Mesoscale biogeochemical responses to iron fertilization in the upper layers of the Southern Ocean Iron Experiment areas

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[1] During the Southern Ocean Iron Experiment (SOFeX), January–February 2002, two iron fertilization experiments were conducted at the south (66.45°S, 171.8°W) and north (56.23°S, 172°W) patches. The south patch was replete with all macronutrients, whereas the north patch was nearly depleted of silicate. Using a towed water sampling/measurement system, high resolution three-dimensional observations of temperature, salinity, CO₂ partial pressure (pCO₂) and the concentrations of total CO₂ (TCO₂), nitrate, phosphate and silicate in the upper 100 m were obtained 10 and 28 days after initial iron additions in the south and north patches, respectively. TCO₂ and nutrient drawdowns observed in the south patch were small due to wind events that limited biological response in the early postfertilization period. At the north patch, drawdown signals were stronger, resulting from the longer time since fertilization. The north patch was dispersed along a frontal zone between two distinct waters, with the denser subducted under the lighter. Subduction limited CO₂ uptake from the air, but provided alternative mechanisms for vertical carbon export. Based on the biogeochemical drawdowns and published estimates of the rate of the entrainment of nonfertilized waters into the patch, the mean net community productivity over 28 days was estimated to be 94 ± 12 mmol carbon m⁻² day⁻¹, to which the air-to-sea flux contributed only 2%. Despite low silicate concentrations and potential limitation of growth of silicifying plankton in the north patch, our estimates of the enhanced carbon uptake are similar to estimates from higher silicate environments.


1. Introduction

[2] Surface waters of the Southern Ocean have long been recognized as important centers of atmospheric CO₂ exchange. While the high latitude areas south of 60°S exhibit only a small sea-air CO₂ flux due to the ice cover preventing sea-air gas exchange during a prolonged period in a year [Takahashi et al., 2009], the Southern Ocean between 30°S and 60°S is one of the most important regions of uptake of anthropogenic CO₂ [Mikaloff Fletcher et al., 2007; Lovenduski et al., 2008; Lovenduski and Ito, 2009; Takahashi et al., 2009]. The presence of high concentrations of macronutrients, but low productivity and low concentrations of chlorophyll make the Southern Ocean a classic high-nutrient, low-chlorophyll (HNLC) setting. Martin et al. [1990a, 1990b] first demonstrated in in vitro experiment that an addition of iron to samples of HNLC Southern Ocean waters caused an increase in growth rates of phytoplankton, and proposed that iron fertilization of the Southern Ocean may be used to sequester industrial CO₂ emitted to the atmosphere.

[3] To test the effects of iron fertilization on marine ecosystems and carbon cycle in actual ocean areas, a number of field experiments have been performed in the HNLC waters in the eastern equatorial Pacific [Coale et al., 1996] and the subarctic North Pacific Ocean [Tsuda et al., 2003; Boyd et al., 2004; Law et al., 2006; Wong et al., 2006]. The Southern Ocean has been the site of several fertilization experiments as well, in the Atlantic [Bakker et al., 2001], Indian [Boyd et al., 2000; Boyd and Law, 2001; Gervais et al., 2002], and Pacific sectors [Coale et al., 2004; Harvey et al., 2011]. All but the SOLAS Air-Sea Gas Exchange Experiment (SAGE) [Harvey et al., 2011] southeast of New Zealand showed strong increases in the primary productivity and biomass in mixed layer, and depletion of dissolved inorganic carbon and nutrients relative to ambient, unfertilized waters.

[4] De Baar et al. [2005] reviewed the results of eight iron fertilization experiments conducted during 1993–2004. The iron fertilization efficiency expressed as the ratio of the CO₂ drawn down to iron added was found to be inversely related to the mixed layer depth, and is also affected by lateral dilution of iron-enriched area. Reviewing 12 iron enrichment experiments, Boyd et al. [2007] considered how the results of mesoscale experiments could be related to the regional
and global scales. They emphasized needs for understanding of the processes that govern the availability of iron to the biota, as well as mechanisms for the retention of iron in upper ocean photic zone and iron mobilization in the water column. Emphasizing these conclusions, the SAGE experiment showed a modest increase in productivity and biomass, but actually ended up with increasing concentrations of macronutrients and inorganic carbon in the patch site [Law et al., 2011]. This may have been the result of lateral and vertical mixing rates that were higher than in previous fertilization experiments [Law et al., 2011] due to the high winds experienced during the ~14 day experiment [Ho et al., 2006], which was similar to the conditions experienced in the early stages of the southern component of the Southern Ocean Iron Experiment (SOFeX) [Coale et al., 2004; Wanninkhof et al., 2004]. Alternatively, the SAGE response may have been limited by biogeochemical effects that led to plankton assemblages with low characteristic net productivity [Pelagic et al., 2011a, 2011b], in particular the low response of fast-growing diatoms.

[5] These studies demonstrated that an iron addition to HNLC ocean areas stimulated phytoplankton growth rates, and, with the exception of SAGE, enhanced oceanic uptake and transfer of atmospheric CO₂ to the deep ocean [Buesseler et al., 2005]. However, large-scale ocean iron fertilization for reduction of atmospheric CO₂ has been questioned on the grounds of the low fraction of carbon exported to the deep oceans [Boyd et al., 2004; Buesseler et al., 2004] as well as the short retention time of the sequestered CO₂ in the ocean water [Broecker, 1990; Peng and Broecker, 1991a, 1991b; Joos et al., 1991; Sarmiento and Orr, 1991; Aumont and Bopp, 2006]. These concerns were amplified by the recent demonstration of limited chemical alteration in SAGE fertilized waters [Law et al., 2011], and by the demonstration of the importance of storm disturbances in limiting the biological response in fertilized waters [Bakker et al., 2001, 2005; Coale et al., 2004]. Environmental problems such as increased ecological stresses that may result from low oxygen environments produced by the oxidation of additional biogenic debris in the water column have also been pointed out [Furhman and Capone, 1991; Chisholm et al., 2001; Buesseler and Boyd, 2003].

[6] The Southern Ocean Iron Experiment (SOFeX) was conceived to test if the marine communities, in particular diatoms, might respond differentially to iron addition to waters with two contrasting macronutrient environments [Coale et al., 2004]. To study the effects of fertilization on two distinctly different macronutrient regimes and potentially distinct phytoplankton assemblages, two sites (hereafter referred to as 'patches') were chosen, one north and one south of the Antarctic Polar Front Zone (~62°S, APFZ). The north patch (56.23°S, 172°W) and south patch (66.45°S, 17.8°W) surface waters had similarly high (22–26 μmol kg⁻¹ for nitrate, and 1.4–1.9 μmol kg⁻¹ for phosphate), whereas the north patch silicate concentration was ~2 μmol kg⁻¹ and the south patch was ~60 μmol kg⁻¹. At the northern site, the silicate to nitrate ratio was ~0.1, similar to that experienced in the SAGE site, whereas that at the south patch was ~2.5. During January 2002, the two sites were fertilized with iron and tagged with ³He/SF₆ gas-tracer mixtures.

[7] While general findings of the experiment have been described by Coale et al. [2004], this paper describes high resolution three-dimensional distributions for temperature, salinity, density, CO₂ partial pressure (pCO₂) and the concentrations of total CO₂ (TCO₂), nitrate, phosphate and silicate in the upper 100 m of water obtained 10 days after the initial iron addition in the south patch and 28 days after in the north patch using a continuous water sampling/measurement system towed behind the ship [Hales and Takahashi, 2002]. Our objectives were to examine the nutrient and carbon depletions throughout the fertilized regions and in the adjacent fertilized waters, to quantify the net photosynthetic CO₂ uptake in fertilized waters in the two distinct macronutrient regimes and compare them with other Southern Ocean fertilization experiments, and to examine the mesoscale structure of the fertilized areas and its impact on fertilization response. At the northern site nearly a month after the initial fertilization, the patch had become trapped along a mesoscale frontal boundary, and distorted into an asymmetric long, narrow band. We present unique observations of subduction of the fertilized waters and discuss the implications for carbon uptake in and export from fertilized waters.

2. Setting and Methods

2.1. Environmental Setting

[8] As described by Coale et al. [2004], iron was added at the north and south patches, in the HNLC Southern Ocean during January and February 2002. The two patches differed in several key ways. The south patch, located at ~66.45°S and 171.8°W, had cold (~0.7°C) surface waters with all macronutrients, including silicate, present in abundance. Following fertilization, this patch moved only minimally from the initial fertilization point, and spread nearly uniformly in the horizontal dimensions, as evidenced by the satellite images of the chloropyll response to fertilization shown by Coale et al. [2004]. The south patch experienced several high-wind events in the early postfertilization period, as described by Wanninkhof et al. [2004]. The north patch, located at ~54°S and 169°W was relatively warmer, at ~7.6°C, and was biogeochemically distinguished by the dramatically lower surface silicate concentrations than seen in the south patch (~2 μmol kg⁻¹ versus ~65 μmol kg⁻¹). The north patch was located in a region of the Southern Ocean notorious for complicated frontal structure, and rather than the nearly stationary uniformly expanding structure of the south patch, the expression of the north patch was a long narrow streak that had migrated significantly to the northeast from the initial fertilization point.

2.2. Iron Fertilization and Tracer Addition Operations

[8] Iron sulfate dissolved in seawater was discharged into the ship’s wake as described by Coale et al. [2004], improving upon procedures developed by Coale et al. [1998]. Each patch was fertilized multiple times, with the north patch being fertilized twice in ~5 days before departing for the south patch, and then reinfused 28 days later upon return from the south patch. The south patch was fertilized four times over a ~15 day period. The iron addition events are listed in Table 1.
Table 1. Periods of the Iron Fertilization Conducted Aboard the R/V Revelle and the Deployment Periods for the Lamont Pumping SeaSoar System

<table>
<thead>
<tr>
<th>Patches</th>
<th>Operations</th>
<th>Iron Added (kg)</th>
<th>Dates</th>
</tr>
</thead>
<tbody>
<tr>
<td>North</td>
<td>Iron fertilization 1 and SF$_6$ addition</td>
<td>631</td>
<td>12–14 Jan 2002</td>
</tr>
<tr>
<td></td>
<td>Iron fertilization 2</td>
<td>631</td>
<td>16–17 Jan 2002</td>
</tr>
<tr>
<td></td>
<td>LPS tow 3, parts A, B, and C</td>
<td>315</td>
<td>24–26 Jan 2002</td>
</tr>
<tr>
<td></td>
<td>Iron fertilization 3</td>
<td>315</td>
<td>26–30 Jan 2002</td>
</tr>
<tr>
<td></td>
<td>LPS tow 1, part A, B and C</td>
<td>315</td>
<td>1–2 Feb 2002</td>
</tr>
<tr>
<td>South</td>
<td>Iron fertilization 1 and SF$_6$ addition</td>
<td>450</td>
<td>9–10 Feb 2002</td>
</tr>
<tr>
<td></td>
<td>Iron fertilization 2</td>
<td>315</td>
<td>3 Feb 2002</td>
</tr>
<tr>
<td></td>
<td>Iron fertilization 4</td>
<td>315</td>
<td>4 Feb 2002</td>
</tr>
<tr>
<td></td>
<td>LPS tow 2, part D</td>
<td>5 Feb 2002</td>
<td></td>
</tr>
</tbody>
</table>

*Iron was added as ferrous sulfate dissolved in local seawater. The north patch is located at 56.234°S and 172°W, and the south patch is at about 66.45°S and 171.8°W [Coale et al., 2004]. The LPS measurements were made 28th day after the initial iron addition in the north patch, and on 10th and 12th days after the initial iron addition at the south patch. LPS, Lamont Pumping SeaSoar system.

[10] Two inert tracers, SF$_6$ and $^3$He, were added along with the first iron infusions and used to estimate the dilution of the iron by lateral mixing and the rate of sea-air gas exchange [Wanninkhof et al., 2004]. These tracers were not reinfused with subsequent iron additions. We utilize here the SF$_6$ data analyzed continuously in the ship’s surface intake line by K. F. Sullivan of AOML, as described by Wanninkhof et al. [2004], obtained from the SOfEx web server, http://www.mbari.org/SOfEx.

2.3. Postfertilization Surveys

[11] We completed two surveys of the south patch in the early days following fertilization, and one survey of the north patch 28 days after fertilization (see Table 1), using a combination of a towed sampling vehicle (described below) and the ship’s surface water intake. During these surveys we made a variety of physical, bio-optical, and chemical measurements to characterize the structure and evolution of the patches. In addition to surveys aboard the R/V Revelle, two additional ships were involved in characterizing the later development of the patches, as described by Coale et al. [2004].

2.4. Towed Water Sampling and Measurement System

[12] This system has been described in detail by Hales and Takahashi [2002], but we will give a brief overview here. An undulating instrumented vehicle (or fish) towed behind the ship is used for observing the mesoscale distribution of physical and biogeochemical properties from surface down to 100 m depth. The vehicle’s flying depth is governed by wings that are feedback controlled by a shipboard computer, and the diving/ascending rate is normally set at 0.3 m sec$^{-1}$. The vehicle houses not only CTD (SeaBird 9/11+) and bio-optical sensors (PAR, Biospherical QSP200L; chlorophyll-a fluorescence, WetLabs WetStar; and optical backscatter, WetLabs LSS), but also a positive displacement pump that delivers a seawater sample stream (about 8 L min$^{-1}$) to the shipboard chemical analyzers through a Nylon tube (3/8” i. d.) encased in the 500 m long towing cable. The chemical analysis methods will be discussed in section 2.4. The transit time of seawater through the 500 m long tubing is determined precisely every few minutes by comparing the salinity signals measured by the fish-borne sensors and a shipboard sensor, following Hales and Takahashi [2002], and is about 6 min. The electrical power (480 V AC) for the operation of these units as well as for the wing control motors aboard the fish is supplied from the ship through conductors embedded in the towing cable. The towed vehicle/chemical analysis system was designed and constructed at the Lamont-Doherty Earth Observatory [Hales and Takahashi, 2002, 2004; Hales et al., 2009a, 2009b], and is called hereafter the Lamont Pumping SeaSoar system (LPS).

[13] We compared the LPS-based temperature and salinity measurements with those in the ship’s underway system. The LPS-based temperature was essentially the same as that recorded by the ship’s sensors (within 0.02–0.05°C), while the salinity offset was more substantial (ship’s sensors about 0.1 PSS higher than LPS). Spatial variability in both temperature and salinity were consistent regardless of sampling/measurement platform. We believe that our temperature and salinity data are more reliable, since we had our sensors calibrated by Sea-Bird before and after the cruise, and recorded consistent data from multiple pairs of sensors. In any case, the agreement in the spatial patterns between the ship-based and LPS-based sensors not only adds confidence to the in situ measurements it also shows that the shallowest depths sampled by the LPS were within the surface mixed layer.

[14] The original plan was to obtain 4-D (x-y-z-time) distribution of physical and biogeochemical parameters for pre- and post-iron fertilization periods at the two patches. However, high-frequency transient noise on the ship’s 480 V AC power supply interfered with the data and control telemetry, and until this problem was resolved midway through the cruise, we were unable to control the fish. As a result, our sampling was limited to a few days in the patches after the fertilization had already been completed, and we were unable to obtain time series measurements consisting of pre- and postfertilization periods.

2.5. Determination of Chemical Properties

[15] The water samples pumped to the shipboard laboratory were analyzed for several properties using rapid response continuous chemical analyses. The partial pressure of CO$_2$, $p$CO$_2$, was measured with an estimated precision of ±1.5 µatm using a membrane-type equilibrator and a LiCOR 6262 CO$_2$ gas analyzer [Hales et al., 2004a] which was calibrated once an hour using five reference CO$_2$-air mixtures that were tied to C. D. Keeling’s WMO CO$_2$
The concentration of total dissolved CO$_2$, TCO$_2$, was measured using an improved version of the method described by Bandstra et al. [2006]. Briefly, a small split of the water sample stream was delivered at a precisely controlled flow rate of 20 ml min$^{-1}$ (1/400 of the rate used for pCO$_2$ measurements) and acidified using an excess of hydrochloric acid. The acidified sample was passed through a bundle of fine tubes made of CO$_2$-permeable membrane, and a CO$_2$-free carrier gas was passed on the outside of the tubes at a precisely controlled rate of 900 ml min$^{-1}$ (3 times that in the pCO$_2$ analysis). The combination of acidification of the sample stream, the high gas/liquid flow ratios, and the rapid gas transfer rates across the membrane resulted in nearly 100% stripping efficiency for CO$_2$. With high and constant stripping efficiency and constant sample liquid and strip gas flow rates, the CO$_2$ content of the strip gas stream is simply proportional to the sample TCO$_2$. The CO$_2$ content of the strip gas stream was measured by a LiCOR 6262 CO$_2$ gas analyzer and the data recorded at 1 Hz. Laboratory tests demonstrated the precision and response time of this measurement to be <0.1% and 7.5 s, respectively. For the calibration of the system, aliquots of water were collected from the main sample line and preserved with HgCl$_2$, and these samples were returned to LDEO and analyzed for TCO$_2$ with a coulometer that was calibrated with reference seawater provided by Andrew Dickson of the Scripps Institution of Oceanography. Thus, accuracy is expected to be similar to the precision.

Nitrates, phosphate, and silicate concentrations were measured using a colorimetric method with continuous segmented flow modified from Hales et al. [2004b] as described by Hales et al. [2005, 2009a, 2009b]. The sensitivity to nutrient concentrations was improved while decreasing the perturbations due to fluctuations in ambient conditions like temperature, and still maintaining response times of <10 s. A newly developed photometer detection unit based on feedback-controlled LED light sources was used to determine concentration-proportional absorbance. Accuracy and precision of these measurements is estimated to be no worse than a few percent, and the data were recorded at approximately 1 Hz.

Nitrate, phosphate, silicate, and pCO$_2$ were also measured in the ship’s underway scientific water line (drawn from an intake at about 5 m depth near the ship’s bow) by independent methods. Nutrients were measured by Hales’ group, following the methods of Gordon et al. [1998], using an AAII autoanalyzer. The pCO$_2$ was measured using an equilibrator and IR detector system assembled by G. Friederich at MBARI, and operated by P. Strutton in the field. As a further check on the accuracy of our analyzers, we compared the chemistry of samples drawn by the towed vehicle at its shallowest depths with coincident common measurements in the ship’s underway surface sample stream. Phosphate, silicate, and pCO$_2$ measured by the different approaches were all within analytical precision of each other, respectively, but nitrate was consistently lower by about 1 µM in near-surface towed vehicle samples than measured in the ship’s underway line. The reason for this offset is not clear, as the two analytical approaches were very similar and used common primary standards for calibration. Comparison with CTD rosette sample profiles gave no clear resolution, as those data showed variance that encompassed these data sets. Regardless, the magnitude of the dynamic range of the observed nitrate distributions is such that the error is insignificant with respect to nutrient limitation, depletion ratios, or mixing/dilution corrections.

Although the agreement between properties measured in the ship’s surface underway sample intake line in the context of this experiment was primarily used as a means to validate the measurements and sampling approach, there is a broader context in the case of pCO$_2$. Juranek et al. [2010] showed evidence that ship’s intakes often impart respiratory signals on the sample water, to an extent that there could possibly be significant artifacts in estimates of net global air-sea CO$_2$ exchange [e.g., Takahashi et al., 2009]. The agreement seen here is within oceanographic analytical uncertainty for pCO$_2$, and is consistent with that reported for the RVIB Nathaniel B Palmer [Hales et al., 2004a] and the R/V Ronald R Brown [Ho et al., 2011]. These results suggest that, at least for these ships that have played significant roles in creation of the global surface ocean pCO$_2$ database [Takahashi et al., 2011], the respiration artifact identified by Juranek et al. [2010] does not appear to be a contributing factor.

These chemical, physical and other operational data (time, fish’s depth, position, attitudes etc.) were recorded by shipboard computers with each system’s measurements stamped with GPS time. Full data sets were merged from the individual data files. The time lags associated with flow through the towed sampling line and analysis times have been corrected such that all data are reported at the time the LPS fish passed through the water of interest. All the towed vehicle (LPS) data have been submitted to the MBARI web server for public access, http://www.mbari.org/SOFeX.

### 3. Results

The results of our towed vehicle transects conducted at the south and north patches are described in this section. Although the south patch was fertilized after the north patch (Table 1), the south patch results will be presented first. Since our system was not functioning prior to the iron addition, prefertilization distribution of the properties was not measured. However, the prefertilization conditions were partially captured by measurements made in waters with little or no SF$_6$ tracer.

#### 3.1. South Patch

The south patch surface water was replete with macronutrients and had a mixed layer depth of about 50 m. It was first fertilized on 24–25 January 2002, and the fertilized water was tagged with SF$_6$ only during the first iron addition (Table 1). The SF$_6$ concentrations shown here were determined 10–12 days after the initial injection. High concentrations of SF$_6$ tracer spread in all directions over an area centered around 66.25°S and 172.15°W as shown by the SF$_6$ contours (also see a SeaWiFS image of the fertilization-induced chlorophyll response [Coale et al., 2004, Figure 2b]). Iron was added to the area for the second time on 28–30 January and for the third time on 1–2 February. The fertilized area was traversed in three different directions by the tows parts A, C and D; and the low SF$_6$ area (assumed free of
The first transect (parts A, B and C) was conducted on 3 February, 10 days after the first iron addition, 6 days after the second addition and a day after the third addition. The third iron addition was made on 4 February, and the second transect (part D) was conducted a day after on 5 February. Because iron fertilization takes effect on the biological community after a few days \[\text{Boyd et al., 2000}\], and because the intense mixing that occurred during several high wind events in this time period \[\text{Wanninkhof et al., 2004}\] limited photosynthetic activity, it is most likely that only the biogeochemical signals of the first and second iron additions were observed by the transect. All the data represent the postfertilization distribution with various degrees of iron fertilization effects.

3.1.1. Physical Structure of the South Patch

Salinity in the south patch ranged from \(\approx 33.7\) to \(\approx 34.4\), but isopleths are mostly distributed horizontally. Features of the physical structure are more clearly shown in the temperature distributions, and salinity is not presented here. For reference and for comparison to the north patch, where salinity is a better descriptor, we have included density contours for both patches in Figures 2–4. The temperature section (Figure 2) exhibits a mixed layer 40–50 m thick with nearly uniform temperatures ranging between \(-0.6\) and \(-0.8^\circ\text{C}\). Throughout this section, the mixed layer is underlain by a cold layer of the winter remnant water with temperatures between \(\sigma_t\) 27.35 and 27.55 at depths of 50–80 m. Its thickness varies from less than 10 m (near 33,000 m point in Figure 2) to 40 m, fluctuating with...
distances of about 5–10 km, which are consistent with the Rossby radius of deformation at this latitude. Below this layer, the dense, but warmer, Antarctic Circumpolar Water (red to yellow) is found, where the greater density is a result of this waters’ elevated salinity. Mixed layer waters are bound below by a density transition zone, or pycnocline, identified by the closely spaced density contours between ~30 and 50 m confirmed by calculations of density stratification (via Brunt-Vaisala frequency calculations; not shown).

[25] Two types of mixed layer water may be identified. Between Lines A and B (26000 m and 36000 m points in Figure 2; 62.15°S and 66.05°S in Figure 1), the densest of the mixed layer waters (darker green; i.e., the coldest, T°C/C0°C = 0.8°C), is found. Very low concentrations of SF6 are found north of the midway point between A and B (i.e. north of 66.10°S in Figure 1) suggesting that area was outside the fertilized patch. South of this, for the distance of about 31 km (i.e., left of 32,000 m to the left end of Figure 2; 66.10°S to 66.35°S in Figure 1), a warmer water mass (T = −0.65°C) with high values of surface SF6 is found in the mixed layer.

3.1.2. The pCO2 in Seawater, South Patch

[26] The high Revelle factor of cold Southern Ocean waters [(ΔpCO2/pCO2)/(ΔTCO2/TCO2) ~15] causes small biological reduction of TCO2 to produce a large relative change in pCO2. For this reason, small changes in TCO2 that signal iron fertilization may be more readily detected with pCO2 observations. Figure 3 shows the distribution of seawater pCO2 at in situ temperature along the section Ds-Dn. The pCO2 ranges from 340 and 370 μatm in the mixed layer, increases with depth near the base of the mixed layer (50 m–60 m) to 390 μatm and then to about 470 μatm through the density transition zone to the appearance of Antarctic Circumpolar Water at 100 m. The pCO2 at the core of the winter remnant layer, described above, is about 400 μatm, which is nearly 20 μatm greater than the atmospheric pCO2 at the time of this field work. This may be due to some respired CO2 that was added to the winter remnant water since the previous winter; alternatively, winter vertical mixing may have maintained a higher than atmospheric surface pCO2, suggesting a wintertime off-gassing of CO2.

[27] Reduced pCO2 values are seen within the mixed layer between 10,000 m and 27,500 m points (magenta color, left of Line A) in Figure 3. These low values coincide with the fertilized patch, as evidenced both by the elevated surface SF6 and the corresponding weakly elevated bio-optical signatures of production (chl-a fluorescence and optical backscatter; not shown). Unfertilized surface water that contains little or no SF6 at T, S and density conditions similar to those seen in the patch, has pCO2 of about 365 μatm, and is seen in the northern end of the section (near Line B). Water that has the maximum SF6 concentration (Figure 1) and pCO2 values as low as 350 μatm is found near the 17500 m point (left of Line C). This suggests that, for the 10 day period after the water was first fertilized, the pCO2 in the mixed layer water with densities less than sigma-t 27.20 has been drawn down by as much as 15 μatm. No clear fertilization effect is found within the winter remnant layer, suggesting that the iron was mostly retained in the surface mixed layer. The effects of iron fertilization are primarily confined to the mixed layer 10 days after the first fertilization, because of the steep vertical density gradients across the base of the mixed layer and the winter remnant water. However, during the following winter, the fertilized water

![Figure 2. A N-S section for temperature to a water depth of 100 m along part D in the south patch. The letters Dn and Ds indicate the northern and southern ends of the section shown in Figure 1; and the heavy vertical lines marked A, B, and C indicate locations where sections A, B and C intersect with section D. The horizontal scale is the distance in meters from the starting point of the transect run. The colors indicate the temperature. Isopycnal contours are indicated with white curves and the tracks of the fish with gray curves.](image-url)
should be mixed down to the base of the winter remnant water near 90 m.

3.1.3. TCO$_2$ and Nutrient Concentrations, South Patch

[28] The distribution patterns for the TCO$_2$, nitrate and silicate concentrations along the section Dn-Ds (Figures 4a–4c) are similar to that for pCO$_2$: low concentrations in the mixed layer and high in the warm Antarctic Circumpolar Water located near 100 m. All these properties in submixed layer waters (below about 60 m) vary primarily with the water density, and exhibit mesoscale variability.

[29] The fertilization effects for these properties are observed in the mixed layer water with densities less than 27.20 in the area of high SF$_6$ concentrations between 13,000 m and 22,500 m points. Although the distribution patterns for TCO$_2$, nitrate, phosphate and silicate are consistent with pCO$_2$, these features do not benefit from the Revelle factor amplification of biological response that pCO$_2$ does. As a result their signals resulting from iron fertilization over this short incubation time are not much above natural variability. Nevertheless, the effects of iron fertilization after 10 days is estimated, for averages of mixed layer waters within the patch sampled by the LPS: The TCO$_2$ depletion, $\Delta$TCO$_2$, is $4 \pm 4$ $\mu$mol kg$^{-1}$, after accounting for the slight salinity differences between in- and out-of-patch waters, and is consistent with the pCO$_2$ depletion and the Revelle factor for these waters. For the nutrients, $\Delta$NO$_3$ = 0.5 $\pm$ 0.2 $\mu$mol kg$^{-1}$; and $\Delta$SiO$_3$ = 0.8 $\pm$ 0.2 $\mu$mol kg$^{-1}$. Phosphate concentrations were not measured along this section, but were in other sections crossing this patch’s boundaries, so we can estimate its fertilization-induced depletion as $\Delta$PO$_4$ = 0.05 $\pm$ 0.02 $\mu$mol kg$^{-1}$. Because the uncertainties in each of these properties is large relative to the small overall drawdown, the computed depletion ratios are subject to large uncertainties, and will not be discussed further.

3.2. North Patch, 54°S and 169°W

[30] The north patch was fertilized with iron on 12–14 January 2002, for the first time and on 16–17 January for the second time. The ship returned to the north patch after the south patch operations were completed, about 28 days after the first fertilization. The patch was identified by the persistent signatures of SF$_6$, which, although much lower than seen in the early stages of the south patch work, were still clearly detectable. We completed our towed vehicle surveys prior to one final refertilization of the patch. The towed vehicle survey was conducted on 8 February, 28 days after the first iron fertilization. Hence the data reflect well-developed effects of iron addition compared to those observed at the south patch.

[31] Figure 5 shows a SF$_6$ distribution map on 8 February, along our tow path. The original 15 $\times$ 15 km patch was stretched along a SW-NE front between two water types and was formed into an elongated narrow high-SF$_6$ belt. Since the fertilized water was tagged with SF$_6$ during the first fertilization four weeks prior to our survey, its concentrations were much lower (about 1/30) than those observed in the south patch (Figure 1). The section Bsw-Bne was obtained along the long high SF$_6$ belt, and the shorter sections Aw-Ae and Cw-Ce cut diagonally across it. The long B transect depicts the two water types well, and will be presented first. The shorter cross-front sections show clearly the subduction of the fertilized water, and will be presented second.
Figure 4
3.2.1. Along-Axis Survey of the North Patch

3.2.1.1. Along-Axis Physical Structure of the North Patch

At the north patch, temperature ranges from -4.7 to 7.7°C, but isopleths are primarily aligned along isobaths and are nearly invariant in mixed layer waters. For example, there is no evidence of subsurface remnant winter water, or of relatively warmer, deep water, as was the case for the south patch. The salinity, while having a small dynamic range of only about 33.9–34.05, most clearly illustrates the lateral physical structure of the mixed layer waters, and hence no temperature distributions are shown here. We present density contours overlain on Figures 6–11 for reference to the density structure and comparison to the south patch. The SW-NE transect for salinity (Figure 6) shows along-axis variability in the presence of two waters of different salinity. The more saline waters are located near the northeast (right) end, and lower salinity waters are near the southwest (left) end. In the subsurface regime of the areas northeast (right) of the line where survey A crosses this along-axis survey, a finger of higher salinity water (green, 30–70 m deep) is sandwiched between two layers of lower salinity water (blue-magenta). Because of the presence of the high salinity finger in the density interval of 26.54 and 26.80, the vertical density gradients in the fingered zone are gentler than those in the zone where the high salinity water is absent (between 100 and 12,000 m points). Below the high salinity feature, a finger of low salinity water is present between 70 and 100 m deep. Although there are weak vertical density gradients at shallower depths, the density transition zone, or pycnocline, is clearly identified by the closely spaced density contours between 60–80 m, a fact confirmed by calculations of density stratification (via Brunt-Vaisala frequency calculations; not shown). Along this section, the density contours appear to exhibit mesoscale variability with a horizontal length scale of about 10 km. However,

Figure 4. N-S section for (a) TCO$_2$, (b) nitrate and (c) silicate concentrations in seawater along part D of the south patch survey (Figure 1). The colors indicate the respective concentrations. Isopycnal contours are indicated with white curves and the fish’s tracks are with gray curves, and other features of the section are same as those in Figure 2. The effects of iron fertilization are seen by the reduced concentrations of TCO$_2$ (darker blue), nitrate (magenta) and silicate (magenta) located between 13,000 m and 22,500 m points.

Figure 5. The map shows the paths of the towed vehicle Lamont Pumping SeaSoar (LPS) system and the SF$_6$ tracer concentrations in the north patch on 8 February 2002. Each colored dot indicates a SF$_6$ measurement in surface waters: red indicates high and blue indicates low concentrations; the estimated distribution of SF$_6$ is shown by the black contour lines [Coale et al., 2004]. Its distribution delineates clearly a narrow NE-SW fertilized zone. Three LPS sections are marked with part A (section Aw-Ae), part B (section Bsw-Bne) and part C (section Cw-Ce).
amplitudes of variation appear to be smaller than those observed in the south patch.

3.2.1.2. Along-Axis pCO2 Distributions, North Patch

[33] The distribution of pCO2 in seawater along the Bsw-Bne section is shown in Figure 7. For this survey, the MBARI surface underway pCO2 system was operational and we additionally show the comparison of these data (black dots; G. Friederich [http://www.mbari.org/SOFeX/]) with those obtained by the LPS system in waters at depths above 20 m (red dots). They agree within 1 μatm, and the observed variations of pCO2 are reproduced by the both sets of the data. This agreement not only provides mutual confirmation of the two measurement and sampling approaches, but shows that the LPS was again adequately sampling surface mixed layer waters.

[34] Waters lighter than sigma-t 26.54 (located above 30–40 m) have low pCO2 ranging between 330 and 345 μatm (magenta-blue), and also have high concentrations of SF6 (Figure 5), suggesting they corresponded with elevated iron provided by the previous fertilizations. The reduction of pCO2 is especially pronounced between Lines A and C (magenta areas between 14,000 m and 29,000 m, Figure 7). The biological cause for these low pCO2 zones is supported by colocated enhanced chlorophyll fluorescence and optical backscatter, detected by sensors aboard the towed vehicle (data not shown). Below this, a pCO2 maximum layer with values of ~365 μatm (yellow-orange) is found in a density range of 26.55–26.65. Under the pCO2 maximum (depths > 75 m), pCO2 values are lower, 350 μatm (green) or less, with a hint of an increase at depth. This deep low-pCO2 layer, most clearly present at 15,000–28,000 m distance along the survey, sits within the density transition zone bounded by the 26.75–26.85 isopycnals, and coincides with weakly elevated bio-optical signals of phytoplankton (chlorophyll-a fluorescence, and optical backscatter; data not shown). The pCO2 maximum layer mostly coincides with the salinity maximum feature (33.97–34.00) shown in Figure 6, but is present even SW of the end salinity maximum (0–12,000 m in Figure 7). The high-salinity high-pCO2 water can be traced to the low SF6 surface waters on the northeast end of this section (Figures 6 and 7). Within the pCO2 maximum layer values appear to exhibit mesoscale variability, probably reflecting meandering of the boundary of the two water types.

3.2.1.3. Along-Axis Distributions of TCO2, Nitrate, Phosphate and Silicate, North Patch

[35] Significant drawdown of the concentrations of TCO2, nitrate, phosphate and silicate in upper 30 m is observed (Figure 8). The fertilization effects are especially strong between Lines A and C (between 14,000 and 29,000 m) in high SF6 waters as observed for pCO2. While nitrate and phosphate still remain abundant, silicate was depleted nearly to our analytical detection limit in waters between 22,600 m and 27,500 m.

3.2.2. Cross-Axis Surveys, North Patch

3.2.2.1. Cross-Axis Physical Structure of the North Patch

[36] As for the along-axis survey, salinity gives a clearer picture for the physical structure of the upper water column, and its distributions are presented instead of temperatures. Figure 9 shows two salinity sections, in which the heavy vertical lines marked B indicate the intersection with the along-axis section B. The high salinity (green) water type is located to the left (west) of the line B and the low salinity (blue) water type to the right (east). These sections show that the two surface water types reported above are separated to the west and east of the patch axis, with the more saline type prevalent to the west and the less saline type prevalent to the east. It is also apparent that the along-axis survey came closer to the saltier water type at its NE end, as evidenced by its closer proximity to the ‘B’ crossing line on section C, and confirmed by the greater prevalence of the more saline water...
at the NE end of the along-axis transect. As for the along-axis transect, the density transition zone is present in these sections between 60 and 80 m depths, essentially constant across the front.

[37] These cross-axis surveys give a picture of the interleaving of the different water types, and appear to suggest that a tongue of the saltier water at a depth of about 50 m penetrates into the fresher water mass, dividing it into two lobes, one remaining on the surface, and one below the salty tongue but above the more saline waters at and below the density transition zone. The shallower boundary of the high salinity water closely follows the isopycnal contour 26.55, which slopes strongly downward toward the less saline water. This isopycnal deepens by nearly 50 m in horizontal distances of \( \sim 5000 \) m in both cross-axis surveys.

[38] At the interface of these two waters at greater depths, the isopycnal surfaces are nearly horizontal, requiring density-compensating temperature variability that is nearly impossible to discern in the temperature distributions because of the stronger vertical temperature gradients. Across the section Aw-Ae, the boundary between these two water types appears to be more complicated: a vertical finger of the high salinity water (between 7500 and 10,000 m points) appears to intrude into the lower salinity water. These features are suggestive of meandering or eddy circulation that could be formed by frontal dynamics (see section 4.3).

### 3.2.2.2. Cross-Axis pCO\(_2\) Distributions, North Patch

[39] Distributions of pCO\(_2\) for the cross-axis surveys A and C are shown in Figure 10. As seen in the along-axis section, the LPS- and underway-based pCO\(_2\) measurements in the mixed layer are in excellent agreement, within 2 \( \mu \)atm of each other, with no clear tendency of either system to show higher or lower values than the other. Significant pCO\(_2\) drawdown, with values as low as 332 \( \mu \)atm, is observed in the fertilized zone sampled by the along-axis survey indicated by the line B in these sections. In unfertilized waters both to the east and west of the B survey, the pCO\(_2\) reaches values of \( \sim 368 \) \( \mu \)atm. In these sections, the...
apparent subsurface pCO$_2$ maximum waters are present only beneath the fertilization-induced surface pCO$_2$ minima, and these maximum values are similar to those in unfertilized waters of both salinity types.

[40] This difference indicates a fertilization-induced drawdown of 36 ± 2 μatm. Combined with the salinity distributions, it is clear that both high- and low-salinity surface waters experienced fertilization-induced CO$_2$ drawdown. It is also clear, particularly from section C that the lowest pCO$_2$ feature extends down in the water column along the downward sloping 26.55 sigma-t surface, much as the salinity tongues seen in Figure 9.

[41] The deeper minimum values seen in the along-axis section are also evident in these surveys, most strongly expressed at 15,000–28,000 m. Between isopycnal surfaces 26.75–26.85, pCO$_2$ shows minimum values of ~345 μatm, with suggestions of weak increases at greater depths. As for the along-axis section, these correspond with weakly elevated optical signals of biomass. While the strength of this minimum is not great, it does not appear to be an artifact of analytical resolution, since it persists in all sections and coincides with elevated biomass. It does not appear to be related to the iron fertilization, because it persists across the study region, below both fertilized and unfertilized waters.

Figure 8. Distribution of (a) TCO$_2$, (b) NO$_3$, (c) PO$_4$ and (d) SiO$_3$ in seawater along the SW-NE section, Bsw-Bne of the north patch survey. The isopycnals are shown with white curves; and the tracks of the LPS fish with gray curves. The heavy vertical lines marked with A and C indicates the intersections with the A and C sections. The drawdown due to the iron fertilization is seen in upper 30 m between A and C.
3.2.2.3. Concentrations of $\text{TCO}_2$, Nitrate, Phosphate and Silicate, North Patch

The distributions of $\text{TCO}_2$ and three nutrients along section C are presented in Figure 11. The features observed are consistent with those observed for $\text{pCO}_2$. A substantial drawdown for each of these properties is observed in waters near the fertilized zone delineated by the high $\text{SF}_6$ concentrations (Figure 5). The affected waters are seen to be subducted below the adjoining layer of low salinity water along the 26.55 isopycnal contour. Although the concentration of silicate is low ($2\text{–}3 \mu\text{mol kg}^{-1}$) in unfertilized waters, it is drawn down to less than $0.5 \mu\text{mol kg}^{-1}$ in the fertilized zone.

3.2.3. Drawdown Ratio of $\text{CO}_2$ and Macronutrients in North Patch

Carbon/nutrient ratios utilized by iron-fertilized biological community are of interest from the point of view of ocean carbon sequestration as well as marine ecology. The property-property relationships observed in the mixed layer along the sections that pass across the fertilized and unfertilized zones are shown in Figure 12, and the observed changes in concentrations are listed in Table 2. These estimates differ from those presented by Coale et al. [2004] in that they were limited to surface waters shallower than 50 m, and are thus more representative of bloom-induced biological response than of the regional hydrographic structure.
These quantities do not represent the net biological utilization, since the observed quantities are also affected by lateral mixing of the surrounding waters and, in the case of CO\textsubscript{2}, sea-air gas exchange. The effects of mixing and sea-air gas exchange on our estimation of net biological uptake of these species will be discussed in section 4.4.

4. Discussion

4.1. Biogeochemical Perturbation of the North Patch Region

[44] While we were not able to sample the south patch as extensively as desired, and what sampling we did accomplish came only after a very short and stormy interval following fertilization [see Wanninkhof et al., 2004], the three-dimensional sampling of the north patch did allow us to clearly identify the change to the biogeochemical structure of the region. The surveys show that the region of the north patch spanned a frontal structure aligned in the SW-NE direction, consistent with the alignment of the meandering jets, filaments and eddies that persist there because of fast eastward flow of the Antarctic Circumpolar Current (ACC) over the complex ocean floor topography [Abbott et al., 2001; Barth et al., 2001; Sokolov and Rintoul, 2007]. The nature of the front is defined by surface salinity gradient normal to the long axis of the patch, where surface salinity
Figure 10
drops by about 0.1 PSS over scales at least as fine as the resolution of our sampling approach (~1 km). This small salinity change is not reflected in other surface properties, as surface temperature, pCO₂, TCO₂ and nutrient concentrations are indistinguishable in unfertilized waters of either high- or low-salinity types on either side of the front. Unfertilized water has weakly undersaturated pCO₂ levels of about 368 μatm, abundant nitrate (21.5 μmol kg⁻¹) and phosphate (1.5 μmol kg⁻¹), and low but nonlimiting silicate (~2.5 μmol kg⁻¹) distributed uniformly in unfertilized waters across the front.

[45] Distributions of biogeochemical properties in unfertilized waters appear remarkably uniform across the front, with low biomass and low signals of nutrient or CO₂ consumption in the surface waters. Only weak signals of elevated biomass (from in situ bio-optical measurements, not shown) and weakly depleted pCO₂ in the density transition zone at a depth of about 75 m (Figure 7) indicate the presence of biological activity at all, and the lack of clear minima in nutrients and TCO₂ at that depth suggest that this is a highly recycled, low net productivity biological community. The reason for this depth as a location for preferitization biological activity is unclear, but may be due to the collocated increase in the vertical density gradient with the silcline, which could be beneficial to Fe-starved diatoms that produce excess biogenic opal [Takeda, 1998].

[46] Fertilization of surface waters across the front dramatically altered this structure. Fertilized surface waters showed large nutrient and carbon depletions, but these were limited mostly to the surface waters above the density transition zone. With the exception of the subduction at the front (discussed in section 4.3), the productive response was limited to the upper 30–40 m of the water column, with no apparent impact on the biota in the density transition zone. The fertilization-induced bloom effects were seen across the frontal salinity transition, indicating that each water type responded similarly to Fe addition. The bloom, however, did not expand away from the front in either direction normal to its axis.

4.2. Convergence and Subduction of the North Patch and Implications for Carbon Export

[47] As discussed earlier, the Southern Ocean is a region with abundant frontal structures [Abbott et al., 2001; Barth et al., 2001; Sokolov and Rintoul, 2007], and the colocation of the fertilized patch with such a feature is not surprising, even if this particular front was not one of the well defined Sub-Antarctic Fronts. This particular feature is only weakly expressed in salinity, as discussed above, in surface waters, but has clear frontal structure when examined in cross-frontal section (Figure 6). The front’s salinity transition zone at ~26.55 sigma-t deepening by 50 m at a subscale distance of 5 km under the less saline waters.

[48] Frontal motions are often difficult to discern based on simple cross sections. Do the sloping isopycnals imply an elevation of the more saline waters and along with it upwelling and divergence, or do they imply a convergence of two waters with the more dense water subducted beneath it? The behavior of the fertilized patch waters strongly suggests the latter. The initial patch had a symmetric distribution of ~15 × 15 km, but the upon reoccupation of the tracer tagged waters, it had shrunk by about 50% in the cross-frontal dimension, and lengthened by over a factor of 10 (see Figure 5 for the SF_6 tracer distribution; and a satellite color image in Figure 2a of Coale et al. [2004]). Rather than broadening in the cross-frontal dimension, or splitting into two fertilized regions characteristic of each side of the front, the patch has been trapped at the front and compressed in the cross-frontal dimension, suggesting a convergent front.

[49] While the features in Figure 10 for pCO₂ and Figures 11a–11d show that the pCO₂, TCO₂ and nutrients in both water types were reduced along the frontal zone, the denser of the two (more saline, on the northwest side) appears to be subducted under the less dense layer on the southeast side of the front zone. This feature is similar to the cross-frontal structure studied by Strass et al. [2002] in the Atlantic sector of the ACC. They observed that the lighter water flows across the front toward and over the denser water, and the denser water flows in the opposite direction under the lighter water. This cross-frontal circulation is ageostrophic and linked to mesoscale dynamics, which may be accounted for by baroclinic instability and the slope of isopycnals across the front.

[50] Our observations in the north patch show that low-CO₂ and low-nutrient waters formed by the iron-enhanced photosynthesis would take up an extra amount of atmospheric CO₂ via gas exchange, if they were allowed to remain in contact with the atmosphere for a number of months. These waters, which contain some additional atmospheric CO₂ as well as newly produced biogenic particulates and dissolved organic matter resulting from the iron fertilization, would be subducted under adjoining lighter waters by cross-frontal dynamic forcing. The subduction thus simultaneously limits atmospheric CO₂ uptake, by reducing the exposure time of low-pCO₂ waters to the atmosphere, and enhances it, by fostering subduction of waters that have already consumed some additional atmospheric CO₂. Unfortunately, this implies unpredictable results of iron fertilization in this region, as the ideal sequestration scenario would have the fertilization take place at some optimum distance from a convergent front to maximize the CO₂ uptake by the fertilized water prior to subduction. Given the slow gas exchange response of CO₂, this would suggest that fertilization should take place so far from convergent fronts that prediction of the convergent subduction response would be highly uncertain.

[51] The rate of the lateral motion and subduction may be crudely estimated on the basis of the geometry of

Figure 10. The pCO₂ distributions along the Aw-Ac and Cw-Ce sections of the north patch survey. (a) The surface water pCO₂ data (black dots) obtained using the shipboard system of G. Friederich (http://www.mbari.org/SOFeX/) of MBARI, and the data above 20 m (red dots) obtained using the towed vehicle system. (b) The LPS pCO₂ data at in situ temperature. The isopycnal contours are indicated with white curves. The heavy vertical lines marked with B indicate the intersection with the section B, where the surface waters were fertilized with iron addition. The mixed layer pCO₂ values in the vicinity of the section B are drawn down significantly by the enhanced photosynthesis in fertilized waters.
the subducting low CO₂ and nutrient tongue shown in section Ce-Cw (Figures 10d and 11a–11c), and assumption that the subduction began immediately after iron addition. The lower tip of the subducted tongue appears to be located about 50 m below the surface and about 4500 m to the right of the middle of the fertilization zone (marked with “B”). Since this section has an apparent angle of 45° to the front, the minimum distance from the tip to the front should be

Figure 11. Distributions of (a) TCO₂, (b) nitrate, (c) phosphate and (d) silicate along the Cw-Ce section of the north patch survey. The isopycnal contours are indicated with white curves. The heavy vertical lines marked with B indicate the intersection with the section B. The mixed layer in the vicinity of the section B shows significant reductions in the respective properties due to enhanced photosynthesis in the fertilized waters.
about 3200 m. Assuming that the tongue was formed in 28 days, we estimate that the water moved laterally at a mean rate of 115 m day$^{-1}$ to southeast (right angles to the front) and sank 1.8 m day$^{-1}$ vertically. Satellite observations show [Coale et al., 2004] that while the patch was ultimately stretched to 340 km along the front its mean width was only about 7 km after 38 days, an actual decrease from the original patch size. This suggests that the cross-front convergence counteracted the lateral dispersion away from the front, and thus kept the width nearly constant. The cross-front subduction speed (to southeast) is slow (about 1/100) compared to the along-front speed of about 9–11 km.

Figure 11. (continued)
day\(^{-1}\) (to the northeast), as estimated from the drift rate of a float within the elongated north patch [Bishop et al., 2004] and from the satellite images [Coale et al., 2004].

This process should occur in addition to the gravitational settling of particulate biogenic debris out of the mixed layer into subsurface regimes, and illustrates a step for the transport of atmospheric CO\(_2\) into subsurface regimes of the oceans. Bishop et al. [2004] placed a Lagrangian profiling float in the north patch, and measured the concentration of particulate organic carbon (POC) from surface to 1000 m deep during the 60 days following the initial iron addition. They observed that POC within the mixed layer increased to a maximum level in the high salinity (north) side within about 18 days of the initial iron addition. After 28 days, the high POC water was found under a 50 m thick less saline mixed layer with lower POC concentrations [Bishop et al., 2004, Figure 2], suggesting subduction of denser water underneath of a lighter layer. Our observations (Figures 7–11) document the initial stage of the subduction process. They also measured a 100 m Carbon Flux Index, which indicates, semiquantitatively, the export of organic carbon particles from the mixed layer. They found that, while there were virtually

![Figure 12. The property-property relationship observed in the mixed layer (Z < 50 m) along the Section Cw-Ce (tow 3C) in the north patch: (a) TCO\(_2\) - NO\(_3\), (b) TCO\(_2\) - SiO\(_3\), (c) NO\(_3\) - PO\(_4\), and (d) SiO\(_3\) - NO\(_3\). TCO\(_2\) data are corrected to a constant salinity of 34.00. The net community utilization ratios for CO\(_2\) and nutrients (ΔCO\(_2\)/ΔNO\(_3\) etc.) are computed using a linear regression, and the uncertainties are computed using the following standard equation: +/− [σ\(^2\)/(Σ(Xi\(^2\)) − N(Xmean\(^2\))]\(^{1/2}\), where σ\(^2\) is the variance around a fitted equation Y = aX + b, and N is the number of data points.](image)
Table 2. Changes in the Carbon and Nutrient Concentrations in the Mixed Layer Waters Observed in Transect C on the 28th Day After the First Addition of Iron in the North Patch

<table>
<thead>
<tr>
<th>Properties and Ratios</th>
<th>Locations</th>
<th>Observed Tow 3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCO₂ (µmol/kg)</td>
<td>Background</td>
<td>2111</td>
</tr>
<tr>
<td></td>
<td>Maximum fertilized</td>
<td>2089</td>
</tr>
<tr>
<td>ΔCO₂ (µmol/kg)</td>
<td>Background</td>
<td>22 ± 3</td>
</tr>
<tr>
<td></td>
<td>Maximum fertilized</td>
<td>19.0</td>
</tr>
<tr>
<td>NO₃ (µmol/kg)</td>
<td>Background</td>
<td>21.5</td>
</tr>
<tr>
<td>ΔN (µmol/kg)</td>
<td>Background</td>
<td>2.5 ± 0.3</td>
</tr>
<tr>
<td>PO₄ (µmol/kg)</td>
<td>Background</td>
<td>1.54</td>
</tr>
<tr>
<td>ΔPO₄ (µmol/kg)</td>
<td>Background</td>
<td>1.32</td>
</tr>
<tr>
<td>SiO₂ (µmol/kg)</td>
<td>Backgr.</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>Maximum fertilized</td>
<td>2.9</td>
</tr>
<tr>
<td>ΔSiO₂ (µmol/kg)</td>
<td>Backgr.</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Maximum fertilized</td>
<td>0.4</td>
</tr>
<tr>
<td>ΔCO₂/ΔNO₃ (mol/mol)</td>
<td></td>
<td>8.7</td>
</tr>
<tr>
<td>ΔCO₂/ΔPO₄ (mol/mol)</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>ΔNO₃/ΔSiO₂ (mol/mol)</td>
<td></td>
<td>8.7</td>
</tr>
<tr>
<td>ΔNO₃/ΔPO₄ (mol/mol)</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>ΔSiO₂/ΔPO₄ (mol/mol)</td>
<td></td>
<td>1.0</td>
</tr>
</tbody>
</table>

*See text for the corrections for air CO₂ uptake.

4.3. Estimation of Net Community Production in the North Patch

[55] The primary objective of this investigation is to estimate the changes in the net community production in response to iron additions. First, our method for estimating the net community production is presented, and then the results will be compared with those of other similar and related investigations. In order to estimate the magnitude of the net community production that took place by iron addition, we need to correct the observed reductions in CO₂ and nutrients for dilution by lateral mixing and sea-air gas transfer. The material balance in the fertilized patch may be described by the equation below: the first term on the right is the net biological utilization, the second term is the dilution by lateral mixing, the third term is the sea-air gas exchange term (for CO₂ only), and the fourth term is vertical transport across the base of mixed layer via eddy diffusion. It is important to note that the calculation detailed below will generate the enhancement of productivity above background levels, and not the total net productivity.

\[
dC_in = dB_in - m \cdot (C_{out} - C_{in}) \cdot dt + (G/Z) \cdot (P_{sw} - P_{air}) \cdot dt + (1/Z) \cdot K_Z \cdot (dC/dz) \cdot dt,
\]

where

- \( C_{in} \) concentration of compound in the fertilized patch at time “t,” µmol/kg;
- \( B_{in} \) net biological community utilization at time “t,” µmol/kg;
- \( m \) mean rate of dilution by lateral mixing, day⁻¹;
- \( C_{out} \) concentration of compound outside the patch at time “t,” µmol/kg;
- \( G \) gas transfer rate for CO₂ across the sea surface, µmol µatm⁻¹ day⁻¹ m⁻²;
- \( Z \) depth of mixed layer, m;
- \( P_{sw} \) partial pressure of CO₂ in seawater, µatm;
- \( P_{air} \) partial pressure of CO₂ in overlying air, µatm;
- \( K_Z \) vertical eddy diffusivity at the base of mixed layer, m² sec⁻¹;
- \( dC/dz \) concentration gradient at the base of mixed layer, µmol m⁻¹.

The following approximations are used to simplify equation (1):

- m constant at 0.1 (+10%) day⁻¹ for the north patch [Coale et al., 2004];
- \( (C_{out} - C_{in}) \) constant at −10 µmol kg⁻¹ according to Figure 3 of Hiscock and Millero [2005];
- \( G/Z = 0.0031 (±10%) \) µmol µatm⁻¹ day⁻¹ kg⁻¹ for the north patch [Honjo and Manganini, 1993];
- assuming \( G = 0.0048 \) mol CO₂ µatm⁻¹ m⁻² month⁻¹ = 160 µmol µatm⁻¹ day⁻¹ m⁻² [Takahashi et al., 2009]; and \( Z = 50 ± 5 \) m;
- \( P_{sw} \) assume that \( P_{sw} \) decreases linearly with time from 368 atm at \( t = 0 \) to 332 µatm at the 28th day: \( P_{sw} (\mu atm) = 368 - 1.294 (t \text{ day}) \);
- \( P_{air} \) constant at 362 µatm; the atmospheric pCO₂ during this period is estimated using the atmospheric CO₂ concentration of 369 ppm [Climate Monitoring and Diagnostics Laboratory, 2006], a climatological mean barometric pressure of 0.991 atm (or 1004 mb) and water vapor pressure at 7.4°C;
Table 3. Net Community Utilization of CO₂ and Nutrients Estimated for the North Patch Based Upon the Measurements Made by Tow 3C on the 28th Day After the Iron Addition

<table>
<thead>
<tr>
<th>CO₂</th>
<th>Phosphate</th>
<th>Nitrate</th>
<th>Silicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔCₐ (µmol kg⁻¹)</td>
<td>22 ± 3</td>
<td>0.22 ± 0.03</td>
<td>2.5 ± 0.3</td>
</tr>
<tr>
<td>(Cₐ - C₀) (µmol kg⁻¹)</td>
<td>10</td>
<td>0.07</td>
<td>1.3</td>
</tr>
<tr>
<td>Lateral mixing (µmol kg⁻¹)</td>
<td>28 ± 3</td>
<td>0.20 ± 0.02</td>
<td>3.6 ± 0.4</td>
</tr>
<tr>
<td>Air-to-sea exchange (µmol kg⁻¹)</td>
<td>2.1 ± 0.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mixed layer depth (meters)</td>
<td>50 ± 5</td>
<td>50 ± 5</td>
<td>50 ± 5</td>
</tr>
<tr>
<td>ΔBₐ (µmol kg⁻¹)</td>
<td>52 ± 4</td>
<td>0.42 ± 0.04</td>
<td>6.1 ± 0.5</td>
</tr>
<tr>
<td>Mean dBₐ/dt (mmol m⁻² day⁻¹)</td>
<td>94 ± 12</td>
<td>0.77 ± 0.10</td>
<td>11.2 ± 1.4</td>
</tr>
<tr>
<td>Net utilization ratios (P as 1)</td>
<td>122 ± 15</td>
<td>1</td>
<td>14.5 ± 1.8</td>
</tr>
</tbody>
</table>

All the values are mean for the 28 day period. See text for the definitions of symbols and method of calculation. Net biological community production in the fertilized patch (ΔBₐ) is a sum of the observed drawdown (ΔCₐ), and the contributions by lateral mixing and air-sea exchange; and (Cₐ - C₀) is used for estimating the lateral mixing effect. The mean rate of production (dBₐ/dt) is obtained by dividing ΔBₐ by 28 days.

K₉ estimated to be between 10⁻⁵ and 10⁻⁶ m²/sec within the basal zone (45 m–65 m) of the mixed layer using the Brunt-Vaisala frequency (n²), and vertical shear from the ADCP data;

\[
(dC/dz) = 8 \text{ mol kg}^{-1}/(65 \text{ m} - 45 \text{ m}) = 400 \text{ mol m}^{-4} \text{ for TCO₂.}
\]

[56] The vertical flux term, \((1/Z) K_z (dC/dz) dt\), is small, ranging between 0.02 and 0.2 \text{ µmol kg}^{-1} for 28 days, and hence is neglected. Accordingly, equation (1) may be simplified to

\[
dBₐ = -dCₐ - 0.1 \cdot (10) \cdot dCₐ + (0.0031) \cdot (368 - 1.29 \cdot t - 362) \cdot dt.
\]

[57] Integration from \(t = 0\) to \(t\) days yields the time-integrated net biological production (ΔBₐ)

\[
ΔBₐ (\text{µmol kg}^{-1}) = ΔTCₐ - 0.1 \cdot 10 \cdot t + (0.0031) \cdot (6 - 1.29 \cdot t/2) \cdot t,
\]

where ΔTCₐ is the change in TCO₂ (µmol kg⁻¹) observed within the patch in time “t” (days).

[58] We observe ΔTCₐ of \(-22 (±3) \text{ µmol kg}^{-1} (= 2089 (±2) - 2111(±2)) \text{ in 28 days within the north patch along tow 3C, and obtain}

\[
ΔBₐ(28 \text{ days}) = -22 (±3) - 28 (±3) - 1.0 (±0.2)
\]

\[
= -51 (±4) \text{ µmol kg}^{-1},
\]

in which 28 µmol kg⁻¹ is the lateral mixing term and 1.0 µmol kg⁻¹ is the sea-air gas transfer term. While the air-to-sea flux is small, the lateral mixing term is as large as the TCO₂ drawdown, and the observed TCO₂ drawdown is less than a half of the net community production. The mean daily rate of the net production may be obtained by dividing the above number by 28 days and multiplying with a constant mixed layer depth of 50 ± 5 m

\[
ΔBₐ(\text{per day}) = 1.82 (±0.14) \text{ µmol kg}^{-1} \text{ day}^{-1}
\]

\[
= 94 (±12) \text{ mmol m}^{-2} \text{ day}.
\]

[59] The net community production rate thus estimated should represent the net enhanced community production rate for all forms of reduced and particulate carbon products including dissolved organic matter and particulate biogenic debris (POC and CaCO₃), that accumulate in or are exported from the mixed layer. The rate accounts for the effect of dilution by lateral mixing and entrainment of adjacent waters.

[60] The net community utilization rate for silica and other nutrients may be estimated similarly using measured depletions in the north patch and a dilution rate of 0.1 day⁻¹, as suggested by Coale et al. [2004]. The results are summarized in Table 3. Through iron additions, the mean rate of net community production is boosted to a peak production level equivalent to that seen during natural maximum spring phytoplankton blooms [Hiscock et al., 2003]. However, the uptake of atmospheric CO₂ by the ocean after 28 days is only 2% (1.0 µmol kg⁻¹) of the biological production due to the slow sea-air gas transfer rate. This is similar to 2.4% estimated by Bakker et al. [2001] during the 13 day SOIREE experiment.

4.4. Net Utilization of Carbon in Iron Fertilized Southern Ocean Waters

[61] There have now been five large-scale Southern Ocean iron fertilization experiments, the SOFeX north and south patches that we discussed above, the Southern Ocean Iron Enrichment Experiment (SOIREE), EisenEx and SAGE. These experiments saw varying degrees of response, across a wide range of available silicate to nitrate ratios, as summarized in Table 4.

4.4.1. North Patch

[62] Since the drawdown measurements presented here were made after different numbers of days after iron additions in these studies, the mean daily rates for dilution-corrected net community utilization are used for comparison among the three fertilization experiments conducted in the Pacific sector of the Southern Ocean (Table 4). These values are computed by dividing the net community utilization by the number of days since the first addition of iron as described in section 4.1. The result of this study for the north patch (94 ± 12 mmol m⁻² day⁻¹) is consistent with those of Hiscock and Millero [2005] (78 ± 29 mmol m⁻² day⁻¹) within the respective uncertainties, in spite of the differences in the methods of investigation. Ours are based on the high frequency measurements made on a single day across the north patch on the 28th day, whereas theirs are based on the measurements made on the 9th, 12th and 39th days at stations occupied inside and outside the fertilized zone.

[63] Estimates of biological production yield similar results. Coale et al. [2004] estimated the production of POC...
in the north patch of 60 μmol carbon L⁻¹ in 28 days (corrected for dilution), which gives a mean POC production rate of 107 mmol C m⁻² day⁻¹ using a mean mixed layer depth of 50 m. This is also consistent with our drawdown-based rate and suggests that the reduction of TCO₂ in mixed layer is primarily accounted for by the formation of POC. Lance et al. [2007] determined the primary production rates at the SOFeX north patch using carbon-14 spiked water samples incubated aboard the ship for 24 h. Their results approximate net community production in the absence of heterotrophic interactions [Marra, 2009]. They observed that the daily mean production rate integrated down to 90 m deep (at 1% of surface irradiance level) increased by six-fold in 26 days, linearly with time from about 25 to 142 ± 23 mmol C m⁻² day⁻¹ giving a mean enhanced production rate of 84 ± 11 mmol C m⁻² day⁻¹. These estimates are broadly consistent with the others, within their respective uncertainties.

### 4.4.2. South Patch

Our observations in the south patch came such a short time after fertilization that we were unable to estimate biological uptake rates in any meaningful way, so we will examine the results of other researchers who studied longer-term results. On the basis of the depletion of CO₂ and nutrients observed in the south patch, where macronutrient concentrations, particularly silicate, are much higher than those at the north patch, Hiscock and Millero [2005] obtained a net production of 129 ± 34 mmol C m⁻² day⁻¹. This is within uncertainty of our north patch result, although it is statistically higher than Hiscock and Millero’s estimated production for the north patch. Lance et al. [2007] provide observations that give a mean production rate of 93 ± 4 mmol C m⁻² day⁻¹ for 20 days, again similar to the north patch estimates.

### 4.4.3. SOIR EE

At the SOIR EE site, silicate concentrations (~10 mol kg⁻¹) are about 1/6 those of the south patch and ~4 times higher than those is the north patch, but nitrate and phosphate concentrations are similarly in excess. For fertilized waters at the SOIR EE site, Bakker et al. [2005, 2005] reported a 12 day average production rate of 70 ± 15 mmol C m⁻² day⁻¹, with a maximum production rate of 108 mmol C m⁻² day⁻¹ [Boyd et al., 2000; Boyd and Law, 2001] on the basis of the depletions of CO₂ and nutrients. These rates are within ~50% of the SOFeX south and north patch values.

### 4.4.4. Eisen Ex

EisenEx waters were intermediate in silicate concentration, with values (~15 μmol kg⁻¹) and replete in other macronutrients. Several storms complicated the interpretation of the net production increase in fertilized waters [Bakker et al., 2005, Bozec et al., 2005], but after incorporating these effects, a net community production increase in fertilized waters was estimated at 31 ± 13 mmol C m⁻² day⁻¹ after 12 days and 39 ± 14 mmol C m⁻² day⁻¹ after 18 days.

### 4.4.5. SAGE

The SOLAS Air-Sea Gas Exchange Experiment (SAGE) was an experiment designed to study gas transfer rates and mechanisms in addition to the impacts of iron enrichments [Harvey et al., 2011]. Silicate to nitrate ratios in prefertilized waters were about 0.1, similar to those seen in the SOFeX north patch, although absolute silicate concentrations in these waters appeared to be about half those in unfertilized north patch waters. The SOFeX north patch, however, saw its silicate levels depleted to ~0.5 μmol kg⁻¹ in the depths of the nutrient depletions in the core of the north patch. Although primary productivity, biomass, and variable fluorescence in SAGE waters all saw positive responses to iron addition, these responses were modest in comparison to

---

**Table 4.** The Mean Rates of Biological Utilization and Their Elemental Ratios for Four Pacific Sector Southern Ocean Iron Addition Experiments

<table>
<thead>
<tr>
<th></th>
<th>North Patch (54°S, 169°W)</th>
<th>South Patch (66°S, 172°W)</th>
<th>SOIR EE (61°S, 141°E)</th>
<th>EisenEx (48°S, 21°E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This Study</td>
<td>Hiscock and Millero [2005]</td>
<td>Boyd et al. [2000]</td>
<td>Bakker et al. [2005]</td>
</tr>
<tr>
<td>NO₃</td>
<td>21.9 ± 0.2</td>
<td>21.9 ± 0.2</td>
<td>26.3 ± 0.2</td>
<td>25 ± 1</td>
</tr>
<tr>
<td>PO₄</td>
<td>1.40 ± 0.02</td>
<td>1.40 ± 0.02</td>
<td>1.87 ± 0.02</td>
<td>1.5 ± 1</td>
</tr>
<tr>
<td>SiO₃</td>
<td>7.1 ± 0.4</td>
<td>7.1 ± 0.4</td>
<td>6.2 ± 0.2</td>
<td>10 ± 4</td>
</tr>
<tr>
<td>Duration</td>
<td>28 day mean</td>
<td>39 day mean</td>
<td>20 day mean</td>
<td>12 day mean</td>
</tr>
</tbody>
</table>

**Concentrations in Prefertilized Waters (μmol kg⁻¹)**

<table>
<thead>
<tr>
<th></th>
<th>North Patch (54°S, 169°W)</th>
<th>South Patch (66°S, 172°W)</th>
<th>SOIR EE (61°S, 141°E)</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This Study</td>
<td>Hiscock and Millero [2005]</td>
<td>Boyd et al. [2000]</td>
<td>Bakker et al. [2005]</td>
</tr>
<tr>
<td>ΔCO₂/ΔNO₃</td>
<td>8.5 ± 1.0</td>
<td>10.0 ± 3.8</td>
<td>6.1 ± 1.5</td>
<td>6.2 ± 1.2</td>
</tr>
<tr>
<td>ΔCO₂/ΔPO₄</td>
<td>124 ± 10</td>
<td>154 ± 55</td>
<td>105 ± 24</td>
<td>94 ± 16</td>
</tr>
<tr>
<td>ΔCO₂/ΔSiO₃</td>
<td>10.4 ± 1.0</td>
<td>12.8 ± 6.5</td>
<td>5.3 ± 1.3</td>
<td>7.4 ± 1.7</td>
</tr>
<tr>
<td>ΔSiO₃/ΔNO₃</td>
<td>0.82 ± 0.08</td>
<td>0.8 ± 0.3</td>
<td>1.1 ± 0.1</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>ΔNO₃/ΔPO₄</td>
<td>14.5 ± 1.7</td>
<td>15.4 ± 5.6</td>
<td>16.7 ± 2.6</td>
<td>15.3 ± 2.3</td>
</tr>
</tbody>
</table>

**Elemental Utilization Ratios in the Fertilized Waters**

<table>
<thead>
<tr>
<th></th>
<th>North Patch (54°S, 169°W)</th>
<th>South Patch (66°S, 172°W)</th>
<th>SOIR EE (61°S, 141°E)</th>
<th>EisenEx (48°S, 21°E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This Study</td>
<td>Hiscock and Millero [2005]</td>
<td>Boyd et al. [2000]</td>
<td>Bakker et al. [2005]</td>
</tr>
<tr>
<td>CO₂</td>
<td>94 ± 12</td>
<td>78 ± 29</td>
<td>129 ± 34</td>
<td>70 ± 15</td>
</tr>
<tr>
<td>NO₃</td>
<td>11.2 ± 1.4</td>
<td>7.8 ± 1.5</td>
<td>21 ± 3</td>
<td>28 ± 4</td>
</tr>
<tr>
<td>PO₄</td>
<td>0.8 ± 0.1</td>
<td>0.5 ± 0.2</td>
<td>1.3 ± 0.2</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>SiO₃</td>
<td>9.2 ± 1.0</td>
<td>6.1 ± 2.3</td>
<td>25 ± 3</td>
<td>24 ± 4</td>
</tr>
</tbody>
</table>

**Mean Net Utilization, Accounting for Patch Dilution by Entrainment (mmol m⁻² day⁻¹)**

---

*While the uncertainties for this study include those from drawdown and mixed layer depth, those from other studies include only the uncertainties in the drawdown values. As mentioned earlier, our south patch measurements were made on 6 and 10 days after the iron additions, the drawdown was small and the uncertainties are large. Hence, our results for the south patch are omitted. For the EisenEx study, Bakker et al. [2005] determined mixing and gas exchange corrected uptake of carbon, while Bozec et al. [2005] did not correct for these complicating factors for the nutrient utilization. Uptake rates and ratios not listed for SAGE because there were no measurable depletions of carbon or nutrients in fertilized waters. ND, not determined.*
other experiments. Inorganic nutrients and carbon were not depleted at all, however, with concentrations 14 days after fertilization, actually higher than initial values and net community productivity essentially incalculable from elemental drawdowns.

4.4.6. Summary

[68] The biological uptake rates are thus similar in three of the five Southern Ocean fertilizations, with prefertilization silicate concentrations ranging from ~2 to ~65 μmol kg⁻¹ (Table 4). The two cases that showed remarkably lower net community productivity came from the EisenEx and SAGE sites, the former of which was nonlimiting in silicate while the latter was limiting. These two sites experienced significant storminess and elevated lateral and vertical mixing, and were occupied for only about two weeks after initial fertilization. Similar conditions were observed for the SOFeX south patch in the early stages following fertilization, and the only way productivity responses were observed was by the continued occupation of the patch by a second ship [Coale et al., 2004; Hiscock and Millero, 2005]. It appears, therefore, that the responses to iron fertilization depended not only on silicate concentrations in surrounding waters, but also on physical conditions that could shape biological responses. This includes not only physical processes that could limit net production stimulated by fertilization, but also the lateral and vertical transports of macronutrients to the fertilized zone, as suggested by Abraham et al. [2000]. Again, it must be stressed that all of these experiments were made over relatively short times since iron addition.

[69] While physical transport will continue to supply silicate to the patch at some rate, silicate at the north patch appears to have reached limiting concentrations. We are unaware of any quantitative kinetic mechanism that has dependence on any property besides absolute concentration. Nelson et al. [2001] demonstrated that silicate limitation of Southern Ocean diatom growth rates begins at concentrations as high as 8 μmol kg⁻¹, well above the values seen at the north patch. Brzezinski et al. [2005] clearly showed that silicate limitation of biogenic opal formation was a factor at the north patch, both in fertilized and unfertilized waters. Photosynthesis would not be likely to continue at similar net rates at these low silicate levels in the absence of shifts in the structure or functioning of the planktonic web there.

[70] One additional possibility must be discussed with respect to the differences between the SAGE and SOFeX north patch sites. Although nitrate: silicate ratios were similar at each location, and north patch silicate concentrations were drawn to levels even below those seen at the SAGE site, it is possible that the difference in initial silicate concentrations led to differences in the planktonic assemblages that shaped the two distinct responses. Peloquin et al. [2011a, 2011b] report exceedingly low diatom seed stocks at the SAGE site, and also an active grazing and microbial loop there. Uptake ratios at the SOFeX north patch distinctly show the prominent role of diatoms in shaping the response there, so perhaps the north patch was poised for a greater response than SAGE under any set of physical conditions.

4.5. Net Utilization Ratios for Carbon and Nutrients

[71] The net community utilization ratios between carbon and nutrients are computed for the north patch (Table 4) using the dilution-corrected values listed in Table 3. While the ΔSiO₃/ΔNO₃ and ΔNO₃/ΔPO₄ ratios for the north and south [from Hiscock and Millero, 2005] patches and the SOIREE site are all similar, the ΔCO₂/ΔNO₃, ΔCO₂/ΔPO₄ and ΔCO₂/ΔSiO₃ ratios for the low silicate north patch are greater than those for the high silicate south patch and the SOIREE site. Also the ratios for the south patch are consistent with those for SOIREE, although the silicate concentration for SOIREE is considerably lower. The iron fertilization in the north patch has therefore caused about 30–40% increase in the net communal carbon utilization per unit utilization of N, P and Si.

[72] The near equivalence of nitrate and silicate depletion strongly suggests that the bulk of the response to the iron fertilization is due to an increase in growth of iron-replete diatoms [Dugdale and Wilkerson, 1998], that have lower ΔSiO₃/ΔNO₃ and ΔSiO₃/ΔPO₄ ratios compared to the ones grown in iron-deficient waters [Hutchins and Bruland, 1998; Takeda, 1998]. In the south patch, silicate is abundant and exceeds iron-replete Si demands implied by available nitrate by nearly a factor of 3. Continued iron fertilization of this region would thus potentially stimulate complete NO₃ utilization, assuming physical factors were favorable. In the north patch, however, silicate in the fertilized region has been essentially exhausted while NO₃ remains at levels above 18 μmol kg⁻¹. Here, carbon uptake in response to iron fertilization has likely reached its limit as a result of silicate depletion unless a new phytoplankton assemblage that is not silicate dependent can begin to play a role. If not, then the maximum productivity response of the higher silicate environments will be ultimately greater. From the perspective of nutrient uptake and for the time scale of this experiment, this does not appear to have occurred, however, and it seems likely that limiting factors in addition to and independent of silicate availability will begin to play roles on longer timescales.

[73] Brzezinski et al. [2003] determined the net uptake ratios for Si, C and N by microplankton in the Southern Ocean (53°S–63°S, along 170°W; no iron added) using C-14, O-18, Si-29 and Si-32 as tracers for differentiating the net from the gross production and the postgrowth dissolution of silica from diatoms. After a 24 h incubation, they found that the average ratios in biogenic particulates were C/N = 9.1 ± 1.5, C/Si = 1.9 ± 0.4 and Si/N = 3.7 ± 0.4. While the C/N ratio for the net utilization for iron fertilized waters are similar to that in the particles, the C/Si ratios for the net utilization are 3 to 6 times as large as that for particles and the Si/N in particles is about 4 times as large as the utilization ratio. On the other hand, the sediment trap data of Buessem and et al. [2005] observed that the C/Si ratios in the trapped particles for outside the south patch are about 10, which is consistent with the drawdown-based values, and that they were similar to the ratios obtained for the outside the patch. The discrepancy between the C/Si and Si/N ratios for particles and those from the drawdown measurements may be accounted for if the loss of silica from grown diatoms in the incubation chamber is underestimated in the Brzezinski et al. [2003] study.

5. Summary and Conclusion

[74] The primary objectives of this study were to observe the differences in the effects of iron addition on the net
community production in different biogeochemical settings and to characterize the oceanographic environments of the fertilization sites. Using the undulating towed vehicle system equipped with a water sampling pump, the high-resolution 3-D distributions of temperature, salinity, density, pCO₂ and the concentrations of TCO₂, nitrate, phosphate and silicate were determined in the south (66°S and 172°W) and north (54°S and 169°W) patches in the upper 100 m of the ocean during the SOFeX expedition of the R/V Revelle, 5 January to 5 February 2002. In the south patch, the mixed layer water was replete with nitrate, phosphate and silicate, whereas the north patch water was similarly replete with the first two nutrients but had >20-fold lower, but apparently nonlimiting, silicate concentrations. The locations and subsequent dispersion of the original 15 km × 15 km iron additions were tracked using SF₆, which was added to the mixed layer water at the time of the initial iron addition. [75] In the south patch, the SF₆ tracer and hence the added iron dispersed in a more or less circular pattern. Four high-resolution sections traversing the fertilized zone were obtained about 10 days after iron was first added to the water. Here, below the 50 m deep mixed layer, a cold layer of winter remnant water (about 20 m thick, −1.8°C) was present; and below it, the warmer and more saline Circumpolar Deep Water was found. The iron addition effects depicted by drawdown of CO₂ and nutrients were observed only within the mixed layer above these two water masses. On the basis of the data obtained 10 days after the initial iron addition, the reduction of biogeochemical properties induced by the iron fertilization has been estimated; ∆pCO₂ was 15 ± 2.1 μatm, ∆TCO₂ = 4 ± 4 μmol kg⁻¹, ∆NO₂ = 0.5 ± 0.2 μmol kg⁻¹, ∆PO₄ = 0.05 ± 0.02 μmol kg⁻¹ and ∆SiO₂ = 0.8 ± 0.2 μmol kg⁻¹. Uncertainties are large relative to the small changes that took place during the short incubation time. [76] In the north patch, the tracer and iron were added to two adjacent water types: the northern one was more saline and denser (salinity = 34.0; sigma-t = 26.57) than the southern one (salinity = 33.94; sigma-t = 26.51) (see Figure 6). The patch spread along the front at the boundary of these two water types, and was stretched to a 7 km wide and 250 km long SW-NE band in the 28 days since the first addition of iron. We obtained a long transect along the axis of the new fertilized zone, and two transects that cut across the fertilized zone on the 28th day after fertilization, a 3 times longer incubation time than observed in the south patch. Significant reductions in the pCO₂ (Figure 7) and the concentrations of TCO₂ (Figure 8a) and nutrients (Figures 8b–8d) were observed in both of these water types. Furthermore, the cross-front sections (Figures 10 and 11) showed that the denser of the two fertilized waters was being subducted by as much as 50 m under the lighter layer. This process may be similar to the frontal dynamics that were described by Strass et al. [2002] or Allen et al. [2005]. The subducting layer contained atmospheric CO₂ taken up from the overlying air, as well as the POC and dissolved organic carbon newly formed by the iron fertilization. However, the subduction cut short the exchange time with atmospheric CO₂, and the CO₂ uptake flux from air constitutes only 2% (1.8 mmol m⁻² day⁻¹) of the biological uptake of CO₂ in 28 days (94 × 12 mmol C m⁻² day⁻¹). This process reduces the effectiveness of the iron fertilization for the purpose of the reduction of atmospheric CO₂. [77] The export of POC started only after the 26th day and peaked around the 40th day, according to the Lagrangian float deployed by Bishop et al. [2004] under the mixed layer. Rapid increase in the export flux observed by Bishop et al. [2004] after the 26th day might be attributed to the subduction of the fertilized water to a point where conditions favored bloom termination and/or aggregation and enhanced settling rates. The CO₂ and organic matter dissolved in the subducted water would be mixed eventually with surrounding waters; however subduction appeared to be limited to depths shallower than the pycnocline at about 75 m depth, and probably did not represent a long-term sequestration pathway. The along-front spreading of the patch should enhance lateral mixing with surrounding waters adding silica to the patch thus prolonging the life of the fertilization as pointed out by Abraham et al. [2000]. [78] After 28 days since the initial iron addition, CO₂ and nutrients in the north patch mixed layer water were drawn down by: ∆pCO₂ = 36 ± 3 μatm, ∆TCO₂ = 22 ± 4 μmol kg⁻¹, ∆NO₂ = 2.5 ± 0.3 μmol kg⁻¹, ∆PO₄ = 0.22 ± 0.03 μmol kg⁻¹, and ∆SiO₂ = 2.50 ± 0.07 μmol kg⁻¹. Correcting these values for entrainment (0.10 day⁻¹) of surrounding waters, we estimated the 28 day mean net utilization rate in mmol m⁻² day⁻¹ of 94 ± 12 for carbon, 11.2 ± 1.4 for nitrate, 0.8 ± 0.1 for phosphate and 9.2 ± 1.0 for silicate. These are consistent with the estimate by Piccirillo and Millero [2005], and by Llano et al. [2007], and with the results of previous iron fertilization experiments in the Southern Ocean. We did not see any strong relation between fertilization response and available silicate levels among experiments, despite the fact that the north patch had limiting silicate concentrations before and during the fertilization-induced bloom. We attribute low biogeochemical signatures of net community production in some experiments to short occupations during stormy conditions following fertilization. [79] Although uncertainties are large at the south patch, ∆CO₂/∆NO₂, ∆CO₂/∆PO₄, and ∆CO₂/∆SiO₂ drawdown ratios for the north patch are considerably larger than those for the south patch, indicating that more carbon is utilized for a unit nutrient. This suggests that, on the basis of the utilization ratios, this area may be considered more favorable than the south patch for enhanced CO₂ sequestration by iron fertilization, despite its lower silicate concentration. However, the response of the north patch appeared to have exhausted the silicate supply, and this stoichiometric enhancement may be canceled by the greater prolonged utilization rate in the south patch. Unless a distinct assemblage can continue to take advantage of added Fe in the absence of Si, the total effect of fertilizing in the region of the north patch appears to have reached its maximum and further production will be curtailed.

[80] Acknowledgments. We thank David W. Chipman, John G. Goddard, Stewart C. Sutherland, Erik Scholz and Colm Sweeney of LDEO and Leah Bandstra, Paul Covert, Dale Hubbard and Joe Jennings of OSU for their assistance at sea and on land; Gernot Friederich and Peter Strutton of MBARI for providing the underway pCO₂ data; and R. Wanninkhof and Kevin Sullivan of NOAA-AOML for providing the SF₆ data. Leadership of Kenneth H. Coale of Moss Landing Marine Laboratory and Kenneth S. Johnson of MBARI for the SOFeX project is appreciated. Discussions with Mark Brzezinski were helpful with regards to the silicate limitation issue. We gratefully acknowledge grants from NSF to OSU and LDEO for the
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