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Distribution of dissolved iron during the natural iron-fertilization experiment KEOPS (Kerguelen Plateau, Southern Ocean)

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Abstract

The Southern Ocean is the largest high-nutrient low-chlorophyll (HNLC) region of the world ocean. It is now well recognized that the low biological productivity in this region is mainly due to the limitation of phytoplankton growth by iron. However, in the core of the Southern Ocean, a massive bloom occurs annually above the Kerguelen Plateau. In the context of KEOPS (Kerguelen Plateau and Ocean compared Study) we investigated the three-dimensional distribution of dissolved iron (DFe) concentrations southeast of the island. We show that in surface waters, DFe was low and not significantly different above and outside the plateau (0.090 ± 0.034 and 0.073 ± 0.014 nM, respectively). By contrast, below 150 m major differences in vertical profiles of DFe were observed. The deep waters above the plateau were clearly enriched, with DFe concentrations up to 0.6 nM near the seafloor. The regeneration from sinking biogenic material and the input from the sediments are very likely the major processes delivering DFe to the deep water. The deep iron-rich reservoir existing above the plateau was responsible for the natural iron fertilization of the surface water by two different mechanisms: (i) winter mixing provided 5 times more DFe to the surface waters above the plateau than outside and (ii) enhanced vertical gradients of DFe and elevated vertical diffusivity resulted in an 8-fold higher diapycnal diffusive flux. The natural iron fertilization presented major differences from artificial iron-fertilization experiments carried out in the Southern Ocean. The amount of DFe required to stimulate the biological activity is much less and the mode of addition is clearly different. The quantification of the excess of DFe supplied in the naturally fertilized area leads to the conclusion that the natural iron fertilization is 10–150 times more efficient to export carbon below 200 m than in artificial fertilization experiments. The bloom above the Kerguelen Plateau was contingent to iron fertilization but it was also sustained by continuous input of major nutrients. Thus, the natural fertilization described here mimics quite well glacial period scenarios where iron fertilization of the Southern Ocean might have occurred from below.

Keywords: Iron; Fertilization; Southern Ocean; Kerguelen

1. Introduction

The publication by John Martin of the iron hypothesis, based on experiments carried out in the subarctic Pacific (Martin and Fitzwater, 1988) was immediately followed by a lively debate centred on the pertinence of the diagnosis of iron limitation based on bottle incubations (Banse, 1990; Martin et al., 1989, 1990b). This debate emerged also for the Southern Ocean where similar results were obtained (Dugdale and Wilkerson, 1990; Martin et al., 1990a, 1992). This put forward the need for alternate experimental strategies that would overcome the bottle effect. Deliberate mesoscale iron-enrichment experiments and investigations in naturally fertilized regions were both proposed as promising approaches. For IRONEX1, Martin proposed both approaches—the first artificial mesoscale iron-addition experiment and the investigation of the naturally occurring high-chlorophyll plume observed westward of the Galapagos Archipelago. He suggested that the latter resulted from a natural iron fertilization. Both studies were successfully conducted in fall 1993, but most of the efforts were concentrated on the mesoscale iron-addition

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experiment and much less was done in the vicinity of the Galapagos Archipelago (Coale et al., 1996b, 1998).

During artificial iron fertilization there is no doubt that, at least at the beginning of the experiment, the biological changes observed within the fertilized patch compared to HNLC waters are only due to the addition of iron. In a natural iron-fertilization experiment, the first challenge is to demonstrate the enhancement of iron input in a region suspected to be fertilized (e.g., due to higher phytoplankton biomass as compared to surrounding waters). There are basically two possible scenarios. If the rate of supply exceeds the rate of consumption, dissolved iron (DFe) accumulates in surface water. This situation has been observed in stratified waters where high dust deposition occurs (Boyle et al., 2005; Guieu et al., 2002; Sedwick et al., 2005), in areas impacted by coastal upwelling (Johnson et al., 1999), and by river plumes (Lohan and Bruland, 2006). In the Southern Ocean, enhanced concentrations in surface waters also were observed in the Atlantic sector of the Polar Front Zone (de Baar et al., 1995), in the seasonal ice zone (Sedwick and Di Tullio, 1997), and in the vicinity of islands (Bucciarelli et al., 2001). If concentrations of DFe in surface water are low, the demonstration of natural iron fertilization is more complicated and requires the identification of the source(s) and mechanism(s) of transport of DFe to the surface layer. Different modes of iron transport are reported in the literature. The most common mode is vertical transport by vertical diffusion through the ferricline (de Baar et al., 1995; Johnson et al., 1997), but other modes also have been observed, including DFe vertical advection in coastal upwelling regions (Johnson et al., 1999) and in open-ocean upwelling areas (Coale et al., 1996a). Iron transported from the coastal to the open ocean by mesoscale eddies was also reported (Johnson et al., 2005). Horizontal transport via isopycnal mixing (Bucciarelli et al., 2001; Johnson et al., 1999) also can be a significant source, if the horizontal gradients of DFe are large.

The first objective of the Kerguelen Ocean and Plateau compared Study (KEOPS) was to demonstrate that the high-chlorophyll region located above the Kerguelen Plateau (Blain et al., 2007) is an area that is naturally fertilized with iron. We present here a three-dimensional distribution of DFe in the water column, the identification of the possible sources of iron for the fertilized area, and the mechanisms for fertilization. We further attempt to quantify iron fertilization above the Kerguelen Plateau and discuss the efficiency of natural fertilization for carbon storage in comparison to artificial iron-fertilization experiments.

2. Material and methods

During the KEOPS cruise (18 January–13 February 2005), 19 stations, located above and outside the Kerguelen Plateau (Fig. 1) were sampled for trace metal determinations using trace metal clean protocols (Bruland et al., 1979). Samples were collected with acid-cleaned 12-L Go-Flo bottles mounted on a kevlar cable and tripped by Teflon messengers. The bottles were then brought in a clean van for sub-sampling. The Go-Flo bottles were gently pressurized with high-purity nitrogen allowing on line filtration through Sartroban cartridges (0.2 μm with 0.4 μm prefilter, Sartorius). All the filtered samples for DFe analysis were collected in acid-cleaned 60-mL low-density polyethylene bottles and immediately acidified with ultrapure HCl (60 μL, 9.5 mM final concentration, Merck, ultrapur©).

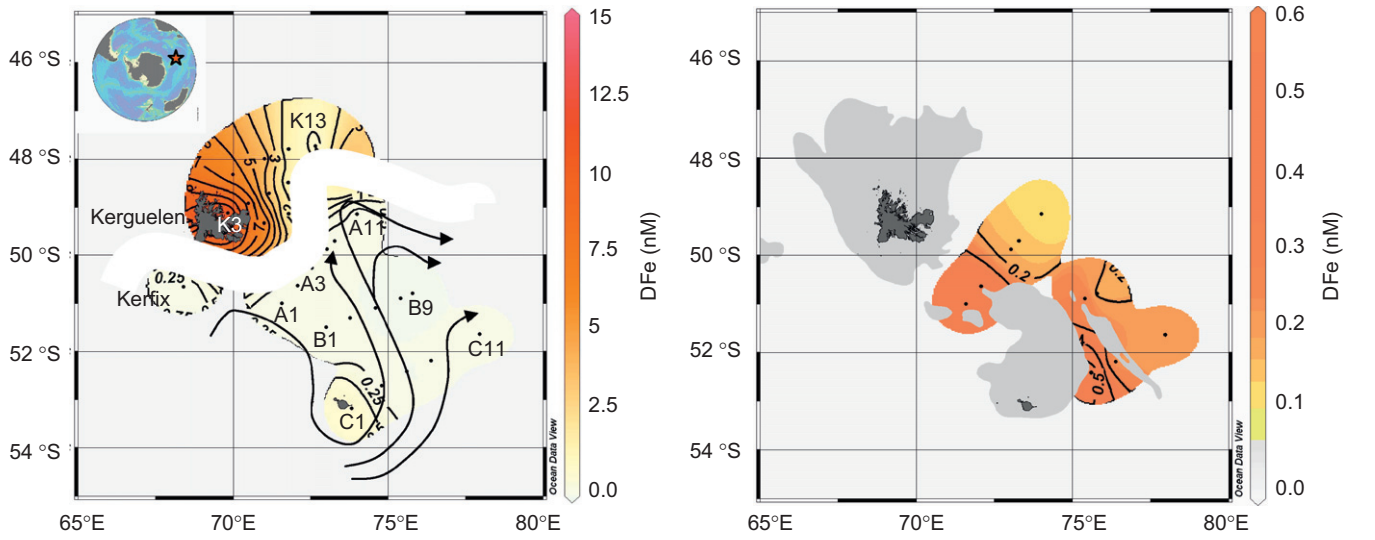

Fig. 1. Horizontal distribution of dissolved iron (DFe) at 20 (A) and 200 m (B). The stations sampled during KEOPS are located along the transects A, B, C and at the time-series site KERFIX (K). Stations sampled during Antares 3 (Blain et al., 2001) are also included. The contours from both data sets are separated by a white band because they are calculated from measurements obtained during different cruises carried out at during different years and at different seasons (see text). This band also denotes the position of the polar front. Black arrows describe the general mean circulation around the plateau (Park et al., 2008b).

The concentrations of DFe were measured on board by Flow Injection Analysis using a modified protocol of the Obata method (Sarthou et al., 2003). The method includes a preconcentration step of DFe by solid–liquid extraction on Hydroxy8 quinoleine resin and the elution of the column with dilute HCl. The eluent was mixed with luminol solution, aqueous ammonia, and hydrogen peroxide and the introduced into the chemiluminescent detector (Hamamatsu photomultiplier H-9319-01). The mean blank, determined daily, equalled 22 ± 10 pM ($n = 21$) and the detection limit was 6 ± 4 pM ($n = 21$). During the cruise we encountered a problem of contamination with some 60-mL bottles. Three stations were concerned (B11, C11 second visit and C9, where concentrations greatly exceeded those at adjacent stations, see sup. Fig. 1) as well as the two deepest samples of the third visit at A3. Among the 237 other samples, three were suspected to be contaminated (station B8 at 200 m (0.24 nM), station B7 at 120 and 150 m (0.43 and 0.48 nM, respectively)). None of these samples are considered in our discussion.

3. Results

Almost all the surface water samples examined during KEOPS exhibited very low levels of DFe (Fig. 1). For all the stations above the plateau (except C1 as discussed below), the mean concentration of DFe above 150 m was 0.090 ± 0.034 nM ($n = 48$). This was not significantly different from the mean of 0.073 ± 0.014 nM ($n = 11$) determined at the stations outside the plateau above 150 m (t-test, $p = 0.01$). On all three transects (A, B, C) the concentration of DFe increased with depth and the highest concentrations were measured in the bottom waters immediately above the plateau (Fig. 2). This general feature is also clearly visible from depth profiles at stations A3 and C11 (Fig. 3A). At the stations outside the plateau the surface concentrations and only small DFe concentrations increase with depth (up to 0.18 nM at 600 m, Fig. 3A) were typical of the open Southern Ocean (Sohrin et al., 2000).

The vertical gradient of DFe varied among the plateau stations. Station A3 was repeatedly visited during the cruise and changes in the DFe vertical profiles were observed (Fig. 3A). The lowest values were measured on 23 February in the upper part of the water column. Changes in the slope of DFe versus depth also were observed below 150 m. Such variability was most likely due to internal wave activity (Park et al., 2008a). Thus, variations in the concentrations of DFe over the duration of the cruise cannot simply be interpreted as a result from short-term biological activity (see Section 4).

An exception to the vertical distribution of DFe across the study area was Station C1, located close to Heard Island (Fig. 1). At this shallow station (150 m) concentrations of DFe (~0.8 nM) were homogenous from the surface to the bottom and at least 2 times higher than measured anywhere during the cruise. These values are consistent with the high concentrations of DFe measured around the Kerguelen Island (Blain et al., 2001). At station C1, the vertical distributions of ^{228}Ra activity (Van Beek et al., 2008), ^{232}Th (Venchiarutti et al., in revision), and dissolved rare earth elements (Zhang et al., 2008) indicated a possible enrichment of these elements in the water column due to the contact with the shallow sediment. The sediment was mainly formed of coarse grains of basalt resulting from the weathering of Heard Island. Dissolution of part of this material also could explain the high DFe concentrations.

4. Discussion

4.1. Distribution and sources of DFe

The low concentrations of DFe measured in surface waters during KEOPS are known to be close to rate-limiting for phytoplankton growth, especially for large cells (Blain et al., 2002; Timmermans et al., 2001). The few artificial iron-fertilization experiments carried out in the Southern Ocean (Boyd and Law, 2001; Coale et al., 2004; Gervais et al., 2002; Hoffmann et al., 2006) have demonstrated that high levels of phytoplankton biomass (1–3 $\mu g\,L^{-1}$ Chl a), similar to those observed within the Kerguelen bloom, can only be reached if DFe is added to HNLC surface waters. In contrast to the homogenous distribution of DFe in surface waters (Fig. 1A), large differences in phytoplankton biomass and biological production were observed between stations above and outside the plateau (Lefèvre et al., 2008; Mongin et al., 2008). Therefore, DFe must be supplied at higher rates in surface waters above the plateau compared to the HNLC waters.

We first examine the case of a possible DFe supply by horizontal advection. In the studied area the concentrations of DFe measured in surface waters outside the plateau were very similar to those measured above the plateau. This is true both on the west side, at station K, and on the east side at stations A11 and C11. In a previous study (Blain et al., 2001; Bucciarelli et al., 2001), DFe concentrations were measured in the north-eastern part of the Kerguelen Plateau (Fig. 1A). The values of DFe varied from 18 nM at station K3 in the Baie des Baleiniers to 0.46 nM at the offshore station K13. The comparison of this data set with KEOPS data is, for several reasons, difficult. The ANTARES 3 cruise took place in October. At this period of the year, biological activity was low (Blain et al., 2001) and did not result in a significant consumption of DFe in the surface layer. In addition, during the ANTARES 3 cruise, 0.4 μm porosity filters were used, which may have—operationally—increased the DFe pool. Finally, the filtered samples of ANTARES 3 were acidified with nitric acid instead of hydrochloric acid. For all these reasons, the comparison of this data set with the KEOPS data is difficult but not inconsistent. However, it is very likely that higher DFe concentrations existed in the

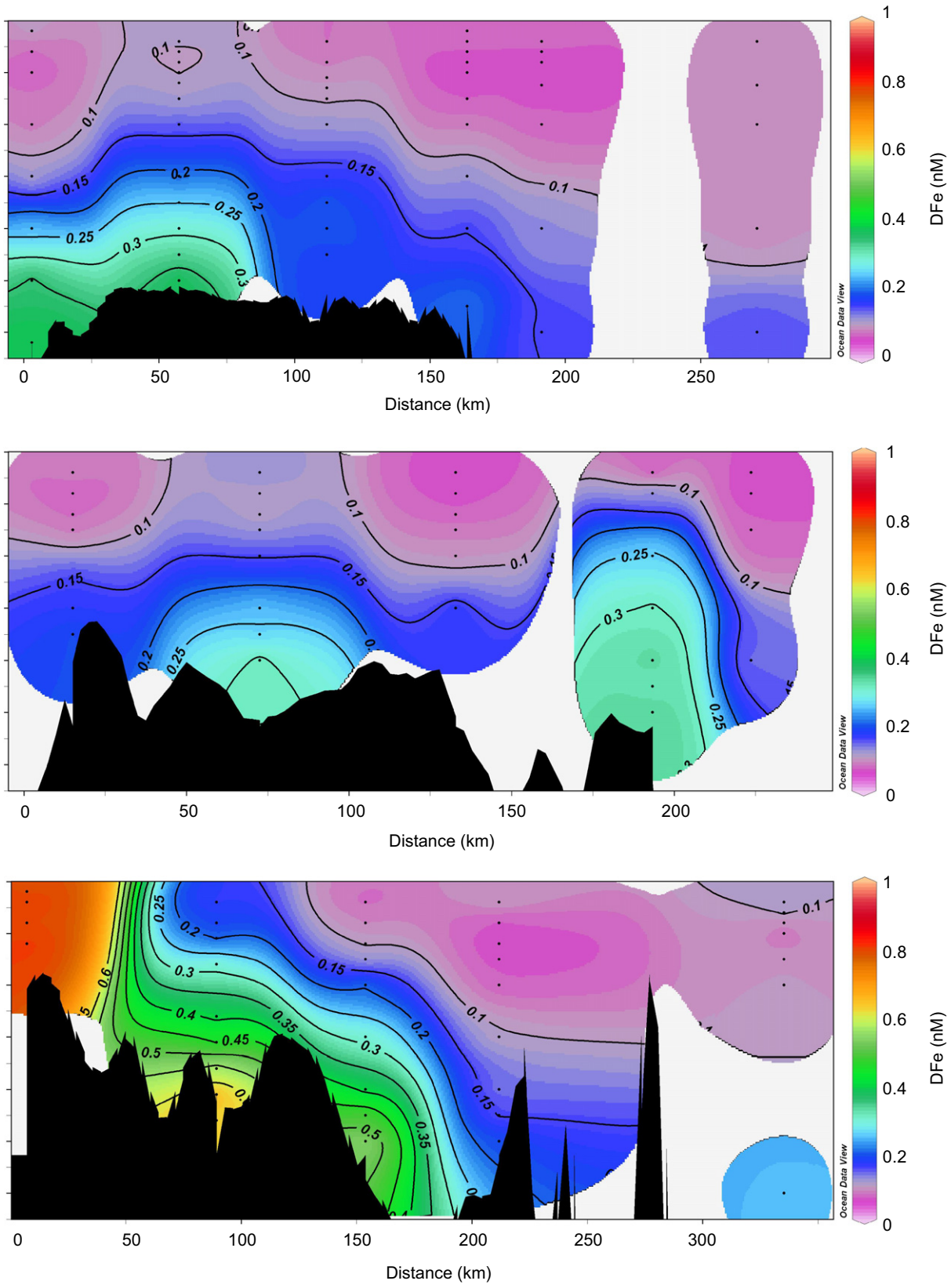

Fig. 2. Dissolved iron (DFe) distribution along transects A, B and C. Black area denotes the plateau. The parts of the water column where the data were not interpolated, due to low spatial resolution, are in grey. The values at A3 are the mean concentrations of DFe for the four visits.

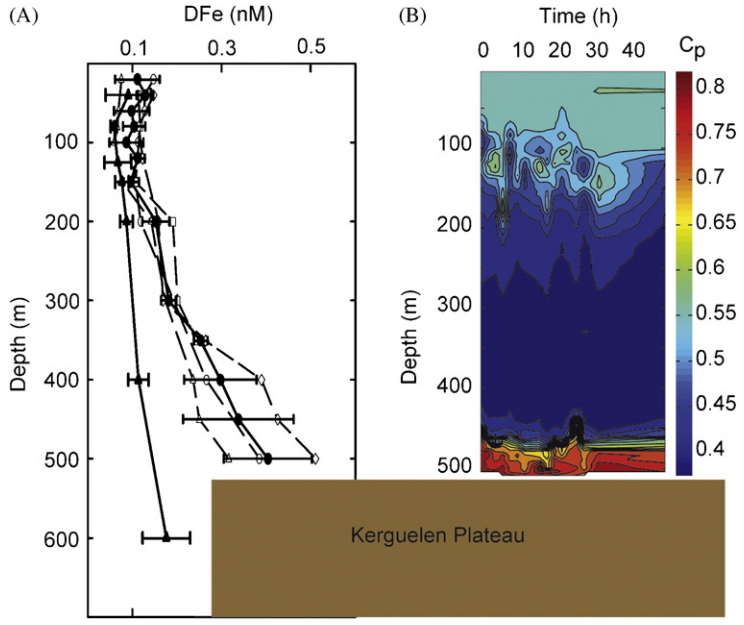

Fig. 3. (A) Vertical profiles of dissolved iron (DFe) at stations A3 and at stations outside the plateau. Filled circle and triangle denote mean values at A3 and C11, respectively. The error bar is one standard deviation. The open symbols denote the different visits at A3 (circle, 19 January; triangle, 24 January; square, 4 February; diamond, 12 February). (B) Time series of particle beam attenuation at 660 nm (c_p) at station A3. A cast was performed every 2 h.

northern part of the plateau. This raises the question: Can this area be a source of DFe for the south-eastern part of the plateau?

The horizontal advection above the plateau is impacted by tides (Park et al., 2008b), leading to rotation of the direction of the currents with time; but the net horizontal transport, measured at station A3, was clearly to the northwest with a net velocity less than 0.05 m s^{-1}. Moreover, the KEOPS area was separated from the direct influence of the island by the polar front. The position of the polar front is well represented by the streamlines deduced from the altimetry (Park et al., 2008b) that border the southeastern flank of the Kerguelen Island shoal (Fig. 1A). Satellite images at different periods of the years (Mongin et al., 2008) show that this water was always low in chlorophyll and thus that the transport of high biomass waters, from the south or from the north, across this front seems negligible. Thus, horizontal advection of DFe from the north cannot be considered as an important source of DFe in surface waters of the plateau, and hence most of the DFe must be supplied by vertical or isopycnal mixing.

DFe supply by vertical mixing requires a deep source and a transport mechanism. The vertical DFe gradient (d(DFe)/dz) between 150 and 200 m of 0.2 nmol m^{-4} at stations outside the plateau is similar to the vertical gradient observed at offshore stations in the Southern Ocean (Sohrin et al., 2000). By contrast, the mean vertical profile of DFe at station A3 (Fig. 3A) shows that, below 150 m, the water column was enriched with DFe. Between 150 and 200 m, d(DFe)/dz was 1.2 nmol m^{-4}, and thus 6 times higher than the mean d(DFe)/dz measured at the stations outside the plateau (Fig. 3A). This clearly shows that a deep DFe reservoir existed above the plateau.

Resuspension of shelf sediment was proposed as the source of the dissolvable Fe over the continental shelf of New Zealand (Croot and Hunter, 1998). The same conclusion also was reached in waters upwelled along the Californian coast (Johnson et al., 1999). During KEOPS, a benthic boundary layer (BBL) extended up to 70 m above the sediment (Fig. 3B), indicating the importance of resuspension. The resuspension was very likely enhanced by internal wave activity. Qualitative evidence of the role of this process in the formation and control of the BBL can be seen in Fig. 3B where the size of BBL clearly varied over time. The sediment was mainly constituted of freshly deposited diatom's frustules (Armand et al., 2008) that could be easily resuspended. The resuspension of particles allowed the degradation of the organic material and the dissolution of the frustules directly in the water column rather than in the sediment. Therefore, trace metals issued from resuspended particles are directly released into the water column, whereas trace metals released into the sediment must first migrate to the surface. During KEOPS, the sediment collected above the plateau also was covered by a fluff layer composed mainly of broken cells (Armand et al., 2008). Millimeter-scale analysis of trace metals in a fluff layer collected above the deep sediment (1967 m) in the northeast Atlantic (Fones et al., 2004) showed that the fluff layer was not acting as a site of intense remobilization because the material was already largely degraded. The same conclusion probably can be applied to the fluff material collected during KEOPS that was mainly dominated by broken cells. Most of the intracellular material such as metal proteins was very likely released during grazing or degradation within faecal pellets in the water column.

Diffusion from pore waters is also another important possible source of trace metals for the BBL. This has been clearly demonstrated along the Californian shelf (Elrod et al., 2004). These authors suggested that diffusion from the shelf sediment is at least as significant as global input from aerosol deposition. The dissolvable fluxes from the sediment along the Californian coast, estimated from benthic chambers, were in the range of 0.1–11.4 $\mu mol\,m^{-2}\,d^{-1}$ with a mean value of 5.18 $\mu mol\,m^{-2}\,d^{-1}$. During KEOPS, DFe profiles in pore water yielded a DFe flux from the sediment of 136 $\mu mol\,m^{-2}\,d^{-1}$ (Viollier et al., pers. comm.). This flux is much higher than the fluxes measured along the Californian coast, particularly if DFe fluxes estimated from DFe gradients in pore waters are underestimates compared to fluxes measured with benthic chambers (Elrod et al., 2004).

Isopycnal mixing is also a very efficient transport mechanism when large horizontal gradients exit. In the case of KEOPS, horizontal gradients of DFe were not present in surface waters, but did exist below 150 m between stations above and outside the plateau (Fig. 2). The amount of DFe transported by this mechanism is difficult to quantify, but the transport is clearly from the plateau to outside the plateau. Therefore, this mechanism cannot be considered as a source of DFe above the plateau, but rather as a sink.

In addition to the sources detailed above that represent external DFe, the regeneration of biogenic particles within the water column is likely also an important source of DFe. Based on Fe uptake and regeneration rate measurements using ^{55}Fe, Sarthou et al. (2008) reported that roughly $51\% \pm 13\%$ of the DFe taken up by phytoplankton is regenerated in the surface layer above the Kerguelen Plateau.

Because the Kerguelen Plateau is located downwind of the dominant wind direction in this region, this raises the question whether dust coming from the island could be a significant source of DFe for surface waters. From a field study carried out on Kerguelen Island simultaneously to KEOPS, Dulac et al. (pers. comm.) concluded that Kerguelen's small desert in the south-east of the main island is indeed a significant source of terrigeneous aerosols. But when combining transport, deposition at sea and dissolution of the mineral dust, the resulting enhancement of DFe in the mixed layer was most likely extremely low (i.e. in the range of 10^{-4}–10^{-5} $nmol\,L^{-1}$). Thus, the atmospheric source of DFe can be neglected above the Kerguelen Plateau. This is confirmed by measurements of aerosols aboard the research vessel during KEOPS. The concentration of mineral dust in the air was 8.3 ± 4.0 $ng\,m^{-3}$, resulting in concentrations of Fe-aerosols of 0.29 ± 0.14 $ng\,m^{-3}$ (Wagener et al., in press). The dissolution of lithogenic particulate Fe (PFe_{lith}) is also a possible source of new DFe in the water column, which is very difficult to properly constrain because PFe_{lith} is only a fraction of PFe and because little is known on its solubility. PFe_{lith} contains Fe included in mineral particles or adsorbed on its surface. During KEOPS, PFe and PAl (>0.2 μm) were measured (Bowie et al., in preparation). This allows an indirect estimate of PFe_{lith} around 0.1 nM in surface waters. The amount of PFe_{lith} that can dissolve is largely unknown, but probably it is a small fraction given the low solubility of PFe_{lith} (Jickells et al., 2005). However, During the FeCycle experiment, efficient conversion of PFe_{lith} to PFe_{bio} was required to balance the PFe budget (Frew et al., 2006). This implied that the dissolution of PFe_{lith} was mediated by the biota and that the residence times of the particles in the surface waters was long enough (around 100 days) to favour this transformation. The possible mechanisms were the solubilization of PFe_{lith} by siderophores (Yoshida et al., 2002) or ingestion of by microzooplankton (Barbeau and Moffet, 2000). Above the Kerguelen Plateau, the residence time of PFe_{lith} is unknown but we can speculate that the very active heterotrophic bacterial community (Obernosterer et al., 2008) with a phylogenetic composition very different from those observed in HNLC waters (West et al., 2008) could produce large amount of siderophores that made a fraction of the PFe_{lith} soluble.

From the preceding comparison of the vertical profiles above and outside the plateau and the examination of the different mechanisms that could provide DFe to the deep water of the Kerguelen Plateau, we conclude that an iron-rich reservoir exists and that this reservoir is mostly maintained by regeneration of biogenic particles settling out of the bloom, from inputs from the sediment and possibly from the dissolution of PFe_{lith}.

4.2. Mechanisms of natural iron fertilization above the Kerguelen Plateau

Above the plateau, DFe concentrations were low in the water layer where phytoplankton productivity was high. This implies that a mechanism efficiently transported DFe from the deep reservoir into the surface layer. In a general manner, diapycnal transfer of a tracer X can be computed from the equation $F_{DFe} = K_z\ \Delta X/\Delta z$ where $\Delta X/\Delta z$ represents the vertical gradient of the tracer concentration and K_z the vertical diffusivity. K_z is a parameter difficult to measure or to parameterize (see for example discussion in Law et al., 2003). During KEOPS, we determined the K_z using the Thorpe scale method (Park et al., 2008a) for the depth stratum 150–200 m where the DFe gradient was most pronounced (Table 1). Our K_z estimates (3.2×10^{-4} and 2.4×10^{-4} $m^2\,s^{-1}$ at Stations A3 and C11, respectively) are considerably higher than previous estimates for the Southern Ocean. During SOIREE (61°S, 140°E), the deliberate release of a mesoscale patch of SF_6 in the mixed layer was used to determine a K_z of $0.11 \pm 0.2 \times 10^{-4}$ $m^2\,s^{-1}$ (Law et al., 2003). During FeCycle (178.72°E, 46.24°S) the same approach lead to a K_z of $0.66 \pm 0.11 \times 10^{-4}$ $m^2\,s^{-1}$ (Boyd et al., 2005). K_z's in the mixed layer and in the seasonal pycnocline derived from different methods were compared during EisenEx (47°S, 21°E) (Cisewski et al., 2005). These

Table 1
Vertical gradient of DFe at the different stations located above the plateau

Station	Date	n[a]	Depth range[b] (m)	d(DFe)/dz[c] (nM m^{-4})	S.D.[d] (nM m^{-4})	R^{2}[e]
A3	19/01/2005	4	150–300	0.79	0.09	0.977
A3	23/01/2005	6	150–450	0.60	0.06	0.676
A3	11/02/2005	6	200–500	1.28	0.2	0.910
A7	22/01/2005	5	150–400	0.35	0.02	0.990
A5	22/01/2005	6	150–450	0.32	0.11	0.676
A1	23/01/2005	5	200–550	0.76	0.16	0.845
B7	30/01/2005	5	200–500	0.21	0.09	0.653
B5	01/02/2005	3	150–300	0.65	0.22	0.893
B3	02/02/2005	5	150–400	0.85	0.14	0.917
B1	02/02/2005	4	150–350	0.61	0.11	0.928
C7	07/02/2005	6	150–500	0.33	0.7	0.860
C5	07/02/2005	6	150–500	1.2	0.2	0.925
C3	08/02/2005	6	160–460	1.3	0.3	0.768

[a]Number of data used in the calculation of d(DFe)/dz.
[b]Minimum and maximum depth of the samples used in the calculation of d(DFe)/dz.
[c]Slope of the linear regression line (DFe) = $f(z)$.
[d]Standard deviation of the slope.
[e]Coefficient of correlation.

authors conclude that a K_z in the order of 10^{-4} m^2 s^{-1} appears a robust estimate for the seasonal pycnocline of the Antarctic Polar Front Zone. Whatever the region and method, it appears that the K_z's at stations above and outside the plateau were the highest reported in the Southern Ocean. The enhancement of the vertical mixing is very likely due to internal wave activity (Park et al., 2008a).

The gradients of DFe versus depth for all the stations above the plateau (excepted C1 where the vertical profile was homogeneous) are reported in Table 1. The variations of DFe with depth were well fitted with a linear relationship and the slope varied between 0.21 and 1.28 nmol m^{-4}. The mean value was 0.71 ± 0.37 nmol m^{-4}. For the three transects the highest values were measured at the three stations (i.e. A3, B3, C3). The gradients were lower at the eastern edge of the plateau (stations A7, B7, C7). We do not have the estimate of K_z at all the stations of the plateau, therefore, the vertical flux of DFe was only calculated at station A3 (Table 2). The vertical gradient 1.1 nmol m^{-4} was calculated between 150 and 200 m to satisfy the criteria that DFe/dz and K_z have to be estimated for the same depth stratum. This was not very different from the mean gradient at A3 of 0.9 ± 0.4 nmol m^{-4} estimated between 150 and 500 m. DFe fluxes were 31 and 4 nmol m^{-2} d^{-1} at A3 and C11 (Table 2), respectively; thus, the DFe flux was 8 times higher above than outside the plateau. At the SOIREE site, vertical diffusive DFe supply accounted for 3 nmol m^{-2} d^{-1} with an upper bound of 8.3 nmol m^{-2} d^{-1}. During FeCycle, the DFe vertical flux was estimated to be 3 nmol m^{-2} d^{-1} (Boyd et al., 2005). In the Atlantic Polar Front region, using a K_z from the literature, de Baar et al. (1995) report a vertical flux of 15 nmol m^{-2} d^{-1}. In comparison to these data it appears that the vertical flux measured above the Kerguelen Plateau is higher than all values reported in the Southern Ocean. Therefore, the excess of vertical input of iron above the plateau compared to the open Southern Ocean contributed to the natural fertilization of the surface waters of the Kerguelen Plateau.

Table 2
DFe fluxes

Station	Bloom (A3)	HNLC(C11)
Short-term fluxes		
Vertical diffusivity (10^{-4} m^2 s^{-1})[a]	3.2	2.4
Vertical gradient (nmol m^{-4})[b]	1.12	0.2
Vertical supply (mmol m^{-2} d^{-1})[c]	31	4
Additional supply (mmol m^{-2} d^{-1})[d]	176	nd
Seasonal budget		
Winter concentration (nmol m^{-3})[e]	153	86
Summer concentration (nmol m^{-3})[f]	86	72
Winter stock utilisation (nmol m^{-2})[g]	4700	950
Vertical supply (nmol m^{-2})[h]	1400	190

[a]Mean values corresponding to the depth stratum where the gradient is observed (150 and 200 m) for DFe.
[b]Vertical gradients were determined using the linear part of the vertical profiles (see Fig. 3A), corresponding to the depth stratum defined in footnote a.
[c]Vertical supply was calculated by multiplying the vertical gradient with the mean vertical diffusivity coefficient converted to m^2 d^{-1}.
[d]The additional supply corresponds to flux of DFe needed to balance the mean Fe demand measured during the cruise within the mixed layer. This flux was not determined at C11 because the net Fe demand was not determined at this station.
[e]Winter concentration (C_{winter}) was taken from the concentration measured at the depth of the temperature minimum characterising the remnant winter water.
[f]Summer concentration (C_{summer}) was the mean value measured within the mixed layer during the KEOPS survey.
[g]Seasonal apparent consumption was calculated using the equation (C_{winter}–C_{summer}) × MLD. The mean mixed layer depth was 70 ± 20 and 68 ± 13 m at A3 and C11, respectively.
[h]Vertical supply was calculated assuming linear build-up of the gradients over 90 days.

The second mechanism of fertilization results from the deep convective mixing that occurs in this area during winter. During this season, the strong winds deepen the mixed layer to 200 m. Therefore, the surface water is mixed with deep water containing high levels of DFe. At the beginning of spring, surface waters contain relatively high DFe concentrations, called winter stock, available for phytoplankton growth. The magnitude of this stock depends on the winter concentration of DFe in the winter mixed layer. The thermal structure of the water column in our study area, located south of the Polar Front, clearly shows an intermediate layer with a minimum temperature, corresponding to the remnant winter water (WW) (see Jouandet et al., 2008 (annex 1) for more details). The DFe concentrations of 0.15 and 0.086 nM at Stations A3 and C11, respectively, measured in the WW were used as estimates for the DFe winter concentrations. The difference between the winter stock and the stock of DFe at the time when the bloom declined (i.e. the period of the cruise) represents the winter stock utilization. The mean mixed-layer depth was 70 m at Stations A3 and C11; thus, we calculated that the winter stock utilization was 5-fold higher at Station A3 than at Station C11 (Table 1). Therefore, the larger winter stock above the plateau is another important mechanism of fertilization of the surface water of the Kerguelen Plateau.

4.3. Biological response to iron fertilization

Following the identification of the mechanism of fertilization, we can now estimate the stock and fluxes of new DFe available for phytoplankton. During KEOPS, ^{55}Fe uptake and regeneration experiments provided an estimate of the net iron demand of the phytoplankton community of 208 ± 77 nmol m^{-2} d^{-1} above the plateau (Sarthou et al., 2008). The vertical diffusive supply provided 31 nmol m^{-2} d^{-1} and was thus not sufficient to account for the biological demand. The utilization of the winter stock could be an additional source. The quasi-steady-state concentrations of DFe observed during the cruise suggests that the supply and the net DFe demand were balanced during one month. Therefore, an additional supply of 177 nmol m^{-2} d^{-1} was required.

The two sources that can support this supply above the Kerguelen Plateau are the winter stock utilization and the possible dissolution of lithogenic PFe, or most likely a combination of both. The partition between both terms cannot be determined, but one can calculate two extreme cases: (i) the additional supply results solely from the winter stock utilization: this would require a depletion by 0.23 nM and (ii) the additional flux results from the daily dissolution of the PFe$_{lith}$ of 2%. These values are in a realistic range (Frew et al., 2006), but they are upper limits because the additional supply is most likely a combination of both processes.

Later in the season, when the bloom declined, the PFe$_{bio}$ accumulated in the surface mixed layer also could serve as source of DFe. A rough estimate of the flux can be provided using the equation $dPFe_{bio}/dt = dPOC/dt * Fe/C$. dPOC is the amount of POC accumulated in the surface mixed layer at the end of the bloom (670 mmol m^{-2} Blain et al., 2007). $dt = 30$ days is the time to decrease the stock down to the winter value. This term is estimated from the decrease in Chl *a* inferred from satellite images (Mongin et al., 2008). Fe/C ($4.4\,10^{-6}$ mol mol^{-1}) is the elemental content of phytoplankton cells determined during the cruise (Sarthou et al., 2008). Using these values, the flux of DFe is 98 nmol m^{-2} d^{-1}.

These calculations may overestimate the flux because they do not take into account any PFe export. If we assume similar cycling of N and Fe, and if we consider the average *f*-ratio of 0.7 inferred from δ^{15}N within the bloom (Trull et al., 2008), we calculate a flux of 29 nmol m^{-2} d^{-1}, which is very similar to the vertical diffusive flux. Our estimate of the flux is also highly dependent on Fe/C. This ratio may have changed through the seasons, and modelling suggests uptake of Fe when DFe is abundant (i.e. early spring) allowing a plasticity of Fe/C between 1.5×10^{-6} and 105×10^{-4} mol mol^{-1} (Mongin et al., 2008). This discussion on the different possible processes that can supply DFe underlines that more work is needed especially on the temporal variability of Fe/C in phytoplankton cells and on the processes that can make PFe$_{litho}$ bioavailable. A DFe budget also was made at C11 (Table 2), but the balance between the vertical flux and phytoplankton demand cannot be estimated because the net demand was not determined for this site. Thus, the excess of DFe supply over the plateau in comparison to open waters is possibly overestimated.

During KEOPS, the impact of the natural fertilization on the biological activity and the biogeochemistry was extensively studied. Among the most important results was the excess of carbon export observed above the plateau compared to outside the plateau (Jouandet et al., 2008; Savoye et al., 2008). Based on ^{234}Th deficit measurements they calculated an excess of export of 14.2 mmol m^{-2} d^{-1}. Combining this result with our excess of DFe supply (Table 1) it is possible to calculate the efficiency of the natural fertilization for carbon sequestration, defined as the ratio between the excess of carbon export to the excess of DFe supply (De Baar et al., 2005). The efficiency falls in the range $70{,}000 \pm 46{,}000$ (mol mol^{-1}).

On the seasonal scale the winter stock provided 4700 and 950 nmol m^{-2} DFe at A3 and C11, respectively (Table 2). The contribution of the vertical diffusive supply can only be estimated if we make some assumptions on the variations of the K_z and the DFe gradient through the season. Because K_z is mainly driven by tide (and possibly by wind speed) it seems reasonable to assume that K_z did not vary dramatically during spring and summer. The variation of the vertical DFe gradient with time is more difficult to assess. We make the assumption that it was set up linearly along the season. With these assumptions, the contribution of the vertical supply was 1400 and

190 nmol m^{-2} at A3 and C11, respectively. The total amount of new DFe utilized by biological activity was 6100 and 1140 nmol m^{-2} at A3 and C11, respectively corresponding to a fertilization of 4960 nmol m^{-2}. Based on a seasonal budget of dissolved inorganic carbon (DIC) in the water column (Jouandet et al., 2008) it is estimated that 4900 and 1650 mmol C m^{-2} were exported below 200 m. The natural iron fertilization supported an excess of carbon export of 3200 mmol m^{-2}. The efficiency of the natural iron fertilization calculated on the seasonal scale is 652,000. This is 150 times higher than the mean efficiency of 4300 for the artificial iron fertilizations carried out in the Southern Ocean (De Baar et al., 2005).

The examination of possible biases in the calculation of the efficiency (Blain et al., 2007) indicated that the natural iron fertilization observed during KEOPS is at least 10 times more efficient at sequestering carbon below 200 m than artificial iron fertilizations. The higher efficiency of the natural iron fertilization is explained by both a modest increase in the carbon export and a considerably lower amount of iron added, compared to artificial iron fertilizations. During natural iron fertilization, the chemical form of DFe made available for phytoplankton is unknown. Above the Kerguelen Plateau, the concentration of iron-complexing ligands were always in excess compared to DFe (Gerringa et al., 2008). This helps to maintain a high amount of iron in the dissolved phase and therefore more easily available for phytoplankton. Photochemical reactions in the surface layer may also enhance the bioavailability of the natural Fe complex (Croot et al., 2001; Maldonado et al., 2005). The regeneration of iron (Obernosterer et al., 2008; Sarthou et al., 2008) was also an important process within the bloom. Recent findings in the Sub-Antarctic Zone of the Southern Ocean (Strzepek et al., 2005) pointed out the importance of the microbial community in the regeneration of iron, the so-called "microbial ferrous wheel" (Kirchman, 1996). This study was carried out in an iron-poor area dominated by the microbial food web. From our investigations in the Kerguelen bloom it appears that in addition to the microbial ferrous wheel, mesozooplankton also contributed actively to the regeneration of iron. Reporting on the results of FeCycle Boyd et al. (2005) questioned: "if more iron is added to the microbial foodweb, would the wheel spin faster or become larger?" Within the Kerguelen bloom it becomes larger and this contributed to prolong the duration of the bloom.

During artificial iron experiments, the triggering and the maintaining of the artificial blooms required multiple injections of acid solution of iron sulphate. From the iron budget constructed for SOIREE, it appears that 95% of the iron is lost (Bowie et al., 2001). It is also obvious that the chemical speciation resulting from massive addition of $FeSO_4$ in seawater is dramatically different from natural iron speciation (Boye et al., 2005). The pulse mode of iron supply in artificial fertilization experiments might mimic episodic dust deposition in the surface layer, but it is unknown if the low dissolution of mineral dust particles will lead to similar or different response of the ecosystem. The impact of episodic dust deposition in the Southern Ocean cannot easily be derived from natural iron fertilization studied above the Kerguelen Plateau.

It is clear that the occurrence of the Kerguelen bloom is contingent to natural iron fertilization, but its persistence over three months would not be possible without the concomitant supply of other major nutrients. Therefore, our results are more relevant to test paleoceanographic scenarios based on iron fertilization from below. Such scenarios have been proposed for glacial periods. The iron enrichment of deep waters might result from terrigenous inputs (Latimer and Filipelli, 2001) or from indirect effect of dust deposition (Lefèvre and Watson, 1999; Ridgwell and Watson, 2002). In the latter, the global deposition of dust leads to a greater flux to the ocean interior where it is remineralized. The iron-enriched deep water could subsequently be transported to the surface, (e.g., by the Southern Ocean upwelling) and supply phytoplankton in a very similar way as observed above the Kerguelen Plateau.

In the context of the iron-fertilization hypothesis, controversial large-scale fertilization has also been proposed to mitigate the CO_2 increase in the atmosphere. These proposals have been severely criticized (Chisholm et al., 2001). Besides possible side effects and the difficulty in assessing the real effect of the fertilization on the concentration of CO_2 in the atmosphere (Gnanadesikan et al., 2003), it also was argued that artificial iron fertilization will trigger much less carbon export than claimed in the geo-engineering proposals (Buesseler et al., 2004). This was mainly based on the low efficiency observed during artificial mesoscale iron fertilization. Clearly the efficiency of natural iron fertilization is higher, but we want to point out here that our result does not imply that the geo-engineering proposals will achieve such high efficiencies, mainly because the mode of iron addition is very different, but also because it requires concomitant supply with major nutrients.

Our study provides detailed possible mechanisms for the natural iron fertilization of the surface water over the Kerguelen Plateau. Careful determination of not only the DFe stocks but also of the DFe fluxes clearly demonstrated that iron fertilization existed. Our study also points out the need for further investigations on the role of particulate iron in Fe cycling. This encompasses the identification of the sources and the modes of transport of the particles, the quantification of the bioavailability of the PFe_{lith} and the determination of the amount of Fe that is exported below the mixed layer, via sinking particles, and the seasonal variability of this flux.

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