

Control of silica production by iron and silicic acid during the Southern Ocean Iron Experiment (SOFeX)

Mark A. Brzezinski, Janice L. Jones, and Mark S. Demarest

The Marine Science Institute and the Department of Ecology Evolution and Marine Biology, University of California, Santa Barbara, California 93106

Abstract

We examined the role of Si limitation in mediating the response of siliceous biomass and silica production to mesoscale Fe fertilization in the high-silicic acid high-nitrate waters of the Antarctic and in the low-silicic acid high-nitrate waters of the Subantarctic during austral summer. Iron fertilization stimulated biogenic silica production and silicic acid depletion in both regions. Si limitation significantly curtailed the response of silica production to Fe in the Subantarctic, but not in the Antarctic. Additions of silicic acid to Fe-enriched waters of the Subantarctic more than doubled specific silica production rates beyond the increase caused by Fe alone. This result, combined with the presence of Si limitation both inside and outside of the fertilized patch in the Subantarctic, indicates that silica production in the Subantarctic is regulated by both Fe and Si during austral summer. Fe increased the ability of Subantarctic diatom assemblages to take up low concentrations of Si over an order of magnitude by increasing maximum uptake rates and lowering half-saturation constants for silicic acid uptake. Our observations indicate that the dramatic gradient in Si availability across the Antarctic Circumpolar Current exerts a strong control on the contribution of diatoms to new production following Fe enrichment in the Southern Ocean during austral summer. With sufficient Fe to allow nitrate depletion, the abundant silicic acid in the Antarctic would allow diatoms to dominate nitrate use; however, low silicic acid concentrations in the Subantarctic would restrict the fraction of available nitrate that would be consumed by diatoms to ca. 5%.

In his original iron hypothesis John Martin postulated that the high-nutrient low-chlorophyll (HNLC) character of the Southern Ocean exists because iron limitation prevents the consumption of macronutrients by phytoplankton (Martin et al. 1990a,b). A series of recent mesoscale Fe fertilization experiments demonstrated that low iron limits primary production, phytoplankton biomass, and nitrate use in the Southern Ocean (Boyd et al. 2000; Smetacek 2001; Coale et al. 2004). A consistent result of these experiments is that diatoms are the group of phytoplankton whose biomass increases most strongly when iron is added to HNLC waters (Boyd et al. 2000; Smetacek 2001; Tsuda et al. 2003; Coale et al. 2004). Because diatoms have an absolute requirement for silicon to build their cell walls (Lewin 1962), their ability to dominate the response to Fe enrichment requires an adequate supply of silicic acid to support their growth. Recent experiments confirm that the biogeochemical response to the addition of Fe in Southern Ocean waters can be influenced by the availability of Si (Franck et al. 2000, 2003; Hutchins et al. 2001; Brzezinski et al. 2003).

The ability of Si to influence the response to Fe arises because most of the Southern Ocean is not a true HNLC region in that, although nitrate may be abundant ($15\text{--}20\ \mu\text{mol L}^{-1}$), silicic acid can be depleted to very low levels ($<3\ \mu\text{mol L}^{-1}$). Dugdale et al. (1995) used the term low-

silicic acid high-nitrate low-chlorophyll (LSiHNLC) to describe these waters. The low silicic acid concentrations in these regions may truncate the response of diatoms to Fe enrichment while ample nitrate remains to support considerable growth by other phytoplankton groups. A shift in nitrate-based new production from diatoms to nonsiliceous phytoplankton would alter phytoplankton community structure and elemental cycling; thereby influencing carbon export through changes in food web structure and the mineral ballast associated with particles (Armstrong et al. 2002).

The LSiHNLC condition in the Southern Ocean shows considerable spatial and temporal variance that is related to the position of major fronts and regional circulation (Fig. 1). In the Pacific sector along 170°W longitude where we conducted our study, the waters adjacent to the continent of Antarctica are part of the Ross Sea Gyre (Orsi et al. 1995). Both silicic acid and nitrate concentrations are persistently high in this area, making it a true HNLC region. Further north is the Southern ACC Front (SACCF), which marks the southern boundary of the Antarctic Circumpolar Current (ACC). Between the SACCF and the Antarctic Polar Front (APF) to the north there exists the most intense and most geographically extensive meridional gradient in mixed-layer silicic acid concentration in the global ocean (Pondaven et al. 2000; Smith et al. 2000). The gradient can be as steep as $0.5\ \mu\text{mol L}^{-1}\ \text{km}^{-1}$ across, which $[\text{Si}(\text{OH})_4]$ changes by over $40\ \mu\text{mol L}^{-1}$ (Dafner and Mordasova 1994; Smith et al. 2000). Near-total silicic acid depletion ($<1\ \mu\text{mol L}^{-1}$) can occur in this zone during austral summer while nitrate remains $>20\ \mu\text{mol L}^{-1}$ (Sigmon et al. 2002), resulting in a seasonal shift from HNLC to LSiHNLC conditions. A similar seasonal shift from HNLC to LSiHNLC conditions occurs further north in both the Antarctic Polar Frontal Zone

Acknowledgments

We thank the officers and crew of the RV *Melville* for their valuable assistance. Dick Barber kindly took samples for biogenic silica concentration aboard the RV *Revelle*. We thank the entire SOFeX team for their help and support. This manuscript benefited from comments by Philip Boyd and one anonymous reviewer.

This work was supported by OCE-9985887 from the NSF.

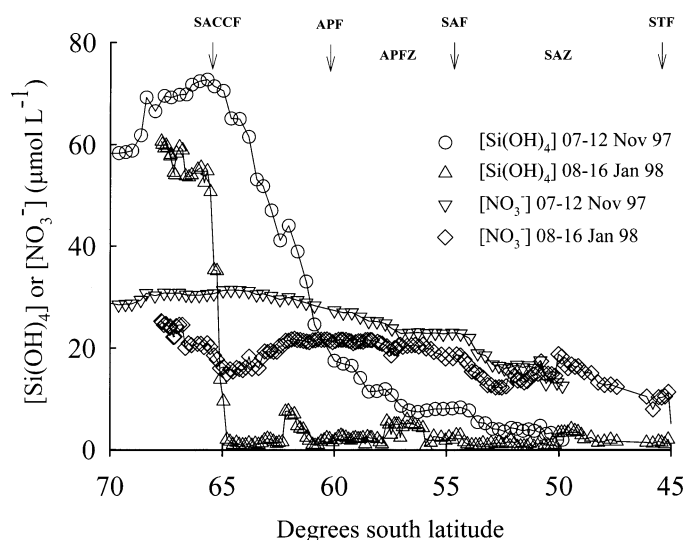


Fig. 1. Surface silicic acid and nitrate concentrations along 170°W longitude measured on 7–12 November 1997 and 8–16 January 1998 (adapted from Smith et al. 2000). Arrows indicate the position of major fronts (Southern ACC Front [SACCF], Antarctic Polar Front [APF], Subantarctic Front [SAF], Subtropical Front [STF]) that define the major latitudinal zones of the Southern Ocean: The Antarctic Polar Front Zone (APFZ) and the Subantarctic Zone (SAZ).

(APFZ) and in the Subantarctic zone (SAZ, Fig. 1). Nitrate concentrations remain $>8\text{--}15\ \mu\text{mol L}^{-1}$ in both areas, whereas silicic acid concentrations are depleted to $<1\text{--}3\ \mu\text{mol L}^{-1}$ during austral summer (Boyd et al. 1999; Brzezinski et al. 2001; Hutchins et al. 2001). These trends create a striking pattern of decreasing silicic acid:nitrate concentration ratios from the south to the north across the ACC (Sarmiento et al. 2003), with silicic acid concentrations in the north being depleted seasonally to values that would limit silicic acid uptake by most diatoms (Martin-Jézéquel et al. 2000), while nitrate remains abundant.

Experimental evaluations of the kinetics of Si use in the Southern Ocean suggest that the potential for Si limitation parallels the equatorward decrease in silicic acid availability. Nelson et al. (2001) found no evidence of Si limitation of silica production in the high-Si(OH)₄ waters to the south of the SACCF. The seasonal depletion of silicic acid in the Pacific sector between the SACCF and the APF can cause a shift from silica production being Fe-limited during spring to it being Si-limited in summer (Franck et al. 2000; Nelson et al. 2001). In the APFZ, silica production rates are severely limited by low silicic acid concentration during summer in both the Australian (Quéguiner 2001) and Pacific (Franck et al. 2000; Nelson et al. 2001) sectors. Studies in the SAZ indicate a succession of limiting factors, with light limitation dominating in early spring followed by Fe limitation upon stratification of the water column and then Si limitation by austral summer (Boyd et al. 1999; Boyd 2002a). Consideration of all of these experimental data sets suggests that the potential for interactions between Si and Fe limitation, at least as it pertains to silica production rates, is a possibility

in any region to the north of the SACCF, especially during austral summer.

In situ mesoscale Fe enrichment experiments offer an opportunity to examine the relative roles of Si and Fe as limiting nutrients in the Southern Ocean. Two iron fertilization experiments had been performed in the Southern Ocean prior to the Southern Ocean Iron Fertilization Experiment (SOFeX; Coale et al. 2004). EisenEx [eisen (= iron) experiment] was performed in the Atlantic sector within the APFZ and Southern Ocean Iron Release Experiment (SOIREE) was performed in the Australian sector just to the south of the APF (Boyd et al. 2000; Smetacek 2001). Initial mixed-layer silicic acid concentrations were ca. $10\ \mu\text{mol L}^{-1}$ during both of these experiments. Each experiment produced a bloom dominated by diatoms. The bloom produced during SOIREE was dominated by the diatom *Fragilariopsis kerguelensis* (Boyd et al. 2000), whereas EisenEx produced a bloom of diatoms of the genus *Pseudonitzschia* (Smetacek 2001). The diatom bloom produced during SOIREE depleted silicic acid concentration from just over $10\ \mu\text{mol L}^{-1}$ to $7.5\ \mu\text{mol L}^{-1}$ (Boyd et al. 2000), whereas concentrations remained $>10\ \mu\text{mol L}^{-1}$ during EisenEx (Smetacek 2001). The silicic acid concentrations present at the end of both SOIREE and EisenEx are at the high end of the range that has been observed to limit silica production in the Southern Ocean (Nelson et al. 2001). Nelson et al. (2001) conducted 87 assessments of Si limitation of silica production at locations extending from the APFZ to just south of the SACCF along 170°W. Detectable limitation of silica production occurred in nearly all experiments where ambient silicic acid concentrations were $<8\text{--}10\ \mu\text{mol L}^{-1}$, but was rare at higher concentrations. On the basis of these results the $\geq 7.5\ \mu\text{mol L}^{-1}$ [Si(OH)₄] present at the end of both SOIREE and EisenEx suggest that Si limitation of silica production, and by inference growth rate, was not present or at least not strong during either experiment.

To further examine interactions between Fe and Si in the Southern Ocean we conducted experiments aimed at assessing Si limitation and the response of silica production to mesoscale iron fertilization during SOFeX in the Pacific sector of the Southern Ocean. In situ iron enrichment was performed at 170°W longitude in both the low-Si waters (ca. $3\ \mu\text{mol L}^{-1}$ Si(OH)₄) of the Subantarctic and in the permanently high-Si waters (ca. $65\ \mu\text{mol L}^{-1}$) to the south of the SACCF. The strong difference in silicic acid concentration between the two sites offered the opportunity to evaluate how Si availability mediates the response of diatoms to mesoscale Fe fertilization. We tested two hypotheses. We anticipated that the apparently Si-replete conditions to the south of the SACCF would prevent Si limitation and allow diatoms to dominate the response to added Fe. The opposite was postulated for the Subantarctic, where we anticipated that Si limitation would decrease the relative contribution of diatoms to an iron-induced phytoplankton bloom. An overview of some of the results of these experiments has been reported briefly in Coale et al. (2004).

Methods

Iron was added as acidified iron sulfate by injection into the wake of the RV *Revelle* along a 15×15 km grid as

described previously (Coale et al. 2004). The “North Patch” was created in the Subantarctic (56.23°S, 172°W) on 12 January 2002, with the “South Patch” created 12 d later in the Antarctic just to the south of the SACCF (66.45°S, 171.8°W) on 24 January 2002. Sulfur hexafluoride was added with the initial infusion of Fe to mark each patch; subsequent additions of Fe did not contain SF₆. Time zero for the creation of each patch was defined as the time of first Fe release (North Patch: 12 January, 1400 h, UTC (coordinated universal time); South Patch: 24 January, 0730 h, UTC), although creating each patch required just over 24 h.

The majority of sampling for silicon cycling studies were conducted aboard a second ship, the RV *Melville*; however, samples for biogenic silica concentration were also collected aboard the *Revelle* (courtesy of R. Barber). The North Patch was occupied by the *Melville* only twice, on patch days 11.5–12.5 and then again on days 38.3–40.0. *Melville* sampled the South Patch more extensively from patch day 5 to day 21.6.

Profiles of silicic acid concentration, biogenic silica concentration, and silica production rates were obtained between the surface and the 0.1% light depth both inside and outside each patch. Water samples were collected using a trace metal clean rosette (Hunter et al. 1996). Stations were denoted as being inside the patch (IN stations) or outside the patch (OUT stations) using SF₆ concentration as a proxy for iron concentration. Those IN stations for which profiles of properties were obtained were chosen by seeking areas with high SF₆ concentration and high chlorophyll fluorescence as measured in near real-time on water collected through the ship's underway clean seawater intake system (ca. 3 m depth).

Maps of surface properties (3 m) were constructed in both patches by sampling from the ship's underway clean intake system while the ship steamed a prescribed course. When possible, navigation during mapping was done in a Lagrangian mode relative to a drifter deployed in the center of the patch (Coale et al. 2004). Properties were examined along transects of profile stations across the South Patch using the trace metal clean rosette system. Transect work was not conducted aboard the *Melville* in the North Patch.

Silicic acid concentrations were measured colorimetrically as previously described (Brzezinski and Nelson 1989), except that a 0.5-cm cuvette was used in the South Patch where silicic acid concentrations were high and a 10-cm cuvette was used in the North Patch where silicic acid concentrations were low. Precision determined by the analysis of replicate samples was better than 0.1 μmol L⁻¹. Independent analyses at sea of our sodium fluosilicate standard in artificial seawater by others determining nutrients on the *Revelle* revealed a variance between groups of <0.3%.

Seawater samples for biogenic silica concentration (1.2 liters) were analyzed using the NaOH digestion technique as described by Brzezinski and Nelson (1989). Silica production rates were measured on 320-ml seawater samples collected from six depths corresponding to 100, 47, 16, 5, 1, and 0.1% of the light intensity just below the sea surface using Chelex-cleaned ³²Si tracer (specific activity = 15,500 Bq/μg Si) as described by Brzezinski et al. (2001). Samples for production rate measurements were incubated in trace metal-cleaned polycarbonate bottles for 24 h in deckboard

incubators that had been adjusted to the desired light levels using neutral density and blue plastic screens and that were cooled with circulating surface seawater (Hiscock et al. 2003).

Substrate limitation of silica production was assessed in two ways. In one series of experiments the response of silica production to a single large addition of silicic acid was examined within the 45-m mixed layer (Coale et al. 2004) at the 47% and 16% light depths. For these experiments a water sample from a given depth was divided into two subsamples and one of the pair was augmented with trace metal-cleaned sodium metasilicate (+21 μmol L⁻¹ in the North Patch, +42 μmol L⁻¹ in the South Patch). ³²Si was then immediately added to all subsamples and each pair was incubated at the appropriate light level to determine the rate of silica production in each bottle. Under the assumption that the addition of silicic acid was sufficient to induce maximum silica production rates, the ratio of the rate measured in the bottle with added cold silicic acid to that in the unamended control is an indicator of the degree to which ambient silicic acid concentration limits silica production rates. We call this ratio the *enhancement statistic*, *E* (Brzezinski and Phillips 1997). A ratio of 1 indicates that ambient silicic acid concentrations were supporting maximum production rates, whereas ratios >1 indicate that ambient Si levels were restricting production rates to be less than maximal. The analytical and experimental uncertainties require that *E* exceed 1.2 to be significantly >1.0. The expression 1/*E* represents the fraction of maximum silica production rates supported at ambient silicic acid concentrations.

More detailed assessments of the kinetics of silicic acid use were made in a second series of experiments in which 4 liters of seawater from the 47% light depth were collected and divided into a series of eight 320-ml subsamples. Unlabeled Chelex-cleaned sodium metasilicate was added to the series to create a gradient of silicic acid concentrations followed by the addition of ³²Si(OH)₄ to each subsample. The subsamples were incubated at 47% light and the silica production rate determined over a 24-h incubation. The concentration dependence of silica production was examined by fitting the resulting production versus concentration curve to the Michaelis-Menten function by nonlinear regression, yielding values of the maximum rate of silica production (*V_m*) and the half-saturation constant (*K_s*). The results of these experiments confirmed that the concentrations used to saturate silica production in the determination of the enhancement statistic indeed achieved this goal in both the North and South Patches (see below).

Results

Patch dilution—Mixing will erode gradients in properties that develop between the enriched patch and the surrounding waters (Boyd and Law 2001). The dilution of a patch with the surrounding water will decrease the rates at which phytoplankton biomass increases and nutrients are depleted within the patch. The nutrients supplied by dilution will also retard nutrient limitation of phytoplankton rate processes. Coale et al. (2004) calculated average dilution rates of 0.11

d^{-1} and $0.08 d^{-1}$ for the North and South Patches, respectively, based on averaging the values obtained from patch deformation and the loss of SF_6 after correcting for outgassing. These rates were estimated to have diminished the apparent depletion of nutrients and the increase in phytoplankton biomass by two to four times in both patches (Coale et al. 2004). Coale et al. (2004) showed that the effects of patch dilution were especially pronounced in the Subantarctic, where by the end of the experiment silica production rates were in approximate balance with the resupply of silicic acid by patch dilution, halting further changes in biogenic silica and silicic acid concentrations.

In this paper we have not corrected the observed changes in silicic acid or biogenic silica concentrations for patch dilution. The SF_6 data set for the trace metal rosette casts is insufficient to determine the extent of dilution in each sample. The exponential nature of the biological response adds further uncertainty as to how to make an appropriate correction as the effect of patch dilution on concentration changes is smallest at the beginning of each experiment when the gradients in properties from inside to outside the patch are at their minimum and grows as the gradients increase exponentially with the biological response. Without correction our data represent conservative estimates of nutrient and biomass changes and the severity of nutrient limitation caused by Fe enrichment.

North Patch—Silicic acid concentration in the mixed layer measured aboard the *Revelle* before the creation of the North Patch was $2.8 \mu\text{mol L}^{-1}$ (Coale et al. 2004). Concentrations measured aboard the *Melville* during the first 12 d varied between 2.1 and $3.0 \mu\text{mol L}^{-1}$, with no indication of significant depletion relative to waters outside of the patch (Fig. 2a). The *Melville* departed the North Patch at this time to join the *Revelle* in the south. When the *Revelle* returned to the North Patch on day 28.5, mixed-layer silicic acid concentrations inside the patch were $0.6 \mu\text{mol L}^{-1}$, with similar levels, 0.4 and $0.9 \mu\text{mol L}^{-1}$, measured on day 39 aboard *Melville*, corresponding to a maximum observed depletion of $2.4 \mu\text{mol L}^{-1}$. Outside the patch mixed-layer silicic acid concentrations remained between 2.0 and $2.5 \mu\text{mol L}^{-1}$ over this same time period (Fig. 2a).

No data on biogenic silica concentrations are available for the refertilized waters of the North Patch, but levels were consistently low, ca. $0.2 \mu\text{mol L}^{-1}$, both inside and outside the patch for the first week of the experiment, suggesting little change from initial conditions (Fig. 2b). A slight increase in biogenic silica concentration occurred after nearly 12 d with mixed-layer concentrations, reaching $0.3 \mu\text{mol L}^{-1}$ on day 11.5. By the time the *Melville* returned to the North Patch on day 37 the patch had stretched to become a long filament of a few kilometers wide by over 340 km long that was visible from space because of its elevated phytoplankton pigment concentration (Coale et al. 2004). The *Melville* sampled the southwest end of the filament, which, on the basis of satellite imagery, did not encompass the highest biomass region of the patch, which lay further to the northeast. The survey of the southwest end of the patch on days 37–39 showed low silicic acid concentrations ($<1 \mu\text{mol L}^{-1}$), but relatively high biogenic silica concentrations ($0.8 \mu\text{mol L}^{-1}$)

compared to initial conditions, along the southwest to northeast axis of the patch in areas of elevated $[SF_6]$ (Fig. 3). The maximum biomass of $3.2 \mu\text{mol L}^{-1}$ of Si was observed in the northeast end of the survey, coincident with the minimum in silicic acid concentration of $0.40 \mu\text{mol L}^{-1}$ (Fig. 3).

A profile station on day 28.5 confirmed the large increase in siliceous biomass observed during the survey, with biogenic silica concentrations reaching $1.0\text{--}1.2 \mu\text{mol L}^{-1}$. Similarly high concentrations were sustained through day 39.3. These shifts correspond to an increase in integrated biogenic silica concentration for the upper 50 m from 8.3mmol m^{-2} on day 3.2 to 38.7 and $30.7 \text{mmol Si m}^{-2}$ on days 28.5 and 39.3, respectively (Table 1). In contrast, biogenic silica concentrations remained $\leq 0.2 \mu\text{mol L}^{-1}$ at OUT stations where integrated concentrations in the upper 50 m remained $\leq 13.1 \text{mmol m}^{-2}$ if Si (Table 1). We emphasize that the observed increase in biogenic silica concentrations in the patch underestimates the production of biogenic silica in response to Fe due to patch dilution.

Only limited data are available on the effect of Fe fertilization on silica production in the North Patch, but they show a clear and strong response of silica production to Fe. Silica production was first measured 11–12 d after fertilization. Absolute rates of silica production rates (ρ) were low ($0.007 \mu\text{mol L}^{-1} d^{-1}$) outside the patch, with low, but slightly higher, values in the patch ($0.02 \mu\text{mol L}^{-1} d^{-1}$; Fig. 2c). At this time integrated silica production rates (50 m) were 0.91 and $0.35 \text{mmol m}^{-2} d^{-1}$ at IN and OUT stations, respectively. By day 39.3 maximum production rates inside the patch had increased over an order of magnitude to $0.22 \mu\text{mol L}^{-1} d^{-1}$ of Si, with integrated rates in the upper 50 m of $4.4 \text{mmol m}^{-2} d^{-1}$ (Table 1). Rates remained low outside of the patch at ca. $0.01 \mu\text{mol L}^{-1} d^{-1}$, with integrated production rates of $0.50 \text{mmol m}^{-2} d^{-1}$.

Specific rates of production of biogenic silica (V_b) in the upper 50 m increased over 500% from $0.06 d^{-1}$ to $0.34 d^{-1}$ in the North Patch (Fig. 2d). The strong increase in V_b inside the patch indicates that the observed increase in ρ was a result of both increased biomass and a physiological response toward more rapid doubling times for biogenic silica. The highest values of V_b were observed at the last station occupied on day 39.3, with implied doubling times for the diatom assemblage of about 2 d. V_b remained low, $<0.06 d^{-1}$, in the upper 50 m outside the patch (Fig. 2d).

The results of the enhancement experiments showed that silica production rates at both IN and OUT stations increased significantly when ambient silicic acid concentrations were increased by $21 \mu\text{mol L}^{-1}$ (Fig. 4). Iron increased rates by over a factor of two at the 47% light depth both early and late in the experiment, with a stronger response occurring at OUT stations compared to IN stations. The response to added Si at the 16% light depth was also large, but similar levels of stimulation were observed at both IN and OUT stations. The universally strong increases in silica production in response to Si addition clearly indicate that the low silicic acid concentrations in the Subantarctic were a significant factor restricting silica production both inside and outside the fertilized area.

The kinetic experiments confirmed limitation of silica production by ambient Si(OH)_4 concentrations in the North

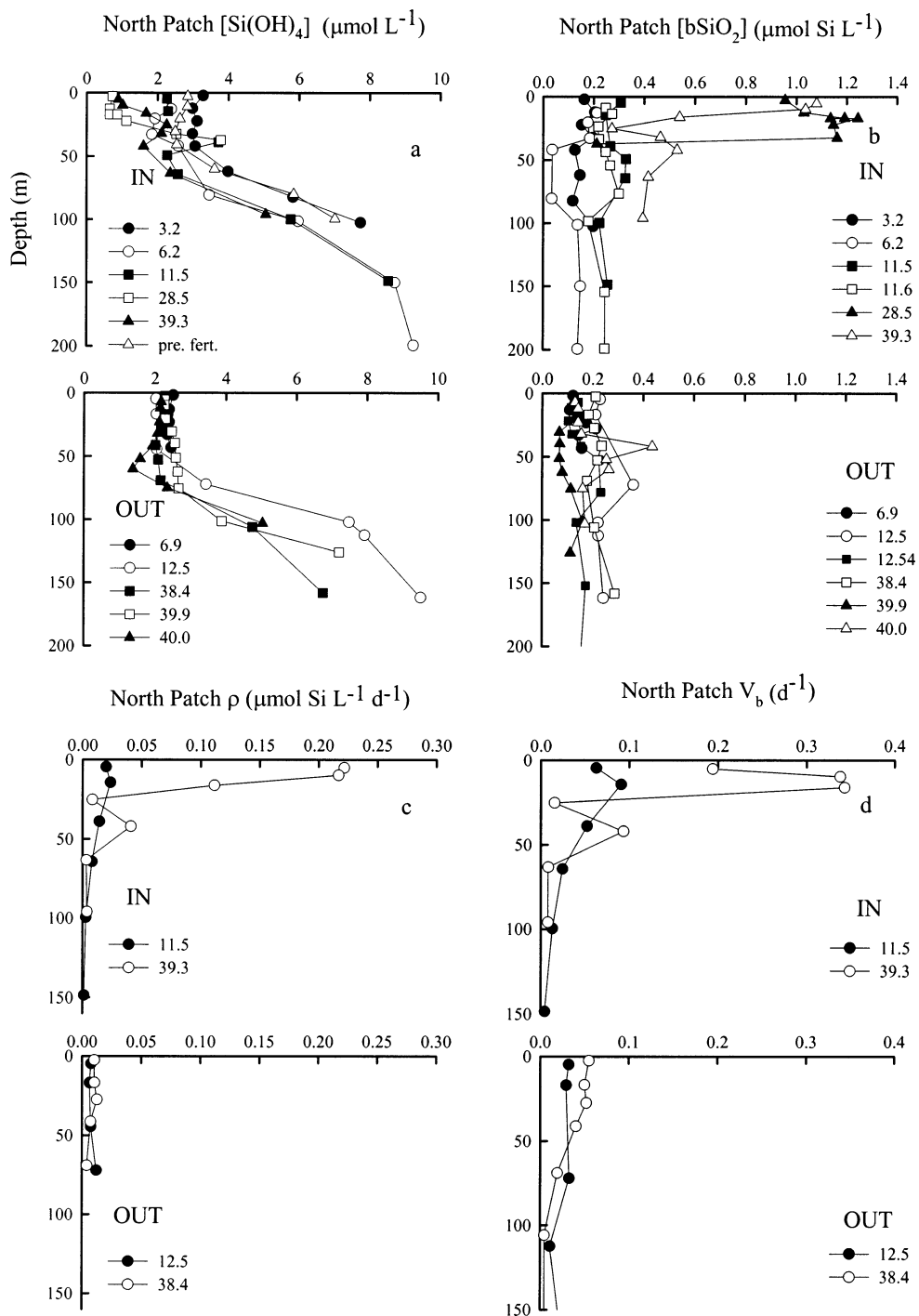


Fig. 2. Profiles of properties in the North Patch. (a) Silicic acid concentration, (b) biogenic silica concentration, (c) absolute silica production rates, (d) specific rates of silica production. Numerals in legends indicate day of each profile.

Patch and showed effects of Fe addition on both the half-saturation constants, K_s , and maximum uptake rates, V_m (Fig. 5). On day 12 the value of V_m was $0.52 \pm 0.04 \text{ d}^{-1}$ inside the patch and $0.37 \pm 0.06 \text{ d}^{-1}$ outside. By days 39–40 V_m in the patch, $0.31 \pm 0.03 \text{ d}^{-1}$, remained higher than outside, $0.11 \pm 0.02 \text{ d}^{-1}$, but both values had declined compared to the earlier observations. Fe also caused a significant change

in K_s . Our estimates of half-saturation constants are subject to significant error because of the lack of rate information at silicic acid concentrations $< \text{ca. } 3 \mu\text{mol L}^{-1}$. However, for the IN stations it is clear that in each case the value of K_s was less than the lowest $\text{Si}(\text{OH})_4$ concentration examined, as the lowest rates measured were not $< 0.5 V_m$ (Fig. 5). The lowest concentrations examined (i.e., ambient silicic acid

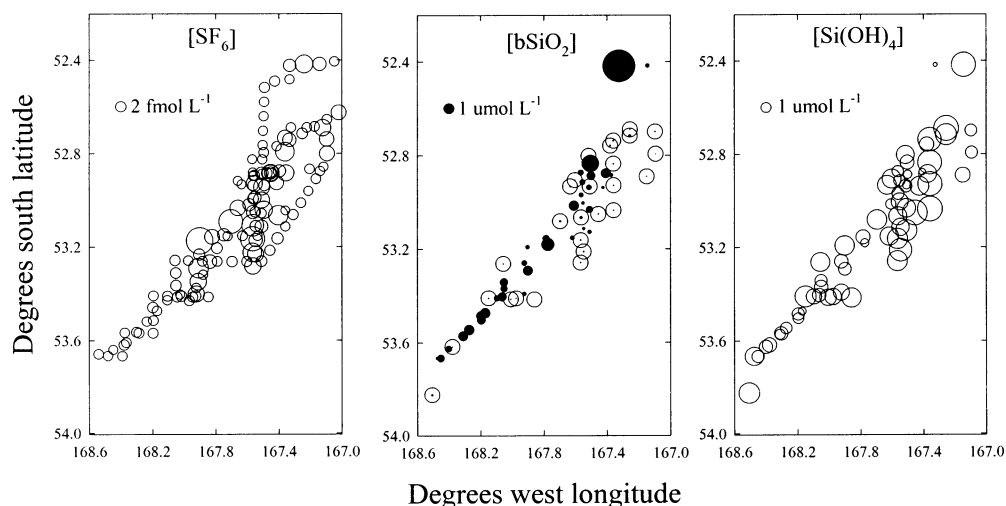


Fig. 3. Bubble plot of sulfur hexafluoride concentration $[SF_6]$, silicic acid concentration $[Si(OH)_4]$, and biogenic silica concentration $[bSiO_2]$, in the surface waters of the North Patch (3 m) on days 37.3–39.2. Bubble diameter is proportional to concentration. In the plot of biogenic silica concentration, values $<0.25 \mu\text{mol L}^{-1}$ are depicted by an open circle that encompasses a scaled filled circle too small to be readily visible. Note the $[SF_6]$ was measured at a different time interval from $[bSiO_2]$ and $[Si(OH)_4]$, so that the sampling locations for $[SF_6]$ are not the same as for the other parameters.

Table 1. Siliceous biomass and silica production rates for IN and OUT station in the North and South Patches.

Station	Location	Day of the year	Patch Day	Latitude ($^{\circ}\text{S}$)	Longitude ($^{\circ}\text{W}$)	$[bSi_2]$ (mmol Si m^{-2})	$\int \rho$ ($\text{mmol Si m}^{-2} \text{d}^{-1}$)	Average V_b (d^{-1})
9	North IN	15.8	3.2	56.040	171.880	8.3		
10	North IN	18.7	6.2	55.875	171.913	7.7		
1	North IN	24.1	11.5	55.329	171.490	13.7	0.91	0.062
1	North IN	24.2	11.6	55.313	171.432	12.0		
33	North IN	41.1	28.5	54.210	169.240	38.7		
45	North IN	51.9	39.3	52.884	167.452	30.7	4.4	0.174
11	North OUT	19.5	6.9	55.960	171.870	6.3		
2	North OUT	25.05	12.47	55.266	171.760	12.2	0.35	0.031
2	North OUT	25.13	12.54	55.258	171.768	6.6		
44	North OUT	51.0	38.4	52.385	166.947	13.1	0.50	0.046
46	North OUT	52.5	39.9	52.875	167.141	4.9		
47	North OUT	52.6	40.0	52.867	167.416	10.4		
19	South Pre-Fert.	23.5	-0.8	66.400	171.500	68.7		
20	South IN	26.2	1.9	64.470	171.900	84.2		
21	South IN	27.0	2.7	66.430	171.950	100.3		
24	South IN	27.6	3.3	66.420	171.940	88.3		
4	South IN	29.4	5.0	66.335	171.960	68.5		
4	South IN	30.1	5.7	66.337	171.962	91.9	8.4	0.091
7	South IN	31.8	7.5	66.320	171.916	87.9	7.2	0.078
18	South IN	35.1	10.8	66.260	171.964	90.5		
19	South IN	36.0	11.7	66.289	172.134	37.0	10.7	0.33
22	South IN	39.3	15.0	66.240	172.120	33.3	12.9	0.46
23	South IN	39.8	15.5	66.172	172.213	33.7	14.1	0.41
34	South IN	42.9	18.6	66.102	172.065	36.2	14.8	0.38
43	South IN	45.9	21.6	65.951	172.189	48.1	19.1	0.38
23	South OUT	27.5	3.1	66.600	171.780	78.2		
6	South OUT	31.1	6.8	66.612	171.818	89.8	5.6	0.071
10	South OUT	32.9	8.6	66.593	172.200	90.3	5.7	0.063
20	South OUT	36.9	12.6	66.312	171.373	19.1	4.0	0.28
36	South OUT	43.9	19.5	66.033	170.998	28.8	5.2	0.28

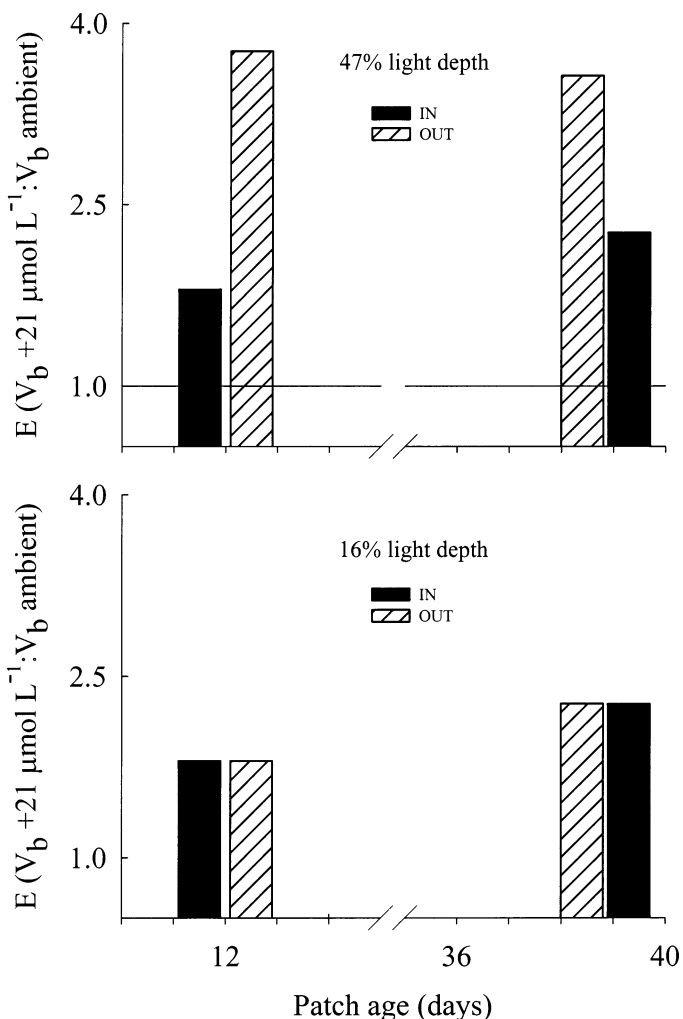


Fig. 4. Response of silica production to silicic acid addition at the 47% and 16% light depths in the North Patch.

concentrations) were 2.3 and 1.2 $\mu\text{mol L}^{-1}$ on days 12 and 40, respectively, indicating that K_s was less than these values in each case. K_s values obtained by nonlinear regression were 1.7 ± 0.40 and 0.63 ± 0.32 $\mu\text{mol L}^{-1}$ on days 12 and 40, respectively. The lowest rates measured in each kinetic experiment at both OUT stations were all $<0.5 V_m$, indicating that the concentration range examined encompassed the actual value of K_s . By this reasoning, K_s must be >2.0 $\mu\text{mol L}^{-1}$ on day 13 and >2.6 $\mu\text{mol L}^{-1}$ on day 39. Values of K_s for OUT stations obtained by nonlinear regression were 12.1 ± 3.6 $\mu\text{mol L}^{-1}$ on day 13 and 4.4 ± 1.9 $\mu\text{mol L}^{-1}$ on day 39. These values are each sevenfold higher than the values of K_s measured at the corresponding IN stations.

The effect of Fe on the ability of the diatom assemblages to take up silicic acid at low concentration can be assessed by examining the initial slope of the kinetic curves (V_m/K_s), where greater initial slope indicates a higher capacity for uptake at low substrate concentration (Healey 1980). At IN stations V_m/K_s was 0.31 and 0.49 on day 12 and day 40, respectively, compared to values of 0.031 (day 13) and 0.025 (day 39) at OUT stations. Thus, the ability of the diatom

assemblage to take up low concentrations of silicic acid in the Fe-fertilized waters was an order of magnitude greater than that of the assemblage in unfertilized waters.

South Patch—The longer occupation of the South Patch allowed for a more comprehensive sampling program including surface mapping and transect work. Transects of the patch on days 9–10 (Fig. 6a), 16–17 (Fig. 6b), and day 20 (Fig. 6c) each show that regions of maximum silicic acid drawdown correspond to areas with high $[\text{SF}_6]$, but that high biogenic silica concentrations extended well beyond the patch. These trends were confirmed by a mapping exercise on days 14 and 15 that showed a strong coherence between silicic acid depletion and $[\text{SF}_6]$, but with high biogenic silica concentrations both within and outside the patch (Fig. 7).

Silica production rates were much lower in the regions of high biogenic silica concentration located outside the patch compared to those occurring within the patch. We measured silica production at three depths at each station along the radial transect on days 9 and 10 (Fig. 6a). Both V_b and ρ were maximal and $[\text{Si}(\text{OH})_4]$ lowest in the region of high $[\text{SF}_6]$, whereas the relatively high biomass waters outside the patch had comparatively low production rates. The lower production rates in the high biomass waters outside the patch are consistent with the idea that the South Patch iron additions cut across a natural mesoscale diatom bloom.

The results from our profile stations showed that during the first 15 d after fertilization, mixed-layer silicic acid concentrations within the South Patch generally varied between 61.5 and 64 $\mu\text{mol L}^{-1}$, without a clear downward trend (Fig. 8a). A clear reduction in $[\text{Si}(\text{OH})_4]$ was observed by days 18–21 when silicic acid concentrations reached 59.5 $\mu\text{mol L}^{-1}$. On the basis of a prefertilization value of 64 $\mu\text{mol L}^{-1}$ (Coale et al. 2004), data from profile stations indicate a maximum silicic acid depletion in the patch of about 4 $\mu\text{mol L}^{-1}$. This value agrees with the estimate of 4.2 $\mu\text{mol L}^{-1}$ derived from the transects and mapping exercises that covered a greater area. Outside, silicic acid concentrations generally remained above 62 $\mu\text{mol L}^{-1}$, varying between 62.0 and 62.5 $\mu\text{mol L}^{-1}$ (Fig. 8a). The small gradient in silicic acid concentration between the South Patch and outside waters suggests that dilution had only a minor effect on silicic acid depletion in the South Patch through the entire experiment.

There was a clear decrease in biogenic silica concentration with time at both IN and OUT profile stations, with a shift to generally lower concentrations occurring between days 10.8 and 11.7 (Fig. 8b). This decline likely reflected a shift in the location of the sampling stations to regions of lower biogenic silica concentration rather than a loss of biogenic silica from the patch and surrounding waters. This view is supported by data from the transect conducted on day 20, which was conducted after the apparent decline in biogenic silica concentrations at the profile stations. Whereas biogenic silica concentration at profile stations had fallen to values <1 $\mu\text{mol L}^{-1}$, the concentrations observed on the transect exceeded 4 $\mu\text{mol L}^{-1}$ both inside and outside the patch (Fig. 6c).

Rates of silica production increased dramatically inside the patch in response to Fe (Fig. 8c). Within 2 wk after the

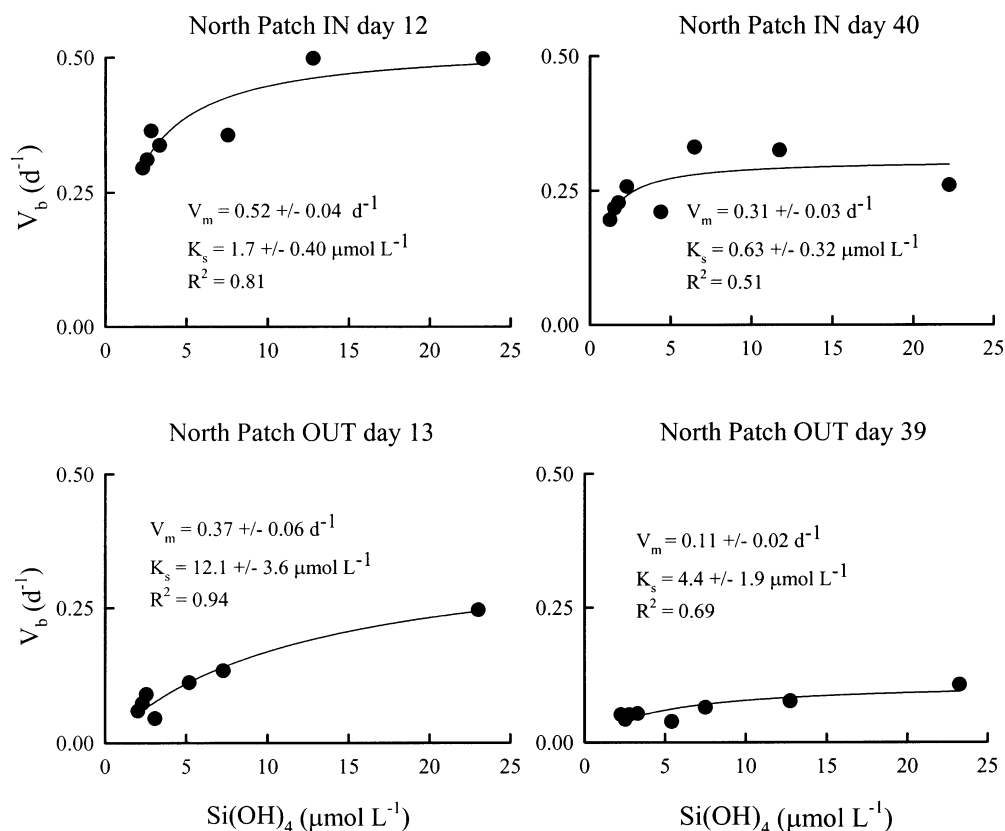


Fig. 5. Kinetic curves for silicic acid uptake in the North Patch.

first Fe addition, rates quadrupled from $0.1 \mu\text{mol L}^{-1} \text{d}^{-1}$ to ca. $0.4 \mu\text{mol L}^{-1} \text{d}^{-1}$. The highest rates were observed on the last station on day 21.6, when rates up to $0.55 \mu\text{mol L}^{-1} \text{d}^{-1}$ were measured. Integrated rates of silica production in the upper 50 m increased from 7.2 to $8.4 \text{ mmol m}^{-2} \text{d}^{-1}$ to $19.1 \text{ mmol m}^{-2} \text{d}^{-1}$ over this same time interval (Table 1). Outside the patch silica production rates generally remained $<0.12 \mu\text{mol L}^{-1} \text{d}^{-1}$, with integrated rates varying between 4.0 and $5.7 \text{ mmol m}^{-2} \text{d}^{-1}$.

Specific rates of silica production inside the patch increased dramatically (Fig. 8d). V_b averaged 0.091 d^{-1} in the upper 50 m on day 5.7 and increased to 0.33 d^{-1} by day 11.7. High average rates between 0.3 and 0.46 d^{-1} were maintained from day 11.7 until the end of the experiment, with maximum rates approaching 0.6 d^{-1} . The highest rates imply doubling times for diatoms of about 1 d, which is twice as rapid as observed in the much warmer ($\Delta T = 7.9^\circ\text{C}$) North Patch. Outside the South Patch, specific rates in the mixed layer increased from an average of about 0.1 d^{-1} to 0.2 d^{-1} , which are on the high end of the range of past measurements in the ACC (Brzezinski et al. 2001; Quéguiner and Brzezinski 2002), but never reached the values of 0.3 to 0.6 d^{-1} observed in the patch. Interestingly, specific production rates outside the patch at depths below the mixed layer after day 12 were comparable to the highest rates observed in the patch. Siliceous biomass was very low at these depths, causing absolute production rates to be comparatively low (compare Fig. 8c,d).

Unlike the response observed in the North Patch, enhance-

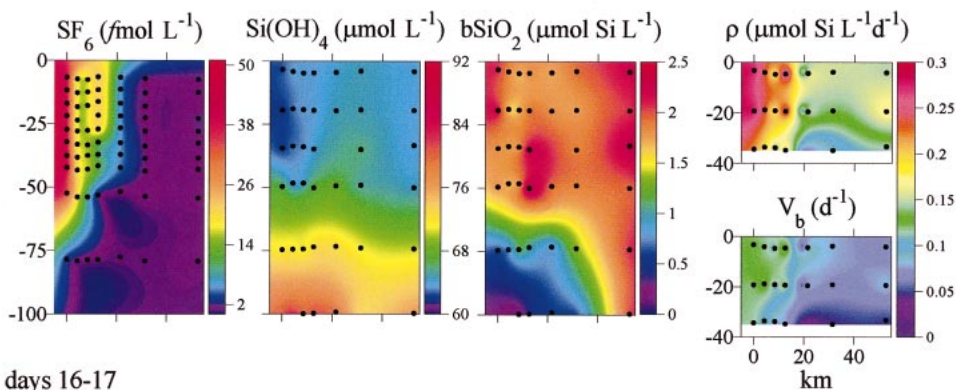
ment experiments with $42 \mu\text{mol L}^{-1}$ added silicic acid did not increase silica production rates in the South Patch (Coale et al. 2004). This result was confirmed by the full kinetic experiments that likewise showed no significant increase in silica production rates with added Si (data not shown). Both sets of experiments indicate a lack of Si limitation in the South Patch.

Discussion

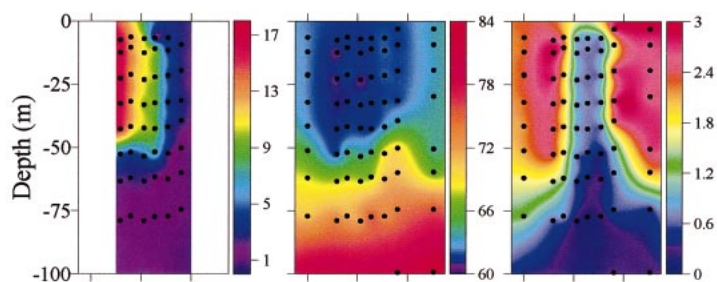
Our results indicate that iron limits silica production and biogenic silica accumulation in both the Antarctic and Subantarctic during austral summer. Si also plays a strong role in that abundant silicic acid in the Antarctic allowed diatoms to respond to Fe addition unimpeded by Si limitation, whereas the low concentration of silicic acid present in the Subantarctic strongly curtailed the response of diatoms to Fe enrichment despite a significant supply of silicic acid via mixing. We will argue that Si limitation affects both the response of diatom silica production to added Fe on the time scale of our experiments and the long-term contribution of diatoms to Fe-induced new production under conditions that would allow complete nutrient depletion, as may have occurred during the last glacial maximum (Martin 1990).

Our measured increases in siliceous biomass and depletion of silicic acid are biased by the effects of patch dilution and silica dissolution. The effect of patch dilution was discussed earlier. Silica dissolution affects silicic acid depletion and

a) days 9-10



b) days 16-17



c) day 20

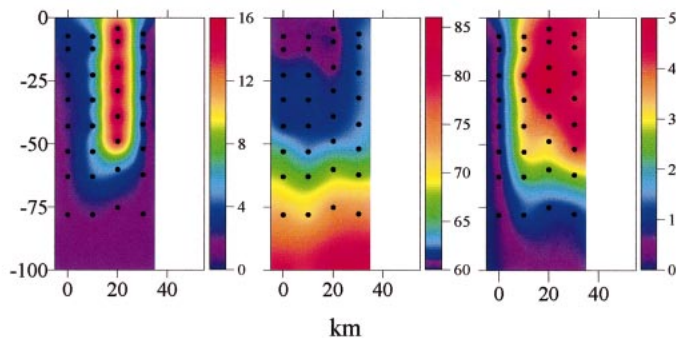


Fig. 6. Distribution of properties along three transects of the South Patch.

biogenic silica accumulation by converting particulate silica to silicic acid. Specific rates of silica dissolution in the Southern Ocean can be quite variable, with values of up 0.2–0.4 d^{-1} (Beucher et al. 2004). Those rates are 30%–>50% of the specific rates of silica production observed in the South Patch and are nearly equal to the specific production rates in the North Patch. If silica dissolution was occurring at the highest rates observed by Beucher et al. (2004), then silica dissolution would have significantly slowed biogenic silica accumulation and silicic acid depletion. We note, however, that about half of the silica dissolution rates observed by Beucher et al. (2004) were $<0.1 \text{ d}^{-1}$ and other studies within the ACC have typically observed dissolution rates of $<<0.1 \text{ d}^{-1}$ (Nelson and Gordon 1982; Brzezinski et al. 2001). The high variability in silica dissolution rates in the Southern Ocean makes it difficult to assess the effect of dissolution accurately without direct measurements.

Iron had a clear and dramatic effect on silica production, with absolute and specific production rates increasing by over 200% in both patches compared to OUT stations. There was a lag of 7–10 d before a significant increase in silica production was observed in each patch. Long lag times in Southern Ocean mesoscale Fe enrichment experiments are also observed for other phytoplankton rate processes such as primary production (Boyd 2002b; Coale et al. 2004) and have been attributed to the cold water temperatures of the Southern Ocean. By the end of our experiments doubling times of biogenic silica were short in both patches, but were significantly longer in the North Patch likely as a result of Si limitation of diatom growth in the Subantarctic.

The rapid doubling times for biogenic silica in both the North and South Patches indicate a large potential for increases in diatom biomass in the weeks after the end of each experiment. That potential would be truncated by low silicic

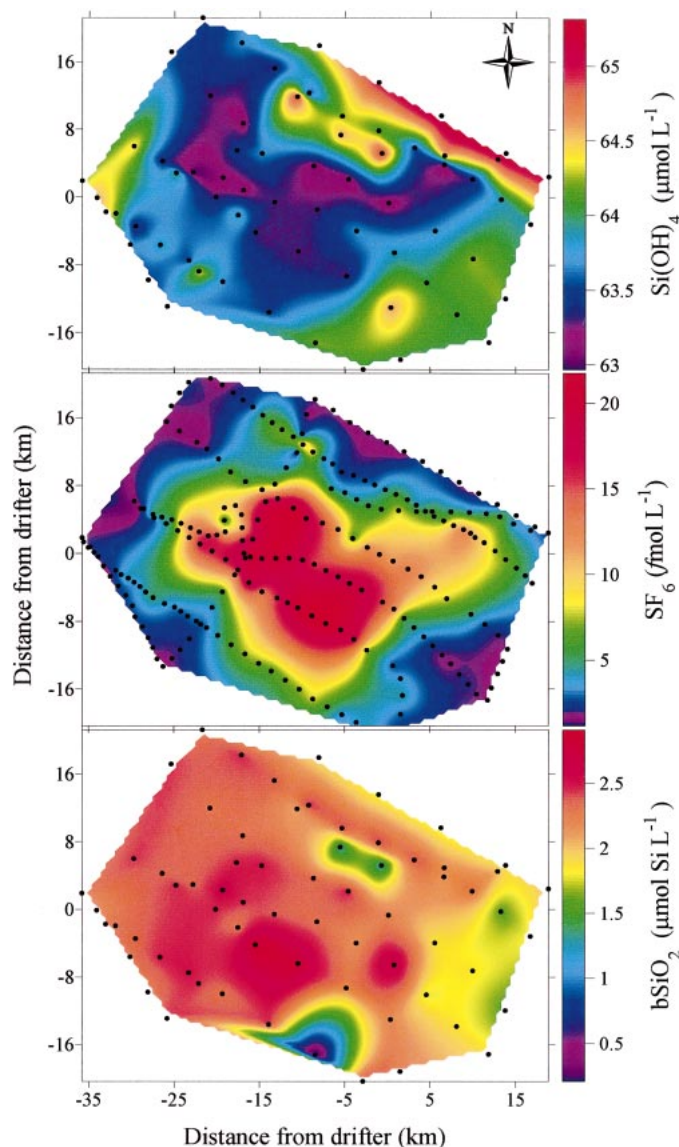


Fig. 7. Map of surface (3 m) properties in the South Patch on days 14 and 15.

acid availability in the North Patch where ambient silicic acid concentrations at the end of our observations could only support a single doubling of diatom biomass (compare Fig. 2a with 2b and 2c). Moreover, at the end of the North Patch experiment, mixing was supplying silicic acid at the same rate as it was being consumed (Coale et al. 2004), indicating that increases in biogenic silica concentration would be entirely offset by dilution as the patch increased in volume. In contrast, ample silicic acid remained in the South Patch to support very large increases in biogenic silica even without any resupply of silicic acid by patch dilution. Grazing losses for diatoms were low in the South Patch, as macrozooplankton were rare (Landry pers. comm.) and losses due to the export of biogenic silica were only 6–7% of daily silica production (Buesseler et al. 2005). Given an average biomass of $2 \mu\text{mol L}^{-1}$ Si and a specific production rate of 0.4 d^{-1} at the end of the South Patch experiment, diatom growth

would have depleted the $60 \mu\text{mol L}^{-1}$ silicic acid that remained in the water column in just 1–2 wk. Determining whether such high levels of nutrient depletion can be achieved will require fertilization experiments of longer duration and larger spatial scale (to minimize dilution) than we were able to accomplish.

Our kinetic and enhancement experiments clearly demonstrate that Si was not limiting silica production south of the SACCF, as adding Si did not increase silica production rates measurably IN or OUT of the South Patch. This result was not surprising given the high ambient silicic acid concentrations of $60 \mu\text{mol L}^{-1}$ or more, but the result was not a foregone conclusion, as Nelson et al. (2001) saw signs of limitation in the Pacific sector of the Antarctic near the site of the SOFeX South Patch at $[\text{Si}(\text{OH})_4]$ up to $50 \mu\text{mol L}^{-1}$. The lack of a response to Si addition indicates that values of V_b obtained during profile stations are estimates of V_m for the diatom assemblages. The higher values of V_b inside the patch compared to outside thus indicate that on average the diatoms in the patch had higher maximum rates of silica production than did those outside. These observations are consistent with bottle experiments in the field and laboratory experiments that show that Fe limitation decreases V_m for silicic acid use by three- to fourfold (e.g., De La Rocha et al. 2000; Franck et al. 2003; Leynaert et al. 2004).

Si clearly limited silica production in the Subantarctic. The addition of Si stimulated silica production rates both outside and inside the North Patch by a factor of 2 or more. The lower half-saturation constants observed at IN compared to OUT stations suggest that Fe fertilization either lowers the K_s of individual diatom species or causes shifts in species composition that favor diatoms with higher affinities for silicic acid. This trend is opposite of that observed in culture experiments by Leynaert et al. (2004), who observed that Fe increased K_s in *Cylindrotheca fusiformis*. Clearly more work is required in this area. Maximum uptake rates were lower at OUT stations when comparing IN and OUT stations sampled within a day of one another in the Subantarctic, but V_m values declined both inside and outside the patch, suggesting a shift toward species with lower maximum specific uptake rates both inside and outside the patch.

The ability of diatoms to deplete silicic acid concentrations from 2.8 to $<1.0 \mu\text{mol L}^{-1}$ in the North Patch despite substantial resupply of silicic acid from mixing is likely related to the order-of-magnitude increase in V_m/K_s caused by Fe enrichment. This physiological shift would partially ameliorate Si limitation by enhancing the ability of diatoms to exploit low silicic acid concentrations. Such physiological shifts lessen the impact of Si limitation as a factor controlling the response of diatoms to Fe in the Subantarctic. The trend of increasing V_m/K_s upon release from Fe limitation differs from results obtained in recent laboratory culture work that show that V_m/K_s is not affected by Fe in *C. fusiformis* (Leynaert et al. 2004). One possible explanation for this discrepancy is that species that did not change V_m/K_s were displaced over time by those that substantially increased their ability to exploit low silicic acid concentrations.

Closer examination of the results of our kinetic experiments reveals a strong interaction between Si and Fe on

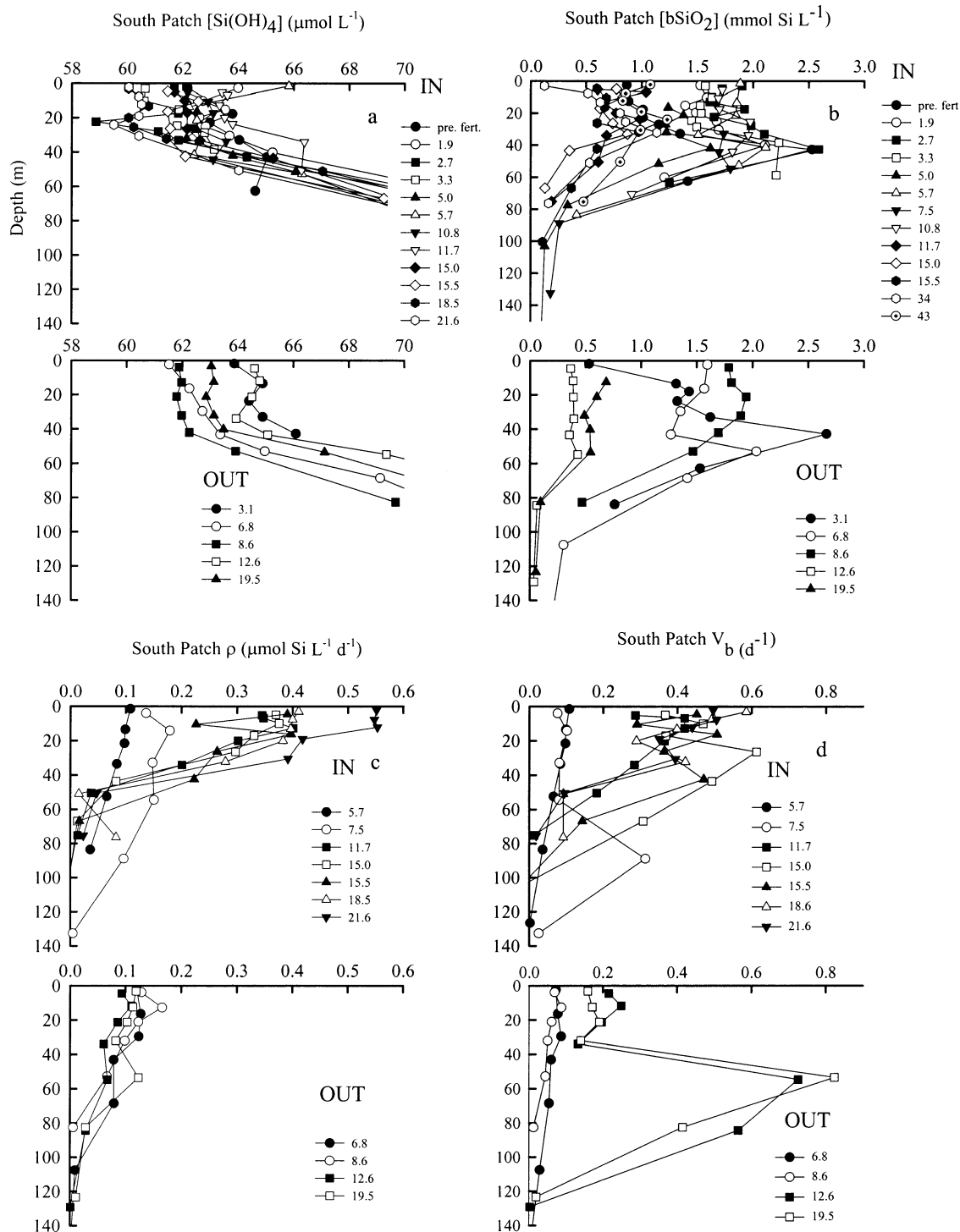


Fig. 8. Profiles of properties in the South Patch. (a) Silicic acid concentration, (b) biogenic silica concentration, (c) absolute silica production rates, (d) specific rates of silica production. Numerals in legends indicate the patch day of each profile.

silica production rates in the North Patch. The addition of Si alone increased production rates in the Subantarctic two- to threefold at both the IN and OUT stations (see E statistic, Fig. 4). For the IN stations this effect of Si enrichment occurred atop the threefold increase in production rates produced by iron fertilization (Fig. 2d) for a combined (Fe +

Si) effect of a six- to ninefold increase in silica production rates compared to unamended OUT station waters. These findings confirm the results of bottle experiments by Hutchins et al. (2001), who observed that although the addition of either Si or Fe to Subantarctic waters increased silica production rates and diatom biomass, the addition of both Si

and Fe together produced a far greater response. Our study and that of Hutchins et al. (2001) were conducted in austral summer after the seasonal depletion of $\text{Si}(\text{OH})_4$. In spring $\text{Si}(\text{OH})_4$ is more abundant in this region of the Subantarctic (Smith et al. 2000) and the influence of Si as a limiting nutrient is likely less. We concur with the idea presented by Boyd et al. (1999) and Hutchins et al. (2001) that there is a seasonal transition in the importance of Si as a limiting resource in the Subantarctic. Low Fe likely restricts phytoplankton growth rates in spring following stratification and favorable light conditions, but Fe limitation also induces high $\text{Si}(\text{OH})_4:\text{NO}_3^-$ uptake ratios in diatoms (Hutchins and Bruland 1998; Takeda 1998; Franck et al. 2000), producing a high-nitrate low-silicic acid condition in the Subantarctic by austral summer. Low summer $[\text{Si}(\text{OH})_4]$ then curtails diatom silica production and the ability of diatoms to utilize the still-abundant nitrate. Had we conducted our experiment earlier in the year before silicic acid depletion the role of diatoms in the North Patch response could have been much greater.

The addition of Fe clearly facilitated silicic acid use in the North Patch, allowing silicic acid to be depleted from 2.8 to 0.4 $\mu\text{mol L}^{-1}$ despite significant patch dilution, but our experiments show clearly that the low concentrations of silicic acid present in the North Patch were limiting silica production rates at all times. This could be interpreted as colimitation by Si and Fe; however, it is important to note that limitation of silica production rates does not conclusively demonstrate limitation of diatom growth rates. Diatoms can compensate for limitation of their Si uptake systems by making thinner frustules and thus reducing their cellular Si quota. In addition, any reduction in cellular Si content in response to the increased Fe in the patch (Hutchins and Bruland 1998; Twining et al. 2004) would help alleviate Si limitation by further lowering each cell's demand for Si. It may be that diatom growth rates are limited by Fe, whereas silica production rates and cellular silicon content are controlled by the combined influence of both Fe and Si.

Comparison of our results from SOFeX with those of the U.S. Joint Global Ocean Flux Study (JGOFS) Antarctic Ecosystems Ocean Process Study (AESOPS) that also sampled along 170°W provides a context for relating our findings to natural conditions in this region of the Southern Ocean. The AESOPS cruises followed the development of a large natural diatom bloom that began at the APF and propagated to the south until it reached the SACCF (Brzezinski et al. 2001). Some aspects of the silicon dynamics during the bloom observed by AESOPS were far more dramatic than observed during SOFeX. The AESOPS bloom consumed $>40 \mu\text{mol L}^{-1}$ silicic acid in approximately 30 d, leaving concentrations of $<1 \mu\text{mol L}^{-1}$ in its wake (Brzezinski et al. 2001; Sigmon et al. 2002). Maximum biogenic silica concentrations exceeded 16 $\mu\text{mol L}^{-1}$, with integrated biogenic silica concentration in excess of 400 mmol m^{-2} (Brzezinski et al. 2001; Sigmon et al. 2002). In contrast, maximum biogenic silica concentrations during SOFeX were only 4 $\mu\text{mol L}^{-1}$, with integrated siliceous biomass reaching just 100 mmol m^{-2} (Table 1). Estimates of silicic acid depletion rates during AESOPS were 1.3 $\mu\text{mol L}^{-1} \text{d}^{-1}$. By comparison, the silicic acid depletion rate was threefold lower [4.2 $\mu\text{mol L}^{-1}$ con-

sumed over (21.6 d – 10-d lag) = 11.6 d, for a depletion rate of 0.4 $\mu\text{mol L}^{-1} \text{d}^{-1}$] in the South Patch during SOFeX even after allowing for a lag of 10 d.

Conditions at the end of the SOFeX South Patch experiment suggest that the bloom was poised to grow to similar proportions as observed during AESOPS. Integrated silica production rates at the end of the South Patch experiment (19.1 $\text{mmol m}^{-2} \text{d}^{-1}$) approached the average values during the peak of the diatom bloom observed during AESOPS (23–27 $\text{mmol m}^{-2} \text{d}^{-1}$, Brzezinski et al. 2001). The 2-d doubling time for biogenic silica implied by the specific silica production rates in the South Patch would have allowed the SOFeX bloom to reach the biogenic silica concentrations and silicic acid consumption levels observed in AESOPS in <2 wk had Fe additions been continued.

The larger siliceous biomass and silicic acid drawdown during AESOPS was in part due to the decoupling of silica and organic matter production under low Fe. Maximum chlorophyll concentrations in the SOFeX South Patch exceeded values observed during the same time of year during AESOPS by nearly an order of magnitude (Coale et al. 2004). Conversely, the accumulation of biogenic silica during SOFeX was four times less than during AESOPS even though the blooms observed during both AESOPS and SOFeX were dominated by diatoms (Brzezinski et al. 2001; Coale et al. 2004). This apparent contradiction is at least in part due to the much higher silicic acid:nitrate uptake ratios observed under low Fe (e.g., Hutchins and Bruland 1998; Takeda 1998). Silicic acid:nitrate uptake ratios during AESOPS (4:1, Smith et al. 2000) were twice as high as observed during SOFeX (2.1:1, Coale et al. 2004), doubling the amount of biogenic silica produced per unit of nitrate consumed during AESOPS compared to SOFeX.

Interannual variability in stratification may also explain some of the differences in the dynamics observed during SOFeX and AESOPS. Natural conditions in the region between the SACCF and the APF were very different during SOFeX from what they were during AESOPS. Mixed-layer depths during AESOPS (25 m) were much less than during SOFeX (30–50 m), which may have raised light levels in the euphotic zone sufficiently to lower the iron requirement of the phytoplankton (Sunda and Huntsman 1997), facilitating the more intense bloom observed during AESOPS. It is also important to note that the enormous silicic acid depletion observed during AESOPS between the SACCF and the APF in 1998 did not occur in 2002. Measurements of silicic acid concentrations at 3 m from between the SACCF and the APF made during transits between the North and South Patches revealed minimum silicic acid concentrations in the region of 20 $\mu\text{mol L}^{-1}$ (Varela et al. 2004), similar to what has been reported for the Indian sector of the Southern Ocean (Pondaven et al. 2000), suggesting that the conditions encountered during AESOPS may have been anomalous.

The most remarkable difference between the AESOPS and SOFeX results is that the values of V_b observed during SOFeX in the South Patch were on average quadruple those observed during AESOPS. Average values of V_b in AESOPS profiles were ca. 0.1 d^{-1} , with maximum values of 0.21 d^{-1} , similar to the highest OUT station values in the South Patch. Average values at IN stations were 0.38–0.41 d^{-1} (Table 1),

with maximum values of 0.6 d^{-1} . Thus, Fe fertilization of the South Patch produced a bloom that had apparent doubling times of biogenic silica that were much faster than observed during AESOPS and more rapid still than the values of 7 d or more that typify most of the Southern Ocean and its marginal seas (Nelson and Gordon 1982; Nelson and Smith 1986; Nelson et al. 1991, 1996; Quéguiner 2001; Quéguiner and Brzezinski 2002). The doubling times for siliceous plankton inside the South Patch were maximal for waters of this temperature (-0.4°C ; Eppley 1972; Banse 1991), indicating that the addition of iron pushed silica production to its physiological maximum. As mentioned earlier, doubling times in the warmer North Patch were slower than in the South Patch, with average values of V_b equal to or less than those observed during AESOPS, likely due to the effects of Si limitation.

The strong increase in silica production rates after Fe addition in both the North and South Patches confirms past observations that diatoms respond significantly to iron enrichment in both the Antarctic (Boyd et al. 2000; Smetacek 2001) and Subantarctic (Hutchins et al. 2001). However, Si limitation in the Subantarctic is also clearly important and would strongly affect the ability of diatoms to contribute to new production and export upon release from Fe limitation. Nitrate was initially abundant in both patches ($>20 \mu\text{mol L}^{-1}$), but only about 10% was consumed in both the Subantarctic and Antarctic (Coale et al. 2004), leaving large uncertainty as to the fate of the vast majority of the nutrient. In the South Patch silicic acid was still plentiful at the end of the experiment ($59.8 \mu\text{mol L}^{-1}$) and exceeded nitrate concentration by ca. 300%. Because Southern Ocean diatoms take up silicic acid and nitrate in a 1–2:1 mole ratio under Fe-replete conditions (Franck et al. 2000), more than sufficient Si was present for Fe-replete diatoms to use all of the nitrate present in the South Patch. Conditions in the North Patch were very different. Silicic acid was nearly exhausted by the end of the experiment (final concentrations = $0.4\text{--}0.9 \mu\text{mol L}^{-1}$), while nitrate remained plentiful ($22 \mu\text{mol L}^{-1}$, Coale et al. 2004). If we had created a patch of sufficient size to eliminate patch dilution, then diatoms could only have consumed 5% of the remaining nitrate before silicic acid would have been exhausted. Such severe Si limitation of diatoms would allow other phytoplankton groups, such as coccolithophores, to consume the nitrate without competition from diatoms. Continued production by coccolithophores after Si depletion has been observed under natural conditions in the Indian sector of the Subantarctic (Nozaki and Yamamoto 2001). If this response is enhanced with Fe enrichment, then long-term Fe fertilization on a scale that would minimize patch dilution in high and low Si waters in the Southern Ocean is likely to produce very different phytoplankton species assemblages, with diatoms dominating in the Antarctic and nonsiliceous phytoplankton dominating in the Subantarctic. Such dramatic shifts in the assemblage of primary producers would affect trophic structure, the ballast characteristics of the phytoplankton, and in turn carbon cycling and export. These issues cannot be resolved for the Southern Ocean until iron fertilization experiments of longer duration and larger spatial scales are performed.

These predictions are based upon the assumption of sus-

tained iron enrichment. If Fe concentrations fall to limiting levels after the stimulation of a diatom bloom by the initial infusion of Fe, $\text{Si}(\text{OH})_4$ uptake can increase abruptly relative to nitrate use, leading to Si limitation. A dramatic example of this was observed during the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) in the North Pacific. Initial silicic acid and nitrate concentrations were ca. 13 and $9 \mu\text{mol L}^{-1}$, respectively. During the period of Fe enrichment the two nutrients were depleted in approximately a 1:1 mole ratio (Boyd et al. 2004). Later in the experiment a resurgence of Fe limitation shifted the system back to high $\text{Si}(\text{OH})_4:\text{NO}_3^-$ uptake ratios, causing the depletion of silicic acid over the less-abundant nitrate (see Boyd et al. 2004 fig. 1). These results indicate that the efficient use of the available silicic acid for diatom new production depends upon sustained Fe enrichment. In environments where iron supply is episodic on time scales less than the duration of a phytoplankton bloom, iron-induced diatom blooms may revert to high silicic acid: nitrate uptake ratios upon Fe depletion, dramatically lowering the contribution of diatoms to new production.

Southern Ocean iron enrichment experiments are often viewed as analogues of conditions during glacial times when dust-borne Fe inputs to the area were much larger (Coale et al. 1996, 2004; Boyd et al. 2000; Hutchins et al. 2001; Smetacek 2001). To interpret our results in the context of such long time scales, the zonal circulation patterns that link the nutrient dynamics of the Antarctic and Subantarctic must be considered. Upper Circumpolar Deep water upwells between the SACCF and the APF and flows northward, forming Subantarctic Mode waters in the APFZ and Subantarctic (Orsi et al. 1995). This creates a linkage between the Antarctic and Subantarctic where nutrient dynamics in the south set the initial nutrient content of the water delivered to the north. The preferential Si depletion known to occur between the SACCF and the APF thus likely contributes to the low-Si high-nitrate character of the modern-day APFZ and Subantarctic (Dugdale et al. 1995; Pondaven et al. 2000; Brzezinski et al. 2003). These linkages would cause any perturbations to nutrient depletion ratios occurring to the south of the APF during glacial periods to have significant effects to the north in the Subantarctic.

It has been argued that silicic acid was much more plentiful in the glacial Subantarctic (Dugdale and Wilkerson 2001; Brzezinski et al. 2002). Opal accumulation rates increase dramatically in glacial sediments beneath the Subantarctic (François et al. 1997; Chase et al. 2003). Because present-day silicic acid depletion is nearly complete in the Subantarctic, increases in opal burial in this region during glacial times require an increased supply of silicic acid to surface waters (Chase et al. 2003). The new supply of silicic acid could be generated to the south in the region between the SACCF and the APF where increased Fe inputs would shift Si:N uptake ratios from the present-day 4:1 ratio to 1:1, allowing diatoms to consume significantly more nitrate but less silicic acid than they do today (Brzezinski et al. 2002; Matsumoto et al. 2002). The northward flow of the low-nitrate high-silicic acid waters would deliver less nitrate but more silicic acid to the glacial Subantarctic compared to modern times (Chase et al. 2003). The greater relative abun-

dance of $\text{Si}(\text{OH})_4$ over NO_3^- would allow diatoms to play a larger role in new production in the glacial Subantarctic than our results for the North Patch would imply. These possibilities make extrapolations of the effect of Fe enrichment of the glacial Subantarctic based on modern day experiments very uncertain.

The region to the south of the SACCF where the South Patch was located was likely more heavily influenced by sea ice and increased stratification during glacial times, lowering productivity (Anderson et al. 2002), but diatoms would still be able to account for the majority of the new production that did occur, assuming that the nutrient content of the lower Circumpolar Deep Water and Antarctic Bottom Water that outcrop in this region was similar to what is observed today.

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Received: 28 April 2004

Accepted: 27 October 2004

Amended: 1 November 2004