Nitrogen isotopic evidence for a poleward decrease in surface nitrate within the ice age Antarctic

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Abstract

Surface sediment diatom-bound $\delta^{15}$N along a latitudinal transect of 170° W shows a previously unobserved increase to the South of the Antarctic Polar Front. The southward $\delta^{15}$N increase is best explained by the combination of two changes toward the South, a decrease in the isotope effect of nitrate assimilation ($\varepsilon$) and an increase in the degree of nitrate consumption, both associated with shoaling of the mixed layer into the seasonal ice zone (SIZ). New downcore records show high amplitude changes in diatom-bound $\delta^{15}$N during the last ice age, with intervals of higher $\delta^{15}$N, including the last glacial maximum, the transition between marine isotope stages 5 and 4, and marine isotope stage 6, while other intervals are similar in $\delta^{15}$N to interglacial sediments. Variation in the range of 0–3\%\textsubscript{o} as seen in previously published records, may be entirely due to changes in $\varepsilon$. However, the observed magnitude of the change of 4–10\% in the three new records and the locations of these records relative to the modern meridional gradient in mixed layer depth appear to require increased nitrate consumption to explain the high-$\delta^{15}$N intervals. The new sites are near the modern Southern Antarctic Circumpolar Current Front (SACCF), and one of the sites has been shown to be associated with sporadic summer sea ice during the LGM. As with other Antarctic sites, the available proxy data suggest that they were characterized by lower export production. Based on these and other observations, we propose that the weak southward nitrate decrease in the modern Antarctic surface was a fully developed “nutrient front” in the glacial Antarctic, associated with the SACCF. Both modern ocean and paleoceanographic work is needed to test this hypothesis, which would have major implications for atmospheric CO$_2$.

1. Introduction

One of the primary features of the modern Antarctic Zone (AZ) in the Southern Ocean is the large excess of the major nutrients, nitrate and phosphate. At present, the nutrient-rich surface releases carbon dioxide (CO$_2$) that was previously sequestered in the ocean interior by the rain of biogenic debris out of the surface ocean in other regions. The rapid exposure of CO$_2$-rich water and incomplete consumption of nitrate and phosphate at the surface limits the degree to which the global biological pump is able to lower atmospheric CO$_2$. More complete utilization of nutrients during glacial episodes, either by increased productivity or reduced deep overturning, would have rendered the global biological pump more efficient by reducing the release of CO$_2$ from this region, potentially explaining the observation of lower atmospheric CO$_2$ concentrations during ice ages (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984). Even a reduction in overturning without more complete nutrient utilization would have reduced atmospheric CO$_2$, albeit not as strongly (Toggweiler, 1999; Sigman and Haug, 2003).

The AZ, which surrounds the Antarctic continent, is one of three major zones of the Southern Ocean (Orsi et al., 1995) (Fig. 1). To the north, it is bounded by the Polar Frontal Zone (PFZ), which is separated from the Antarctic by the Antarctic Polar Front (APF) and from the more equatorward Subantarctic Zone (SAZ) by the Subantarctic Front. The AZ itself is divided into zones, the permanently open ocean zone (POOZ) and the seasonal ice zone (SIZ). The Southern Antarctic Circumpolar Current Front (SACCF) bounds the southern edge of the ACC and...
approximates the northernmost limit of the SIZ. The AZ is a region of large scale, wind-driven upwelling and the only region of the Southern Ocean that directly ventilates the abyssal ocean. As such, it plays a critical role in the air–sea balance of CO₂ (Marinov et al., 2006).

In the AZ, export production during the ice ages, as inferred from opal and biogenic Ba flux estimates, was lower than during interglacials (Charles et al., 1991; Mortlock et al., 1991; Kumar et al., 1993; Francois et al., 1997; Frank et al., 2000; Chase et al., 2003). Lower algal growth rates are also suggested by the lower 13C/12C of bulk and diatom-bound organic matter (Shemesh et al., 1993; Singer and Shemesh, 1995). The reduced productivity in the glacial Antarctic has been explained in two very different ways: as the result of light limitation, for instance, by increased sea ice cover shortening the growing season (Mitchell et al., 1991; Anderson et al., 1998, 2002), or as the result of a decrease in the gross supply of nutrients from below (Francois et al., 1997).

For more than a decade, downcore N isotope studies have been conducted to test explanations for the observed productivity changes, by providing a constraint on the ratio of nitrate uptake to gross nitrate supply (i.e. on nitrate consumption). The 15N/14N of sinking organic matter reflects the utilization of nitrate (NO₃⁻) in regions such as the Southern Ocean where NO₃⁻ is not completely consumed (Altabet and Francois, 1994). Phytoplankton preferentially take up NO₃⁻ bearing the lighter N isotope, 14N. As the initial NO₃⁻ supply is progressively consumed, the δ¹⁵N of the NO₃⁻ increases, leading to a related increase in the δ¹⁵N of the organic matter produced from the NO₃⁻ (δ¹⁵N = (¹⁵N/¹⁴N)_sample/(¹⁵N/¹⁴N)_reference−1) where the N₂ in air is the universal reference). Early work focused on the use of bulk sedimentary δ¹⁵N despite the acknowledged potential for diagenetic artifacts due to alteration of the isotopic signal during sinking and sedimentation. Microfossil-bound organic N has since been targeted as a potentially pristine sedimentary N archive, and several measurement methodologies have been developed thus far (Shemesh et al., 1993; Sigman et al., 1999a; Robinson et al., 2004; DeLaRocha, 2006).

Fig. 1. In this circumpolar view of the Southern Ocean, the Southern Antarctic Circumpolar Front (SACCF), Antarctic Polar Front (APF), and the Subantarctic Front (SAF) are delineated (Orsi et al., 1995). The bold orange lines within the polar Antarctic Zone mark the location of apparent summer sea ice during the LGM (Gersonde et al., 2005). Site locations of existing diatom-bound δ¹⁵N records are color coded according to difference in diatom-bound δ¹⁵N between ice ages and interglacials. The largest δ¹⁵N differences (>4‰) are observed in NBP9802-5GC1 and RC13-259; however, there are also glacial intervals in those cores with δ¹⁵N similar to interglacial intervals (~0‰). The two other measured Antarctic records show smaller glacial/interglacial changes. To the north of the APF, sites within the Polar Frontal Zone (KTB-13 and RC13-254) and the Subantarctic Zone (MD84-527 and E11-2) show moderate (1.8–3‰) differences between the LGM and the early Holocene (Robinson et al., 2005; Robinson unpublished data).
The balance of data for temporal changes in nutrient consumption within the AZ suggests that evidence for reduced export production in the glacial Antarctic was accompanied by a higher $\delta^{15}N$ in sinking N, despite differences in measurement techniques and potential methodological problems (Francois et al., 1997; Sigman et al., 1999a; Crosta and Shemesh, 2002; Robinson et al., 2004). Beginning with Francois et al. (1997), workers have, on the basis of the N isotope results, inferred greater nitrate consumption during the last ice age. Coupling the evidence for more complete nitrate consumption with the evidence for a decrease in export production, they deduced a decrease in gross rate of supply of major nutrients to the Antarctic euphotic zone (Francois et al., 1997; Sigman et al., 1999a; Robinson et al., 2004). Physically, this change would require reduced exchange of water between the surface and deep Antarctic, as would result from year-round stratification of the upper water column. However, the various types of $\delta^{15}N$ data do not allow for a straightforward comparison of the different downcore records. Moreover, downcore records of diatom microfossil-bound $\delta^{15}N$ measured with a single methodology (the persulfate-denitrifier method that is employed in this study) have suggested that the glacial decrease in export production was associated with varied degrees of enhanced nitrate consumption, spatially and temporally within the glacial AZ (Robinson et al., 2004).

Here, we report three new downcore profiles of diatom-bound N isotopes from the Atlantic and Pacific sectors of the Antarctic. The downcore diatom-bound $\delta^{15}N$ records suggest large changes in the degree of nitrate consumption over the core sites in both sectors of the AZ. These data contrast with previously published profiles (generated with the same methods) and suggest broad spatial variations in nutrient consumption across the AZ. Surface sedimentary diatom-bound $\delta^{15}N$ from a transect that spans the SIZ of the Antarctic, the PFZ and into the Subantarctic along 170W provide some perspective on the new downcore results, suggesting the existence of a meridional gradient, contrary with previously published profiles (generated with different methods). These results, however, still allow for a straightforward comparison of the different downcore methods (Fig. 3). In the Indian Sector of the AZ (54.6°S, 73.5°E), for a methodological comparison. Using the age model from Charles et al. (1991), the RC13-259 data was compared to sea ice indicator data from nearby sites in the Atlantic (Fig. 4).

2. Materials and methods

2.1. Sampling

Diatom-bound $\delta^{15}N$ was measured in surface (top 2 cm) sediment samples from multi-cores collected during the AESOPS transect, a Southern Ocean JGOFS project along 170W (Fig. 2). Two paleoceanographic records from the Pacific AZ were generated: an approximately 25–30 ka profile from Pacific core NBP9802-5GC (63°S, 170°W) and a longer record from NBP9802-6PC (62°S, 170°W) (to be referred to as 5GC and 6PC, respectively) (Chase et al., 2003). These cores were also collected as part of AESOPS. Both 5GC and 6PC display a sharp change in biogenic and lithogenic fluxes across the glacial/interglacial boundary where opal fluxes increase and lithogenic fluxes decrease into the Holocene (Fig. 3) (Chase et al., 2003). Another longer profile, this one dating beyond the last glacial to ~135 ka, comes from Atlantic core RC13-259 (54°S, 5°W). Numerous studies have utilized this core to document an increase in AZ productivity across Termination 1, primarily using opal concentration and flux records (Charles et al., 1991; Kumar et al., 1995).

Because of significant uncertainties related to the age models in the cores, the data are presented below against core depth and accompanied by published foraminiferal $\delta^{18}O$ (unavailable in 6PC) and opal concentration or accumulation rate data for stratigraphic comparison. We also used newly sampled materials from core MD84-552 (Fig. 3), in the Indian Sector of the AZ (54.6°S, 73.5°E), for a methodological comparison. Using the age model from Charles et al. (1991), the RC13-259 data was compared to sea ice indicator data from nearby sites in the Atlantic (Fig. 4).

2.2. Diatom-bound $\delta^{15}N$ measurements

The physical separation and cleaning of the diatom fraction follows Robinson et al. (2004, 2005) with slight modification. The <150 μm fraction of diatoms were physically isolated in three steps: (1) sieving; (2) settling, for clay removal; and (3) density separation with sodium polytungstate ($\rho = 2.15$ g/cm$^3$), to further purify opal from more dense aluminosilicates and metal oxides. The resulting diatom fraction was chemically cleaned by a dithionite-citric acid reductive cleaning step followed by a single treatment with 30% H$_2$O$_2$ and then a chemical oxidation with 70% perchloric acid at 100°C to remove external organic nitrogen (ON). The perchloric acid cleaning replaces two additional H$_2$O$_2$ cleaning steps previously utilized by Robinson et al. (2004, 2005). Concentrated perchloric acid appears to be more universally effective in cleaning samples (Brunelle et al., 2007), and a single cleaning improves sample recovery. Comparison of the two cleaning methods in Southern Ocean samples (from SAZ core E11-2 and AZ core MD84-552) shows no significant $\delta^{15}N$ differences between them for most samples (Fig. 3 and Robinson unpublished data, 2004).

N content and $\delta^{15}N$ of the diatom-bound organic matter was determined by the persulfate oxidation-based method (Robinson et al., 2004). Treatment with potassium persulfate in 1.5N NaOH dissolves the opal to release the internally bound ON, which is then quantitatively oxidized to nitrate. Nitrate concentration was determined by chemiluminescence (Braman and Hendrix, 1989) and the N isotopic composition of the nitrate was measured via the “denitrifier” method (Sigman et al., 2001). Roughly one
out of six samples were analyzed with full procedural replication (i.e. starting with separate sediment separations), and are shown as open symbols where applicable, with filled symbols indicating the analysis mean.

3. Results and discussion

3.1. Meridional N isotope gradients in the modern AZ

In the modern Pacific sector along 170°W, diatom-bound δ¹⁵N is at a minimum around the APF, increasing with distance to the north and to the south (Fig. 2). There is a large change, from 3.3‰ to 12.4‰ from the APF across the SAZ toward the Subtropical Front. This increase is comparable to the modern gradient in the δ¹⁵N of nitrate across the SAZ, which is driven by nitrate consumption (Sigman et al., 1999b; DiFiore et al., 2006). This increase, which we hope to define better using additional coring sites, will not be considered further here.

More relevant to the downcore records described below, diatom-bound δ¹⁵N also increases southward, by 3.4‰ between 60 and 64°S across the AZ towards the SACCF.

Fig. 2. A comparison of modern water column nitrate concentration (A), nitrate δ¹⁵N, and sinking flux δ¹⁵N (at ~1000 m) (Smith et al., 2000; Altabet and Francois, 2001) and surface sediment diatom-bound δ¹⁵N along the AESOPS transect at 170°W (B), summer (Dec.–Feb.) mixed layer depth (MLD) (Kara et al., 2003) (C), and calculated amplitude of difference in sinking flux δ¹⁵N relative to 60°S calculated from the instantaneous, accumulated, and steady state product equations, as well as a replotting of the diatom δ¹⁵N, relative to the value measured at 60°S (D). The changes in the δ¹⁵N are calculated using the maximum seasonal change in NO₃/C₀ concentration from AESOPS and either an isotope effect for nitrate assimilation (ε) that is either constant at 5‰ (open symbols) or a linear function of MLD (closed symbols) between end member values of 5‰ and 8‰. The fronts and zones of the Southern Ocean are marked. Coretop δ¹⁵N from SGC (63.1°S) and 6PC (61.9°S) are shown for comparison (B) (gray diamonds) The southward increase in diatom-bound δ¹⁵N corresponds to larger seasonal changes in surface nitrate concentrations (Smith et al., 2000; Altabet and Francois, 2001) as well as nitrate δ¹⁵N (Altabet and Francois, 2001), suggesting that the Antarctic near the SACCF and southward is characterized by more complete nitrate consumption, due to some combination of less re-supply of nitrate during the summer and enhanced algal growth associated with the marginal ice zone. However, the amplitude of change cannot be explained with the simple supply-and-demand models without a southward decrease in ε associated with the shoaling of the mixed layer.
This increase toward the south away from the APF was not observed in diatom-bound $\delta^{15}$N surface sediments along a meridional transect in the Indian Sector, although the northward increase was present (Sigman et al., 1999a; Robinson et al., 2004). The differences are interpreted as a reflection of the physical settings of the Indian and Pacific Sector transects. Along 170°W, the transect samples the Antarctic SIZ, while the entire AZ segment of the Indian
transect is from within the POOZ, the SIZ being further from the APF in the Indian sector (Orsi et al., 1995).

Surface water data collected during the AESOPS cruises in 1997–1998 indicate summertime nitrate drawdown south of the APF (Fig. 2a) (Smith et al., 2000; Nelson et al., 2002). The highest degree of summertime drawdown was achieved around 63–65°S in early January 1998, in the weeks following the retreat of sea ice over this latitude (Smith et al., 2000). By early February, the ice edge was located around 74°S, again just to the South of the region of maximum nitrate drawdown at this time (Smith et al., 2000). The seasonal nitrate concentration minimum, around 65°S, appears to be accompanied by a greater summertime increase in the δ15N of surface nitrate (Fig. 2b) (Altabet and Francois, 2001). We used three simple nitrate supply-and-demand models to investigate the observed amplitude of diatom-bound δ15N change south of the APF: (a) the Rayleigh instantaneous product approximation (1), valid for the progressive consumption of an advecting nitrate pool; (b) the Rayleigh accumulated product approximation (2), applicable where nitrate is vertically supplied and then consumed within a closed system; and (c) the steady state product (3), appropriate when nitrate is continuously being supplied and removed from the system.

\[ \delta^{15}N_{\text{product}} = \delta^{15}N_{\text{initial}} - e \ln f - e, \]  
\[ \delta^{15}N_{\text{product}} = \delta^{15}N_{\text{initial}} - e(f \ln f / (1 - f)), \]  
\[ \delta^{15}N_{\text{product}} = \delta^{15}N_{\text{initial}} - e(f). \]  

\( e \) is the isotope effect of assimilation and \( f = ([\text{NO}_3^-]/[\text{NO}_3^-]_{\text{supply}}) \). Maximum and minimum \([\text{NO}_3^-]\) from the 1997–1998 AESOPS transects were used in two sets of calculations. In the first set, \( e \) is assumed to be 5% across the entire Antarctic. In the second, \( e \) is assumed to vary with latitude, as described below.

Nitrate δ15N data suggest that \( e \) increases towards the North in the Southern Ocean, such that the \( e \) in the SAZ may be as much as 3% greater than in the AZ (Lourey et al., 2003; DiFiore et al., 2006). The best current explanation for the apparent gradient in \( e \) comes from culture studies that indicate a tendency for \( e \) to be higher under light limitation (Wada and Hattori, 1978; Needoba and Harrison, 2004; Needoba et al., 2004), such that the greater mixed layer depths (MLDs) of the PFZ and SAZ yield a higher \( e \) in those zones. Accordingly, in the
calculations plotted in Fig. 2d, we explore the implications for diatom $\delta^{15}N$ of a dependence of $\varepsilon$ on MLD. We calculate summertime MLD as the average of MLD during December, January, and February from climatological data (Fig. 2c). We assume that $\varepsilon$ is at its minimum value of 5% when MLD is 20 m or less, as observed in the marginal ice zone (Sigman et al., 1999b; DiFiore et al., 2007), and that it increases linearly with MLD, reaching a maximum of 8% at an MLD of 65 m, consistent with observations from the Subantarctic (Lourey et al., 2003; DiFiore et al., 2006).

The large amplitude of diatom-bound $\delta^{15}N$ increase cannot be explained using a constant $\varepsilon$ and is best explained using an isotopic effect that varies as a function of MLD (Fig. 2c, d). Moreover, none of the applied supply-and-demand models provides a better fit than the $\delta^{15}N$ for diatom growth (Smith and Nelson, 1986; Sedwick and DiTullio, 1997; Altabet and Francois, 2001; Sigmon et al., 2002; Hiscock et al., 2003). Melting ice reduces the surface MLD, improving light conditions and at the same time releasing the micronutrient iron (Fe) from dust that has accumulated during the winter (Smith and Nelson, 1986; Sedwick and DiTullio, 1997). Fe availability appears to impact the uptake of macronutrients in this AZ, with nanomolar additions of Fe to Southern Ocean surface waters stimulating blooms of large diatoms (Boyd et al., 2007). Beyond its enhancement of nitrate uptake, Fe fertilization can also lower the silicate-to-nitrate uptake ratio in diatoms (Hutchins and Bruland, 1998; Takeda, 1998). This may allow diatom-driven nitrate consumption to proceed faster than regeneration can replenish the nitrate pool, especially south of the APF, where the nitrate uptake ratio is quite variable throughout the glacial period, with $\delta^{15}N$ maxima including late stage 5/ early stage 4 and the LGM but values as low as interglacial values at various times, including the interval preceding the LGM.

In Pacific core 5GC, the LGM interval identified by foraminiferal $\delta^{18}O$ has a $\delta^{15}N$ maximum at $\sim$9–10‰, with a deglacial decrease to $\sim$6‰ during the interval preceding to previous interglacial MIS 5 (Fig. 3). At present, the greatest nitrate drawdown occurs to the South of the highest export fluxes (Honjo et al., 2000). This suggests that the decrease in summer nitrate concentration south of the APF shown in Fig. 2c relates not only to productivity but also to nitrate supply. North of the SACC, winter mixing and year-round Ekman upwelling supply nitrate to the surface. South of the SACC, nitrate is supplied primarily by wintertime vertical mixing. As sea ice retreats during the summer, transient surface stratification occurs as a result of the fresh water inputs to the sea surface, shoaling the depth of the mixed layer to less than 20 m (Fig. 2). Because supply is temporarily shut off, with little augmentation of nutrient supply by Ekman upwelling in this region, nutrient concentrations drop off sharply to the south of the SACC during the summer months. In sum, the SACC is a region of both ice-encouraged productivity and reduced summertime nitrate re-supply. These two conditions work together to increase the degree of nitrate consumption near the SACC, which, along with the southward decrease in $\varepsilon$, may explain the southward increase in diatom $\delta^{15}N$.

3.2. Downcore diatom-bound $\delta^{15}N$ profiles

Both the Atlantic and the Pacific sector cores show a pattern of change with higher $\delta^{15}N$ during the LGM than during the Holocene, with lower $\delta^{15}N$ earlier in the glacial (perhaps MIS 3) and an increase in $\delta^{15}N$ in the late Holocene (Fig. 3). Going further back in the time, the Atlantic sector core continues to show this generalized pattern of high $\delta^{15}N$ during colder or more ice covered episodes and lower $\delta^{15}N$ during milder and interglacial times.

In detail, however, the link to climate is more complex. In Atlantic core RC13-259, $\delta^{15}N$ is elevated during the previous glacial maximum (MIS 6) at the base of the record, decreasing from $\sim$14‰ to $\sim$6‰ during the transition to previous interglacial MIS 5 (Fig. 3), then increasing again in into last glacial period. However, while diatom opal accumulation is uniformly reduced during this period, diatom-bound $\delta^{15}N$ is quite variable throughout the glacial period, with $\delta^{15}N$ maxima including late stage 5/ early stage 4 and the LGM but values as low as interglacial values at various times, including the interval preceding the LGM. In Pacific core 5GC, the LGM interval identified by foraminiferal $\delta^{18}O$ has a $\delta^{15}N$ maximum at $\sim$9–10‰, with a deglacial decrease to 5‰ (Fig. 3). The LGM diatom-bound $\delta^{15}N$ maximum in 5GC is accompanied by a nearly 60% decrease in biogenic opal accumulation (Fig. 3). However, while the age of the core base is unclear, it appears that diatom $\delta^{15}N$ and opal accumulation are at near-interglacial values before the LGM, again in conflict with a simple glacial/interglacial pattern. Diatom-bound $\delta^{15}N$ increases in the late Holocene of 5GC, reminiscent of the increase in RC13-259, but of lower amplitude. Just to the north of 5GC, piston core 6PC, despite its much higher accumulation rate (Chase et al., 2003), bears a diatom-bound $\delta^{15}N$ record that is similar to 5GC, with a $\delta^{15}N$
maximum during the LGM. The 6PC does not show an increase in the latest Holocene. The absolute values and the amplitude of the glacial/interglacial shifts also differ significantly between the two sites, where 5GC and 6PC bear Holocene $\delta^{15}$N values of 5% and ~3–4%, respectively, and LGM values of 11% and 6.5%, respectively. The difference in the $\delta^{15}$N maxima between 5GC and 6PC is approximately 3%, while the average Holocene values differ by ~1%, with consistently lower values at 6PC. The direction of the difference is consistent with the surface sediment transect (Fig. 2b), although the magnitude is greater, perhaps because 6PC lost its coretop, as can happen in piston coring.

In the AZ cores, and as described previously for $\delta^{15}$N (Francois et al., 1997; Sigman et al., 1999a; Robinson et al., 2004), the glacial/interglacial pattern of diatom-bound $\delta^{15}$N is generally anti-correlated with opal concentration and accumulation rate. In 5GC, this anti-correlation also appears to apply within the glacial period (Fig. 3). In RC13-259, however, no anti-correlation is apparent within the last glacial period (Fig. 3). One could speculate that the consistently low glacial opal values may reflect both a decrease in regional productivity as well as a change in the silicic acid-to-nitrate uptake ratio in diatoms (e.g., Brzezinski et al., 2002). Comparison of the diatom $\delta^{15}$N profile with a published record of $\delta^{30}$Si, a proxy for relative utilization of silicic acid, from RC13-259 (Brzezinski et al., 2002) (data not shown) does not show a clear positive or negative relationship between these two nutrient consumption proxies within the last glacial interval, suggesting that more than one factor is controlling the relative degrees of consumption of one or both of the nutrients at this site.

3.3. Spatial and temporal variability within the AZ

The amplitude of change in diatom-bound $\delta^{15}$N observed in cores 5GC and RC13-259 is greater than what has been observed previously in AZ cores from the Atlantic (IO1277-10PC) and Indian (MD84-552; Fig. 3) sectors (Robinson et al., 2004). The surface transect data indicate that the downcore variation in $\delta^{15}$N may be the product of changes in $\varepsilon$, changes in nitrate uptake, or some combination of the two. The observed inter-site differences are likely due to geographical variations in physical and/or biogeochemical conditions at the sea surface. If $\varepsilon$ varies as a function of MLD, then one would expect significant variation in $\varepsilon$ between the Subantarctic Front and the SACCF where MLD changes sharply. MD84-552 sits within the Indian sector POOZ which has a particularly wide and deep mixed layer at present and a maximum at approximately the location of MD84-552 (Kara et al., 2003). If we allow up to 3% of variation to be associated with $\varepsilon$ changes (DiFiore et al., 2006), then all of the downcore variation in diatom-bound $\delta^{15}$N at MD84-552 may be attributable to $\varepsilon$. More work investigating the spatial variability of $\varepsilon$ in the modern Southern Ocean is required to better constrain the potential magnitude and extent of its influence on the sediment record. Nevertheless, spatial variation in $\varepsilon$ resulting from MLD variation cannot explain the magnitude of change observed at RC13-259, 5GC, and 6PC. Moreover, the positions of the Pacific cores relative to the modern core-top $\delta^{15}$N gradient (Fig. 2b) and estimates of $\varepsilon$ overlying the sites (Altabet and Francois, 2001) would suggest that $\varepsilon$ is already relatively low at these sites (closer to 5% than 8%), such that the potential for further reduction in $\varepsilon$ during the last ice age is relatively small. Finally, a reduction in MLD at times in the past would have improved light conditions for phytoplankton. Therefore, if $\varepsilon$ decreased in the past because of reduced MLD, this would likely have been associated with more complete nitrate consumption, the two changes compound- ing to raise the $\delta^{15}$N of diatom-bound N.

We propose that the high amplitude changes in $\delta^{15}$N at RC13-259, 5GC, and 6PC are related to their locations with respect to the SACCF and the SIZ. In the longer record, RC13-259, the $\delta^{15}$N fluctuations within the glacial interval are not matched by changes in the opal concentration or flux, which is taken to reflect export productivity (Charles et al., 1991; Kumar et al., 1995). Neither does the glacial $\delta^{15}$N increase from the last interglacial develop gradually or progressively through the last ice age. In this regard, the intra-glacial variability in diatom-bound $\delta^{15}$N is more similar to sea ice indicator species variation (Fig. 4; Frank et al., 2000), suggesting that the large changes in $\delta^{15}$N may be related to the extent or duration of sea ice cover. During the youngest part of MIS 5, with the first subtle increase in the biostratigraphic indicators, Cycladophora davisianna, and Eucampia antarctica, there is a significant increase in $\delta^{15}$N (Fig. 4). This increase in $\delta^{15}$N appears to correspond to the early increase in the ice edge indicators Fragilariopsis curta, Fragilariopsis cylindrus, and Fragilariopsis obliquuscostata in nearby cores PS1772 (55.48°S, 1.15°E) and PS1768 (53.53°S, 4.48°E) (Fig. 4) (Frank et al., 2000). The influence of sea ice as recorded by the diatom assemblages was spatially heterogeneous, with ice impacting PS1772 earlier than PS1768 (Frank et al., 2000). Today, with regard to ice cover, RC13-259 is intermediate between these two sites. Indeed, a sea ice history intermediate between those of PS1772 and PS1768 would fit remarkably well with N isotope history, with evidence for summertime ice in the early and late glacial occurring when there are maxima in diatom $\delta^{15}$N.

The O isotopes of foraminiferal carbonate and diatom opal should also be sensitive to Antarctic surface ocean conditions. The planktonic $\delta^{18}$O record at RC13-259 indicates variable conditions over the core location during the last glacial interval, such that local changes in temperature and salinity appear to blur the “global” glacial–interglacial $\delta^{18}$O variation that is typically used as a stratigraphic tool. Suggestive similarities exist between diatom $\delta^{15}$N and diatom opal $\delta^{18}$O ($\delta^{18}$Opal) profiles, although the relatively low sampling resolutions hamper our comparison (Fig. 4) (Shemesh et al., 1995). With as the $\delta^{18}$O of marine biogenic carbonate, $\delta^{18}$Opal is sensitive to
the $\delta^{18}O$ of the surface water in which the diatoms precipitate their opalline tests, as well as to its temperature. In the case of RC13-259, the typical ice volume/temperature variation one expects to see in a $\delta^{18}O$ record appears to be masked by local $\delta^{18}O$ (i.e. salinity) changes (Shemesh et al., 1994, 1995). Sea ice is similar in $\delta^{18}O$ to the water in which it formed, so sea ice melting in itself cannot explain the low $\delta^{18}O$ intervals that occur early and late in the last glacial interval. Rather, these intervals may be due to a regional concentration of icebergs due to transport patterns, the melting of snow that had accumulated on sea ice, or simply a decrease in surface salinity associated with ocean/atmosphere freshwater exchange. Regardless of which of the above alternatives was more important, stratification of the glacial Antarctic surface may have played a role in the apparent decrease of surface water $\delta^{18}O$, by increasing the residence time of the Antarctic mixed layer and thus allowing a greater freshwater cap to develop.

In the modern Pacific Antarctic, 5GC lies well within the SIZ, and 6PC sits within the SIZ although closer to the northern limit of seasonal sea ice. On the basis of diatom assemblage distributions (Crosta et al., 1998; Gersonde et al., 2005), Atlantic Antarctic core RC13-259 appears to sit at the southern edge of the POOZ; however, satellite chlorophyll data lead to a SIZ characterization for the region surrounding RC13-259 (Moore et al., 1999). Moreover, RC13-259 is directly downstream of the characteristic path that sea ice and icebergs travel after being exported from the Weddell Sea, “Iceberg Alley” (Anderson, 1999; Anderson and Andrews, 1999). Recent studies mapping sea ice extent at the last glacial maximum (LGM) indicate that the winter sea ice may have reached as far as 6–10° of latitude beyond the present northern edge (Crosta et al., 1998; Gersonde et al., 2005). Summer sea ice extents are inferred to be approximately the same as in the modern, although only a handful of cores are available from the southern region of the AZ to constrain this inference. The entire AZ, and thus all of the studied core sites, would have been within the SIZ during the last glacial period. However, sea ice would have retreated through the more northern Antarctic sites in the spring or early summer. An important exception is the vicinity of RC13-259 and to the west in the Atlantic, where there is evidence for sporadic summer sea ice near the northern limits of the AZ (Allen et al., 2005; Gersonde et al., 2005). In contrast, evidence for sporadic summer sea ice in the Indian Sector suggests only a slight northward expansion from the modern limits and largely ice free summers in this sector (Gersonde et al., 2005; Wolff et al., 2006) (Fig. 1). The available data indicate that, during the last ice age, 5GC, 6PC, and RC13-259 were significantly south of the winter ice edge and likely experienced prolonged seasonal ice cover. The previously published records from the Atlantic and Indian sectors, including MD84-552 (Fig. 3), were also within the SIZ during the LGM. However, evidence from diatom assemblages, ice rafted detritus (IRD) distributions, and sea surface temperature estimates suggests that the seasonal duration of ice cover over MD84-552 was shorter than at the sites of RC13-259 and 5GC/6PC (Cooke and Hays, 1981; Gersonde et al., 2005).

There are at least three SIZ-related explanations for the episodically high glacial $\delta^{15}N$ related to the site locations: (1) assemblage changes related to ice cover or cooling, influencing some aspect of the N isotope systematics; (2) an increase in nitrate consumption due to more rapid algal growth in the expanded summer marginal ice zone environment; and/or (3) a circulation-driven reduction in nitrate supply in some way linked to the summertime persistence of ice, also leading to more complete nitrate consumption in the summertime mixed layer. Given the changing environmental conditions and the evidence for species abundance changes in RC13-259, there is potential for assemblage-related changes in $\delta^{15}N$. These changes may be due to a change in either the relationship between diatom-bound $\delta^{15}N$ and that of bulk diatom-biomass or in $\varepsilon$.

There is growing evidence that $\varepsilon$ varies significantly across the Southern Ocean, and the apparent spatial pattern (higher $\varepsilon$ near the SAF than further south) is consistent with culture studies demonstrating an important role for light availability (Fig. 2) (Sigman et al., 2000; Altabet and Francois, 2001; Lourey et al., 2003; Needoba and Harrison, 2004; Needoba et al., 2004; DiFiore et al., 2006). Culture studies, if anything, indicate higher isotope effects for diatoms than for other oceanic algal forms (Needoba et al., 2003), which does not provide an obvious explanation for the higher $\varepsilon$ of the SAZ. Of course, it is possible that the pattern derives from $\varepsilon$ differences among diatom species. There are as yet no data to assess potential variation in the $\delta^{15}N$ relationship between diatom-biomass N and diatom frustule-bound N. The possibility of a change in $\varepsilon$ or in diatom-biomass-frustule $\delta^{15}N$ differences associated with assemblage changes during the last ice age remains a source of uncertainty in our interpretations. However, as stated above, the magnitude of the observed variability is too great to be explained by the observed amplitude of $\varepsilon$ variation (DiFiore et al., 2006). Moreover, the observed range of core-top diatom-bound $\delta^{15}N$ across the Antarctic and SAZ, including coastal Antarctic ODP Site 1098 from Palmer Deep, where seasonal nitrate consumption is very high, is ~4% (Robinson et al., 2004, 2005; Robinson unpublished data, 2006). If this level of variation was due to assemblage variations alone (which it is not), it still could not explain the changes on the order of 7–10% as observed for the last ice age at 5GC and RC13-259.

Our preferred explanation for the $\delta^{15}N$ maxima is the now-familiar mechanism of greater algal nitrate consumption (Altabet and Francois, 1994; Francois et al., 1997). It is tempting to explain the downcore $\delta^{15}N$ records of RC13-259 and 5GC/6PC as the result of (1) reduced nitrate supply throughout the entire AZ during the last ice age and (2) the occurrence of the summertime ice edge blooms at
the sites of RC13-259 and 5GC/6PC during the LGM and several other intervals during the last ice age, leading to complete nitrate consumption at these sites. One might then explain the temporal variations at RC13-259 as resulting from climate-driven migration of the summertime sea ice edge, with this region being overhead of RC13-259 and 5GC/6PC during the LGM and some other intervals during the ice ages but also further south during other intervals within the ice ages. There are, however, several indications that this explanation is incomplete.

First, it is not clear that it can explain the lack of similarly high $\delta^{15}N$ elevation in the LGM intervals of the previously published cores MD84-552 in the Indian Sector and IO1277-10PC in the Atlantic. All AZ cores were apparently located within the SIZ during the LGM and therefore had some potential for an increase in drawdown related to enhanced surface stabilization and focused Fe-fertilization. Model predictions of glacial dust distributions, with the highest accumulation rates in the Atlantic, moderate in the Indian, and low in the Pacific sectors (Mahowald et al., 1999), also fail to explain the spatial differences.

Second, the glacial variation in $\delta^{15}N$ at RC13-259 and 5GC is too great to be explained by a one-dimensional model of nitrate supply and consumption. If diatom-bound N was recording the simple situation of vigorous winter mixing and re-setting of the surface $[NO_3]$ and $\delta^{15}N$ to near deep ocean values, followed by the subsequent isolation of the surface nitrate pool and drawdown of that nitrate with no lateral transport, then the diatom-bound $\delta^{15}N$ should be well approximated by an accumulated product formulation of the Rayleigh process. This would place an upper limit on the $\delta^{15}N$ of the accumulating material as equal to the starting nitrate pool, for complete consumption. Assuming no large changes in mean deep ocean $\delta^{15}N$ on glacial-interglacial timescales (Kienast, 2000), one can estimate an upper limit to the increase in $\delta^{15}N$ as approximately the amplitude of $\varepsilon$; in the case of the modern Antarctic, $\sim 5$–8%. The total range of $\delta^{15}N$ from 5GC is $\sim 7\%_{\text{oo}}$, at the upper limit of change allowed by the accumulated product model, while the total range for RC13-259, $\sim 10\%_{\text{oo}}$, violates that model. We propose that these two apparent problems with the “ice edge” model for cores RC13-259 and 5GC are explained by a meridional gradient in the interglacial-to-glacial changes in the nitrate supply to the Antarctic surface. In this hypothesis, the presence of the summertime ice edge at RC13-259 and 5GC during the LGM is a driver of biogeochemical change, as described above, but also an indicator of the underlying ocean circulation in these regions.

### 3.4. The hypothesis

Today, nitrate is supplied to the AZ surface by two different processes: wind- (Ekman-) driven upwelling and density-driven deep winter mixing (Fig. 5a). Both occur within the AZ, and together they make the Antarctic a broad region where deep water is delivered to the surface ocean. The Ekman upwelling flux of $\sim 20$ Sv (Karsten and Marshall, 2002; DiFiore et al., 2006) appears inadequate to support the modern rate of export production in the AZ ($\sim 3$ mmol m$^{-2}$d$^{-1}$, Lourey and Trull, 2001; Reuer et al., 2007) while maintaining a $[NO_3]$ of $\sim 25$ $\mu$M; winter mixing must supply roughly half of the nitrate. Within the Antarctic, the relative importance of winter mixing is likely greater to the South, where winter cooling is stronger and Ekman-driven upwelling is weaker.

We propose that, during the LGM, the re-supply of nutrients by winter mixing, the second of the two mechanisms of nitrate supply listed above, was nearly eliminated (Fig. 5b) (Sigman et al., 2004). Several mechanisms have been proposed for the development of a polar Antarctic halocline during the last ice age. An equatorward shift in the westerly winds would have reduced the equatorward export of Antarctic surface water, allowing a polar Antarctic halocline to develop (Toggweiler et al., 2006). Alternatively, the cooling of the glacial ocean may explain the development of this halocline (Sigman et al., 2004; de Boer et al., 2007). Finally, it remains possible that the sea ice itself worked to reduce vertical exchange in the glacial Antarctic. More extensive Antarctic sea ice may have modified atmospheric temperatures so as to move the upwelling winds equatorward and away from the more polar Antarctic. Moreover, the sea ice cover may have interfered with the penetration of turbulent energy into the Antarctic surface mixed layer, an effect that has been shown to be important in the Arctic.

Whether or not wind-driven upwelling in the AZ was reduced during glacial times due to a shift in the location of the westerly winds, its qualitative persistence would have continued to bring nutrient-rich deep water to the surface (Fig. 5b). However, this process is largely limited today to the Antarctic north of the SACCF (Fig. 5a). Thus, with the loss of winter mixing, the re-supply of nutrients to the Antarctic surface would have been restricted to a discrete latitude band, the position of which is largely determined by the position of the westerly winds, likely near the APF. In this case, the only nitrate making its way into the polar AZ (i.e. south of the SACCF) would have been supplied by lateral exchange with the waters upwelling near the APF (gray arrow in Fig. 5b). The glacial SACCF would thus have represented a biogeochemical front between continued nitrate supply to the North and minimal nitrate supply to the South.

The hypothesis helps to explain the apparent coincidence of the summer sea ice during the LGM and the modern SACCF (Fig. 1; Gersonde et al., 2005). The cold ice age climate would have allowed summer sea ice to be more extensive than during the Holocene, but the ice could still not persist through the summer in the region to the North of the SACCF, because of Ekman-driven upwelling, which supplied heat from below (Matsumoto et al., 2002). The SACCF would also have been biologically active.
because the summer marginal ice edge environment with which it was associated would have encouraged algal growth (Fig. 5b). This would have acted to reinforce the sharp southward decline in surface nitrate concentration across the front. The Southern Boundary of the ACC, which is tightly coupled to the SACCF (Orsi et al., 1995), has been described as important to the functioning of Antarctic ecosystems (Tynan, 1998). Thus, it is perhaps not surprising that it was an even more important physical and biogeochemical front during the last ice age.

This hypothesis provides an explanation for the extreme elevation of $\delta^{15}N$ at RC13-259 and 5GC, and to some degree 6PC, during the LGM (Figs. 1 and 3). These core sites currently sit very close to the modern SACCF, and they could easily have been on that front or to the South of it during the LGM. It was during the times when this was...
the case that the $\delta^{15}$N of nitrate and sinking N increased to extremely high levels. We suggest that the $\delta^{15}$N of diatom N was elevated past the allowed range of the integrated product equation of Rayleigh fractionation (see above) because of the origin of the nitrate in those environments. The nitrate was originally upwelled further to the North, where it underwent partial algal consumption and $^{15}$N enrichment before being mixed southward in the mixed layer (Fig. 5b). Thus, the $\delta^{15}$N of the nitrate source at sites 5GC and RC13-259 was already greater than that of the deep water supply. This scenario is analogous (although not necessarily equivalent) to assuming the instantaneous equation of the Rayleigh model. According to the instantaneous equation and a range in $\varepsilon$ of 5–7‰, the $\delta^{15}$N change in the range of 7–10% observed at 5GC and RC13-259 would indicate an approximately 60–90% change in nitrate consumption. In this context, AZ core sites that show less change in $\delta^{15}$N across the deglaciation (MD84-552 and IO1277-10PC, Figs. 1 and 3), are thought to be closer to the region of upwelling and/or less affected by interaction with the summer ice edge (Fig. 5b), such that a smaller fraction of nitrate was consumed, albeit potentially somewhat more than today, in the case of MD84-552.

The two critical observations originally leading to the hypothesis of Antarctic stratification during the last ice age were: (1) lower opal and biogenic barium rain rates, suggesting lower export production in the glacial Antarctic (Kumar et al., 1993, 1995; Frank et al., 2000; Chase and Anderson, 2001; Chase et al., 2003) and (2) higher sedimentary N isotopes suggesting more complete nitrate consumption in glacial Antarctic (Francois et al., 1993, 1997). The hypothesis for the more polar Antarctic posed here is based largely on the N isotopes, and it remains to be determined whether productivity proxies support it as well. This uncertainty derives from a currently unclear picture of the spatial pattern of glacial/interglacial change in the proxies. For instance, in RC13-259, opal concentration and accumulation show no apparent connection to the variability in $\delta^{15}$N within the glacial interval (Fig. 3), while in 5GC, opal concentration and opal accumulation maintain an anti-correlation with $\delta^{15}$N within the glacial interval. Beyond this, there are fundamental uncertainties about the significance of these proxies. For instance, the lower opal accumulation rates may have resulted at least partially from a decrease in the degree of silification due to greater Fe availability, a possibility that is supported by $\delta^{30}$Si data from RC13-259 (Brzezinski et al., 2002).

In addition, a recent examination of the diatom assemblage changes in the Atlantic sector of the AZ concluded that the greater abundance of Chaetoceros resting spores in glacial sediments reflects more complete major nutrient consumption during the LGM, while the greater abundance of radiolarian C. davisiana resulted from a greater organic carbon flux to depth, both associated with the expansion of the productive sea ice environment (Abelmann et al., 2006). They interpret the lower glacial opal fluxes (and higher fluxes in the Subantarctic) to reflect the northward shift in the high opal-low carbon ecosystem associated with F. kerguelensis; that is, they do not take opal (or barium) flux to be a reliable indicator of organic carbon flux. Using this separate dataset, Abelmann et al. (2006) proposed a scenario similar to ours, where the expansion of glacial sea ice and the associated iron fertilization of the surface drove an increase in production associated with annual retreat of the ice edge that would have resulted in considerable nutrient and CO$_2$ drawdown within the Atlantic sector of the AZ. While we cannot speak to the different interpretation of the productivity proxies, our $\delta^{15}$N data do indicate extreme degrees of nitrate drawdown during the LGM, as the authors deduced from the increased presence of Chaetoceros spores. However, the $\delta^{15}$C of diatom-bound organic C suggests that even the ice margin-related algal growth during the last ice age was not as rapid as Holocene algal growth rates (Singer and Shemesh, 1995), so we question their proposal of increased export production. Our own expectation for the meridional gradient in Antarctic export production is not completely clear, as we have argued that the waters south of the SACC were characterized by less nitrate supply but more complete consumption of that supply than the Antarctic waters further north.

The late Holocene rise in diatom-bound $\delta^{15}$N at RC13-259 and 5GC is one aspect of the records that is not well fit by our hypothesis, especially the amplitude of the change in RC13-259 (Fig. 3). To the extent that an increase is present at the sites that record the largest variation in $\delta^{15}$N during the glacial and that are closest to the SIZ, this change may reflect a change in nitrate supply and demand roughly as hypothesized for the last ice age. Evidence exists for increased presence of ice in the late Holocene. Weight % of IRD in Atlantic Sector sediment core TTN057-13 (53°S) declines sharply upon deglaciation to a minimum in the early Holocene and then increases to near LGM concentrations at ~5 ka (Hodell et al., 2001). The increase in IRD may represent the transition from the Holocene climatic optimum to the relatively cooler Neoglacial and an expansion of winter sea ice (Shemesh et al., 1994; Hodell et al., 2001). This IRD increase was accompanied by a decline in $\delta^{18}$O$_{\text{opal}}$, suggesting an increase in halocline strength at that time (Shemesh et al., 1994). Thus, the late Holocene $\delta^{15}$N increases in RC13-259 and 5GC may indicate an increase in the degree of nitrate consumption, associated with reduced nitrate supply (from a freshening-induced reduction in wintertime vertical mixing) and/or better conditions for algal nitrate assimilation (ice-borne iron and shoaling of the mixed layer). The greater Holocene $\delta^{15}$N increase in at RC13-259 than in 5GC may relate to its location just downstream of “iceberg alley,” the track of floating ice from the Weddell Sea that is shed off the Antarctic Peninsula; with a neoglacial, this region may have been particularly susceptible to ice-driven changes. Alternatively, the difference between RC13-259 and 5GC
may be better interpreted as a large-scale interbasin difference, with the Atlantic receiving more aeolian deposition. The site of RC13-259 appears to be one of the non-coastal Antarctic regions with the greatest seasonal nitrate drawdown, of roughly 12 μM (Conkright, 2002), and the Levitus et al. (1994) mixed layer climatology also identifies it as having an anomalously shallow summer MLD for a site so far from the continent (Kara et al., 2003). These observations are qualitatively consistent with an impact of melting ice at this site today. Still, the maximum δ15N values during the Holocene are similar to the maximum during the LGM, yet we do not think this AZ site is as nutrient-deplete today as we have proposed for the AZ south of the SACCF during the LGM. Thus, in the context of our hypothesis, we do not understand the Holocene δ15N increase in RC13-259 at a quantitative level.

4. Conclusions

The modern spatial distribution of diatom-bound δ15N along 170°W, with a 3.4% increase southward from the APF, is best explained by more complete nitrate consumption combined with a lower isotope effect of nitrate assimilation toward the South. Both effects are thought to be related to the shoaling of summertime mixed layer. This suggests a role for seasonal sea ice in determining both the degree of nitrate consumption as well as its isotopic expression as recorded in the sediments.

New downcore diatom-bound δ15N data suggest an ice age AZ characterized by greater spatial gradients in physical and biogeochemical conditions than we observe today, with the SACCF arising as a potentially important mid-Antarctic front. We envision an AZ where year-round density stratification greatly reduced winter mixing, so that the nutrient supply to the surface was limited to wind-driven upwelling, which was located at the Antarctic Divergence close to the modern APF and bounded to the South (as it is today) by the SACCF. In this scenario, nitrate supply to the polar Antarctic occurred through lateral mixing with waters from the region of upwelling. The summertime marginal ice zone was associated with the region south of the SACCF, with continued upwelling near the Polar Front precluding extensive summertime ice in that region. The summertime marginal ice in the polar Antarctic encouraged the consumption of this limited nutrient supply from the North through the summertime input of atmospheric Fe accumulated in the ice over the winter, as well as through shoaling of the summertime mixed layer. The extremely high diatom δ15N was caused by a high degree of nitrate consumption and the 15N enrichment of the surface nitrate supply from the North by previous algal consumption. This high nutrient consumption in the polar Antarctic would have enhanced the previously proposed decrease in CO2 evasion due to density stratification of the AZ (see Sigman and Haug, 2003 for a box model comparison of the CO2 decreases due to Antarctic stratification with and without increased nutrient consumption).

Clearly, much work is required to test this view of the glacial Antarctic. Modern evidence for spatial gradients in ε suggest that temporal changes in ε cannot be ruled out as a source of variation. The diatom δ15N proxy itself requires extensive testing in the modern ocean. With regard to the paleoclimate data, the distribution of N isotope changes is currently far too sparse to yield a clear picture, and records from south of the modern SACCF are badly needed. Finally, a more thorough understanding of the spatial and temporal heterogeneity in the modern Antarctic must accompany the effort to evaluate the potential for spatial variability in the response to climate forcing and its significance for atmospheric CO2.

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