorporation of Fe available from the atmosphere, vertical mixing or dissolved lateral inputs, without there being a conversion of part of the lithogenic fraction to biologically available forms. These data therefore strongly supports the concept of bioconversion of litho to bio forms of Fe as suggested by Frew et al. (2006) and Lam et al. (2006, 2008)

The budget of Fe to the north (“downstream”) of the Crozet Islands is dominated by lateral advection and then downward transport of lithogenic and BioFe fractions with a substantial part of the latter fraction originating from the primary lithogenic pool of Fe. The inclusion of the offshore lithogenic iron flux and its conversion to BioFe is therefore required to calculate fully the yield of carbon exported per unit iron injected into the upper water column (Pollard et al., 2009).

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Table 1: Blank value and certified reference materials (CRM) recoveries. Blanks and CRMs were treated in the same way as the samples, full procedure can be found in Planquette et al. (2009).

Number of replicate analyses is indicated in brackets.

Certified concentrations are in italics.

Concentrations obtained in this study are in bold. % value is recovery. All concentrations are expressed in ppm except for *: weight %.

	Blank	**BIR-1**	**JA-2**	**JB-2**	**MAG-1**	**No. 9 NIES**	**SGR-1**	**TORT-2**
Fe	**0.0011 ± 0.00075 (n=5)**	_7.87 ± 0.16_ * **8.47 ± 2.6 (n=4)**	_4.34_ * **4.25 ± 0.66 (n=3)**	_9.96_ * **10.35 ± 0.37 (n=3)**	**_6.8 ± 0.6*_** **8.47 ±.0.84(n=3)**	_187 ± 6_ **180.5 ± 9.2 (n=3)**	_3.03 ± 0.14_ * **2.70 ± 0.12 (n=3)**	_105 ±13_ **103.7 ± 6.05 (n=4)**
		100%	100%	100%	**103%**	100%	98%	100%

Table 2: Particulate organic carbon (POC) concentrations and export (from Morris et al., 2007), acetic acid leachable (HAc-Fe) BioFe (biogenic Fe) and PFe (total Fe) concentrations (from Planquette et al., 2009) and calculated HAcFe, BioFe and PFe downward fluxes at each station during D285 and D286. Note that repeat visits to a station are designated M3.1, M3.2 etc. Average values for the northern and southern sites are given in italics. Deployment depths are given in brackets for each station. NM= not measurable.

Station	Date	Lat.	Long.	POC	POC flux	HAc-Fe	BioFe	Total-Fe	HAc-Fe flux	Total Fe flux	BioFe Flux	BioFe:C
		°S	°E	*µmol L^{-1}*	*mmol m^{-2} d^{-1}*	*pmol L^{-1}*	*nmol L^{-1}*	*nmol L^{-1}*	*nmol m^{-2} d^{-1}*	*µmol m^{-2} d^{-1}*	*µmol m^{-2} d^{-1}*	*µmol mol^{-1}*
M3.1 (225m)	13th Nov 2004	46.058	51.781	0.86	15.3	1.58	0.09	1.74	28.1	31.0	1.60	105
M3.2 (155m)	18 Nov 2004	46.026	51.811	0.19	4.9	11.7	0.12	1.38	302	35.4	3.08	632
M2.1 (150m)	19-20Nov 2004	47.796	52.855	0.3	5.3	0.4	0.05	0.15	7.1	2.7	0.89	167
M6.1 (200m)	21-23 Nov 2004	49.006	51.501	0.26	5.8	0.96	0.15	0.29	21.4	6.5	3.34	577
M3.3 (200m)	25 Nov 2004	46.070	51.772	0.33	13.9	0.46	0.02	0.25	19.4	10.5	0.84	61
M7 (150m)	27 Nov 2004	45.499	49.002	0.45	13	0.41	0.03	0.38	11.8	12.1	0.95	67
M8E (200m)	29-30 Nov 2004	44.954	49.941	0.34	15.3	2.68	NM	0.8	121	35.8	NM	NM

M8W (150m)	1-2 Dec 2004	44.872	49.647	0.89	13.7	0.35	1.07	1.41	5.4	21.5	16.4	1202
M3.4 (180m)	22-23 Dec 2004	46.068	51.778	0.17	25.8	0.82	0.23	0.4	124	67.1	38. 6	1353
M5 (125m)	27-28 Dec 2004	45.997	56.152	0.41	17.9	0.38	0.08	0.38	16.6	16.6	3.49	195
M3.5 (100m)	31 Dec 2004	46.043	51.778	0.23	22.2	0.36	0.52	1.5	34.7	145	50.2	2261
M6.2 (120m)	3-5 Jan 2005	48.999	51.538	0.55	18.3	2.18	0.13	0.22	72.5	7.3	4.33	236
M2.2 (160m)	6-7 Jan 2005	47.800	52.848	0.47	22	0.08	0.13	0.27	3.7	12.6	6.09	277
M3.7 (80m)	10 Jan 2005	46.032	51.870	0.16	13.7	3.52	0.14	0.38	301	32.5	11.99	875
M3.8 (80m)	12 Jan 2005	46.041	51.961	0.26	15	1.78	0.23	0.66	103	38.1	13.27	885
Baie Americaine	6 Jan 2006	46.381	51.829	0.34			0.20	13.2				588
North		-	-	*0.39*	*15.9*	*2.18*	*0.23*	*0.84*	*97*	*40.5*	*12.7*	*689*
South		-	-	*0.40*	*12.9*	*0.9*	*0.12*	*0.23*	*26.2*	*7.3*	*3.7*	*314*

Table 3. Estimated Fe: carbon ratios of natural Crozet phytoplankton populations based on shipboard incubations Moore et al. (2007). The data used contains both high and low light information. At end of incubations Fe:C are assumed to be at a maximal value. * Where there are increases in POC with no Fe addition, these phytoplankton have a lower Fe: C ratio than in Fe addition experiments. Where no significant change in POC noted, data excluded from Table and average Fe:C value of 248.

		POC µM	POC no Fe	difference	Fe uptake nM	Fe:C µmol/mol
M1	Low Light	33.1	20.6	12.5	2	160
	High Light	28.7	19.1	9.6	2	208
					2	
M3.3	Low Light	15.3	11.8	3.5	2	571
	High Light	28	16	12	2	167
M3b	Low Light	48.2	32.4	15.8	2	127
	High Light	43.3	35.7	7.6	2	263

Figure 1

Bathymetry of the survey area between 40-50{degree sign}S and 43-57{degree sign}E. Black filled circles mark the five sites M2, M3, M5, M6, M7, M8E and M8W that were sampled for suspended particulate matter during CROZEX. The northern branch of the Sub Antarctic Front (SAF) is indicated by the thin black line.

Figure 2

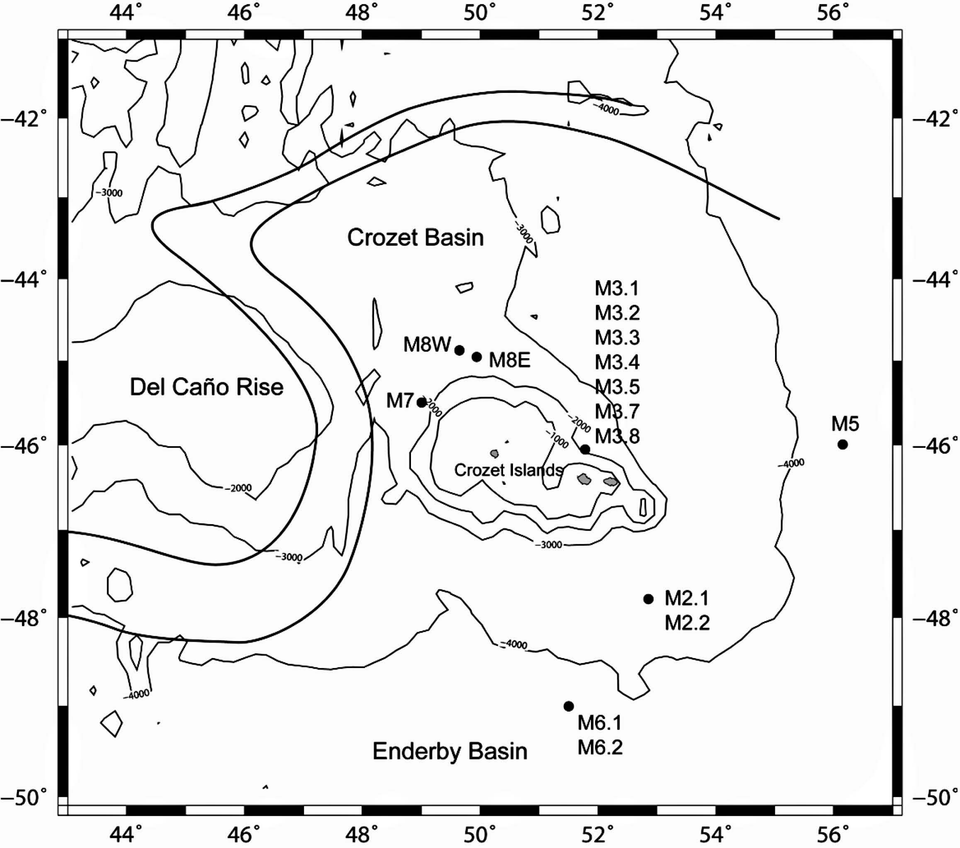
Latitudinal variation of HAc-PFe export (nmol m-2 d-1) and PFe and BioFe export (µmol m-2 d-1). The approximate latitude of the islands is marked by the dashed line. Average values of labile (red triangles), BioFe (green diamond) and total (blue square) particulate iron fluxes are also indicated for the northern and southern areas in the ellipses.

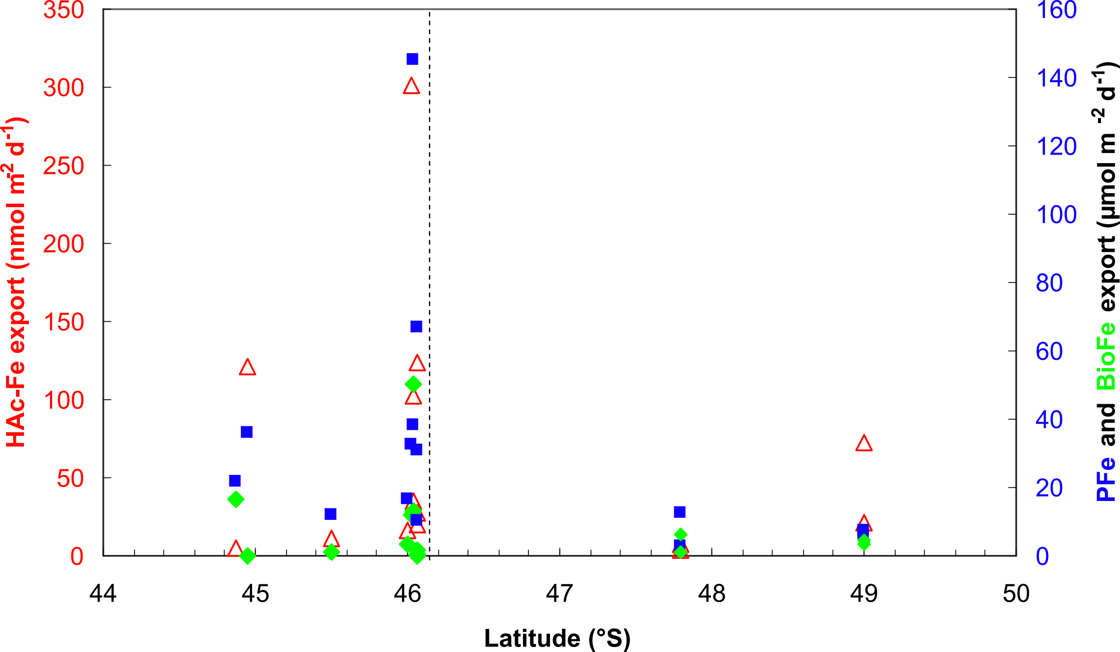
Figure 3

BioFe and particulate organic carbon for the Crozex and FeCycle studies. Labelled lines refer to diatom algal Fe:C ratio of 11, and 48 µmol:mol for respectively background and after Fe addition during SOFEX (Twining et al., 2004) for HNLC waters south of New Zealand, and 248 µmol:mol is average of values derived from Moore et al. (2007) data from Crozex experiment (see Table 2). The Fe:C surface value for FeCycle is estimated from data in Frew et al. (2006).

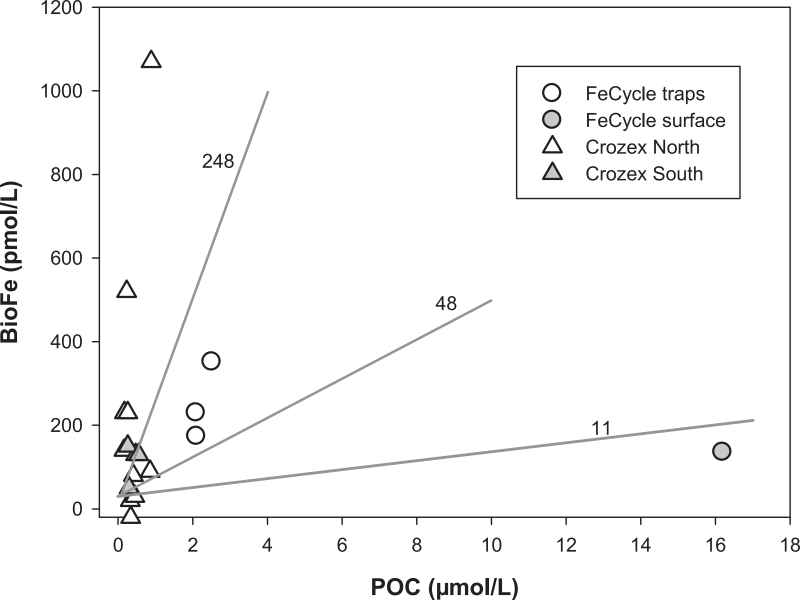
Figure 4

Main pathways of DFe in nmol m-2 d-1 into the bloom area around the Crozet Islands, combining the main circulation paths (green lines), and a summer averaged SeaWIFS chlorophyll a image for the austral summer 2004-2005 (adapted from Planquette et al., 2007). The average fluxes are in italics, the ranges are in brackets. All white and grey fluxes are from Planquette et al. (2007) with additions to each panel being as follows: a) Acid leachable iron removal term in orange font and marked with an asterisk represents the HAc-PFe flux. The green arrow represents the BioFe removal term. b) Total iron removal term in red font. c) Suggested source of total particulate iron is superimposed in red on the horizontal flux.

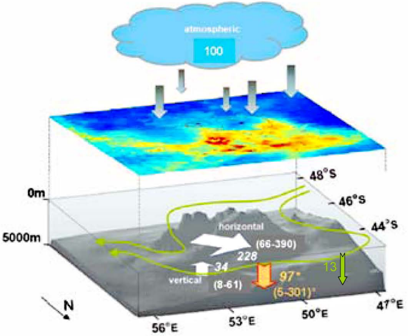

44°
46°
48°
50°
52°
54°
56°
-42°
-44°
-46°
-48°
-50°
Crozet Basin
Del Caño Rise
Crozet Islands
Enderby Basin
M8W
M8E
M7
M3.1
M3.2
M3.3
M3.4
M3.5
M3.7
M3.8
M5
M2.1
M2.2
M6.1
M6.2
-4000
-3000
-2000
-1000



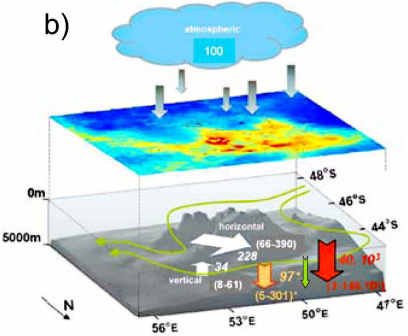
350
300
250
200
150
100
50
0
HAc-Fe export (nmol m-2 d-1)
160
140
120
100
80
60
40
20
0
PFe and BioFe export (µmol m-2 d-1)
44
45
46
47
48
49
50
Latitude (°S)


1200
1000
800
600
400
200
0
BioFe (pmol/L)
0
2
4
6
8
10
12
14
16
18
POC (µmol/L)
248
48
11
FeCycle traps
FeCycle surface
Crozex North
Crozex South

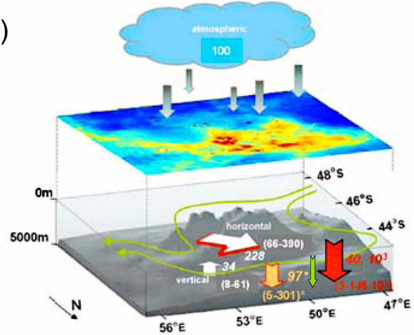
a)


atmospheric
100
0m
5000m
48°S
46°S
44°S
horizontal
(66-390)
228
34
vertical
(8-61)
97*
(5-301)*
13
N
56°E
53°E
50°E
47°E

b)


atmospheric
100
0m
5000m
48°S
46°S
44°S
horizontal
(66-390)
228
34
vertical
(8-61)
97*
(5-301)*
40, 10^3
[3-148.10^3]
N
56°E
53°E
50°E
47°E

c)


atmospheric
100
0m
5000m
48°S
46°S
44°S
horizontal
(66-390)
228
34
vertical
(8-61)
97*
(5-301)*
40, 10^3
[3-148.10^3]
N
56°E
53°E
50°E
47°E