

Diatom-bound $^{15}\text{N}/^{14}\text{N}$: New support for enhanced nutrient consumption in the ice age subantarctic

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[1] Diatom-bound $^{15}\text{N}/^{14}\text{N}$ was used to reconstruct the glacial nutrient status of the Subantarctic Zone in the Southern Ocean. Down-core records from both the Pacific and Indian sectors show $\delta^{15}\text{N}$ of 5 to 6‰ during the Last Glacial Maximum and a decrease, coincident with the glacial termination, to values as low as 2‰. The effect of either diatom assemblage or physiological change on the diatom-bound $^{15}\text{N}/^{14}\text{N}$ is unknown and cannot yet be ruled out as a possible explanation for the observed change. However, the consistency between Indian and Pacific sector records and with other paleoceanographic data suggests that the glacial-interglacial difference in diatom-bound $^{15}\text{N}/^{14}\text{N}$ was driven by higher consumption of nitrate in the subantarctic surface during the last ice age. Such a change in nutrient consumption may have resulted from atmospheric iron fertilization and/or decreased glacial mixed layer depths associated with sea ice melting. Enhanced nutrient consumption in the glacial subantarctic would have worked to lower the concentration of CO_2 in the ice age atmosphere. It also would have reduced the preformed nutrient content of the low-latitude thermocline, leading to decreases in low-latitude productivity, suboxia, and denitrification.

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1. Introduction

[2] Since John Martin [*Martin*, 1990] posed the hypothesis that polar phytoplankton were fertilized by increased dust supply during the last ice age, paleoceanographers have been searching for evidence of this effect. The Subantarctic Zone (SAZ) of the Southern Ocean is one of the best candidate regions for iron fertilization because it falls in the same latitude band as the major southern hemisphere dust sources. Evidence for higher productivity in at least some sectors of the SAZ during the last ice age has been taken to support the glacial “iron hypothesis” [*Kumar et al.*, 1995]. However, subantarctic iron fertilization would have been accompanied by a drawdown of nutrients during the last ice age, which has been suggested by some studies [*Rosenthal et al.*, 1997; *Rosenthal et al.*, 2000] but not by others [*Elderfield and Rickaby*, 2000; *Francois et al.*, 1997].

[3] The SAZ is the northern domain of the Southern Ocean, with the Polar Frontal Zone (PFZ) and Antarctic Zone (AZ) to the south (Figure 1). Today, the subantarctic

surface is characterized by a meridional gradient in the concentrations of the “major nutrients” nitrate and phosphate [*Conkright et al.*, 2002]. Nutrients are supplied to the subantarctic by wind-driven northward transport of nutrient-rich Antarctic surface water and by intense vertical mixing in the winter. The phytoplankton growing on this nutrient supply causes the SAZ region to be a persistent sink for atmospheric CO_2 [*Takahashi et al.*, 1997]. However, this region experiences only partial drawdown of the major nutrients and therefore holds the potential for even greater CO_2 uptake. Moreover, thermocline ventilation in the SAZ is responsible for supplying nutrients to low-latitude ocean ecosystems [*Sarmiento et al.*, 2004], which, in turn, produce most of the ocean’s calcium carbonate rain to the seafloor. Thus a change in the nutrient status of the SAZ can have a significant effect on atmospheric CO_2 [*Matsumoto et al.*, 2002b]. Workers have tried to approach the question of the Southern Ocean’s role in the ice age carbon cycle through analysis of productivity proxy records. In the AZ, south of the Antarctic Polar Front (APF), opal is the primary biogenic component of Holocene sediment, but down-core records indicate less opal deposition during the last ice age. Early reconstructions suggested that opal flux was elevated in the PFZ and SAZ during glacial episodes [*Charles et al.*, 1991; *Kumar et al.*, 1993; *Mortlock et al.*, 1991], which has been taken as evidence of regional iron fertilization during ice ages [*Kumar et al.*, 1995]. The most recent reconstructions of glacial-interglacial productivity changes, which benefit from increased coverage of the SAZ and better quantification of opal fluxes using ^{230}Th normalization, show some degree of zonal heterogeneity within the SAZ,

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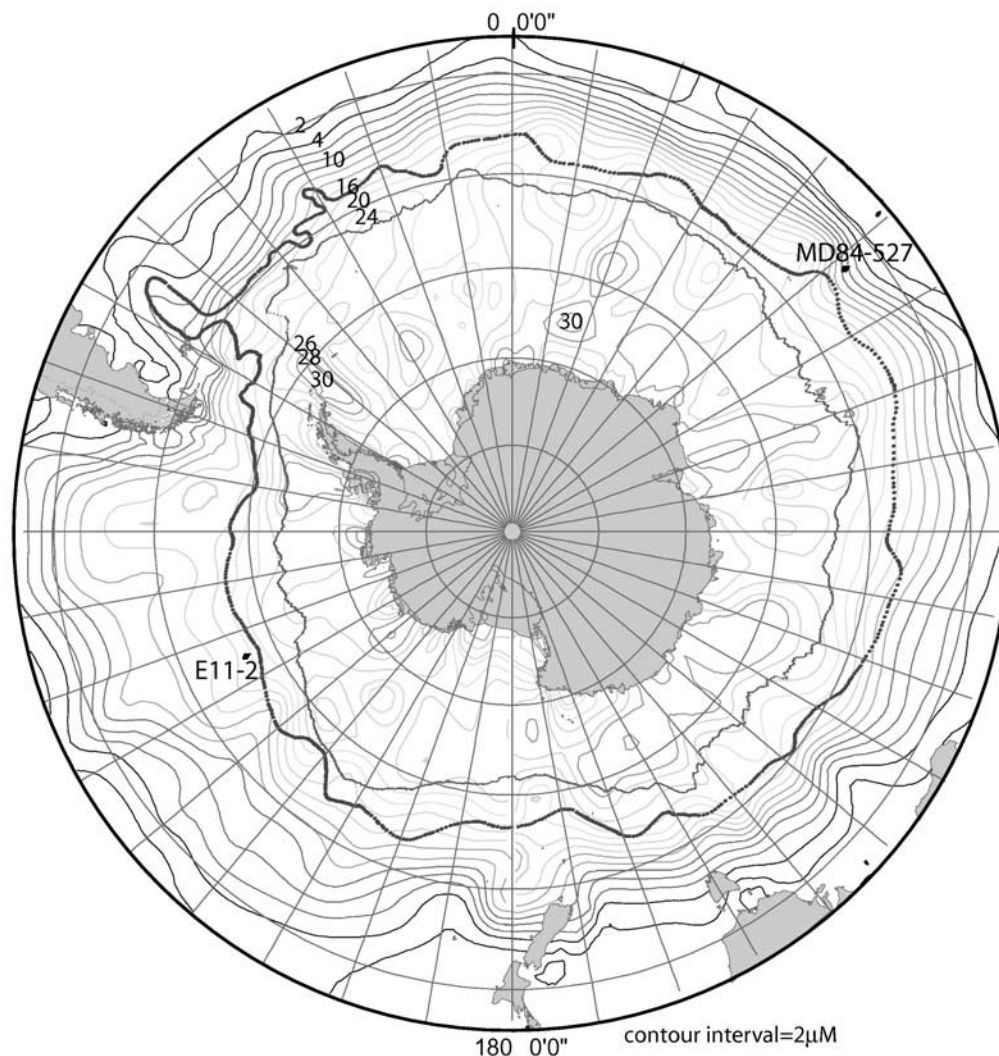


Figure 1. Polar stereographic view of the Southern Ocean showing the locations of the Subantarctic Zone (SAZ) sediment cores used in this study. Topographically steered current jets, or fronts, within the Antarctic Circumpolar Current (ACC) divide the Southern Ocean into distinct zones. The Subantarctic Zone is bounded to the south by the Subantarctic Front [Orsi *et al.*, 1995] (bold red line), and the Antarctic Polar Front [Moore *et al.*, 1999] (thin blue line) divides the Polar Frontal Zone to the north from the Antarctic Zone to the south. Summertime (January–March) NO_3^- concentrations (μM) [Conkright *et al.*, 2002] in the Southern Ocean are contoured with a $2 \mu\text{M}$ contour interval. See color version of this figure in the HTML.

with generally larger changes in the Atlantic sector and more modest to absent changes in the Indian and Pacific sectors [Chase *et al.*, 2003; Dezileau *et al.*, 2003].

[4] Nutrient utilization is typically a better gauge than export production of the role of a region in the global biological pump, because it is more directly linked to the balance between the upwelling of excess CO_2 and the downward flux of organic C. Decreased or constant export production in the polar ocean could be associated with an increase in nutrient utilization if the supply of nutrients is diminished, for instance, because of stratification of the upper water column [Francois *et al.*, 1997]. If the supply of nutrients is constant, increased nutrient utilization requires

an increase in export production. In either of these cases, the major nutrient content of the surface waters of the Southern Ocean would be lower and the efflux of CO_2 to the atmosphere would be reduced.

[5] However, the evaluation of nutrient utilization from different paleoceanographic proxies has not yet yielded a consensus view for any region of the Southern Ocean. Here we use diatom-bound $^{15}\text{N}/^{14}\text{N}$ as a metric for nitrate consumption in the SAZ. Phytoplankton preferentially take up ^{14}N -bearing nitrate, causing the $^{15}\text{N}/^{14}\text{N}$ of the nitrate in surface waters to increase as it is consumed [Sigman *et al.*, 1999b]. As a result, the $^{15}\text{N}/^{14}\text{N}$ of sinking and surface sedimentary N is indicative of the degree of nitrate utiliza-

Table 1. Reductive Cleaning Comparison^a

Sample Identification	Cleaning Treatment			
	H ₂ O ₂		Dithionite+H ₂ O ₂	
	N, $\mu\text{mol/g}$	$\delta^{15}\text{N}$	N, $\mu\text{mol/g}$	$\delta^{15}\text{N}$
SiO ₂ ^b	2.0	-	0.5	-
AZ	12.7	2.1	12.4	2.3
PFZ	8.7	4.2	8.5	4.5
SAZ-glacial	13.3	4.9	12.2	5.4
SAZ-glacial	14.2	5.5	13.4	5.0
SAZ-glacial	12.3	-	11.6	4.5

^aAbbreviations are AZ, Antarctic Zone; PFZ, Polar Frontal Zone; and SAZ, Subantarctic Zone.

^bSynthetic SiO₂ with approximately the same surface area as diatom opal.

tion in overlying nutrient-bearing surface waters [Altabet and Francois, 2001; Altabet and Francois, 1994]. However, in addition to the algal nitrate assimilation signal, microbial alteration increases the $^{15}\text{N}/^{14}\text{N}$ of sedimentary N above that of the N sinking out of the surface ocean, especially in deep, open ocean depositional settings like the Southern Ocean [Altabet and Francois, 1994; Lourey et al., 2003]. Comparison of Holocene and last glacial bulk sediments in the SAZ most often show lower $^{15}\text{N}/^{14}\text{N}$ during the last ice age, which has been taken to signify intensified vertical mixing, such that nutrient supply increased more than did algal nutrient demand [Francois et al., 1997]. However, this pattern is not apparent in many SAZ reconstructions, and full down-core records often show trends that do not relate to glacial/interglacial climate change [Francois et al., 1993]. This incoherent pattern may stem from temporal changes in the diagenetic alteration of the primary isotopic signal during sinking and sedimentation.

[6] To overcome the potentially confounding effect of isotopic alteration, the organic matter protected within the silica frustule of diatoms has been targeted for isotopic analysis [Robinson et al., 2004; Shemesh et al., 1993; Sigman et al., 1999a]. Recent work introducing an improved method for measuring diatom-bound $^{15}\text{N}/^{14}\text{N}$ uncovered analytical problems with the combustion-based methodologies for measuring the $^{15}\text{N}/^{14}\text{N}$ of diatom-bound and bulk sedimentary N in opal-rich materials [Robinson et al., 2004]. This same study revisited the evidence for glacial/interglacial changes in diatom-bound $^{15}\text{N}/^{14}\text{N}$ within the Antarctic zone: modest changes in diatom-bound $^{15}\text{N}/^{14}\text{N}$ across the glacial-interglacial transition were observed in an Indian sector core, but no glacial-interglacial change was observed in an Atlantic sector core. Comparison of diatom-bound with bulk sedimentary $^{15}\text{N}/^{14}\text{N}$ suggested that isotopic alteration of the bulk N during sinking and sedimentation has aliased the bulk sediment records.

[7] The new evidence for artifacts in the AZ bulk sediment $^{15}\text{N}/^{14}\text{N}$ records motivates a diatom-bound N-based study of the Subantarctic Zone, where previous N isotope work has been restricted to measurement of bulk sedimentary N. We measured diatom-bound $^{15}\text{N}/^{14}\text{N}$ profiles in two cores north of the Subantarctic Front, one each from the Indian and Pacific sectors. Unlike previously published

bulk sediment records, the diatom-bound reconstructions show a clear glacial/interglacial structure, with higher diatom-bound $\delta^{15}\text{N}$ during the last ice age and a decrease upon deglaciation to lower interglacial $\delta^{15}\text{N}$ ($\delta^{15}\text{N} = (^{15}\text{N}/^{14}\text{N}_{\text{sample}}/^{15}\text{N}/^{14}\text{N}_{\text{reference}} - 1)1000\text{‰}$ where atmospheric N₂ is the universal reference). While we do not yet know enough about diatom-bound N isotopes to definitively interpret the elevation of diatom-bound $\delta^{15}\text{N}$ in the Subantarctic Zone, the most straightforward explanation is as evidence of increased nitrate utilization during the last ice age.

2. Materials and Methods

[8] Down-core profiles of diatom-bound $\delta^{15}\text{N}$ were measured in subantarctic sediment cores E11-2 (54°S; 115°W) from the Pacific sector and MD84-527 (44°S; 51°E) from the Indian sector (Figure 1). The age model for E11-2 was derived by Ninnemann and Charles [1997], through correlation of the $\delta^{18}\text{O}$ stratigraphy (*N. pachyderma*) to that of the well-dated, high-resolution core RC11-83. The age model for MD84-527 is based on AMS ^{14}C dates from monospecific samples of *G. bulloides* and *N. pachyderma* [Pichon et al., 1992]. There is a large drop in calculated sedimentation rate during the last glacial maximum (LGM), from around 30 cm ky⁻¹ between 2 and 13 ka to ~ 3 cm ky⁻¹, suggestive of a hiatus. Moreover, the $\delta^{18}\text{O}$ maximum is $\sim 0.6\text{‰}$ less than expected for LGM conditions observed regionally, again indicating that the LGM section of the core is compressed or missing [Francois et al., 1993; Pichon et al., 1992].

[9] The physical separation and cleaning of the diatom fraction follows Robinson et al. [2004]. 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 solution ($\rho = 2.15$ g/cm³), 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 several (4–6) repeated oxidations with 30% H₂O₂ to remove external organic nitrogen (ON).

[10] The reductive cleaning step is new to this study and was added preemptively to remove metals that could potentially form oxide coatings during the H₂O₂ oxidative cleaning steps. In relatively opal-rich samples from the AZ, PFZ, and cores E11-2 and MD84-527, samples treated with and without the reductive cleaning step do not show any systematic differences in diatom-bound $\delta^{15}\text{N}$ (Table 1). However, there is a small reduction in N content and, in general, improved precision for samples treated with a reductive cleaning prior to the H₂O₂ steps with respect to those cleaned with H₂O₂ alone. Because of this observation, we have incorporated the reductive cleaning into our standard sample preparation protocol.

[11] N content and $\delta^{15}\text{N}$ of the diatom-bound intrinsic organic matter was determined by our 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

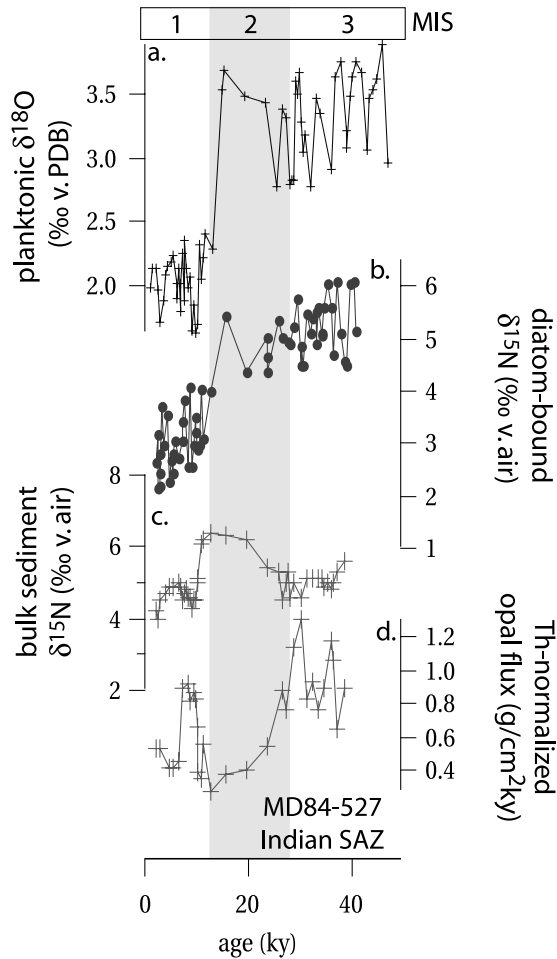


Figure 2. Down-core profiles of (a) foraminiferal $\delta^{18}\text{O}$ (b) diatom-bound $\delta^{15}\text{N}$, (c) bulk sediment $\delta^{15}\text{N}$, and (d) Th-normalized opal burial rate versus age from subantarctic core MD84-527. The age model and ancillary data sources are described in detail in the text. See color version of this figure in the HTML.

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].

3. Results

3.1. Last Glacial Maximum and Termination 1 in the Subantarctic Zone

[12] Focusing on the last 45 kyr, there is a shift from elevated diatom-bound $\delta^{15}\text{N}$ during the last ice age to lower values during the Holocene in both of the SAZ records (Figures 2 and 3). The decrease in the diatom-bound $\delta^{15}\text{N}$ is coincident with the shift in planktonic foraminiferal $\delta^{18}\text{O}$ [Ninnemann and Charles, 1997] at the glacial termination. In E11-2, there is a decrease of 4‰ from a maximum of 6‰ during the LGM down to 2‰ at 10 ka. In MD84-527, the change is only 2.5‰, from $\sim 5.5\%$ to 3‰. This difference

may be due to the absence of the true LGM in MD84-527 (see above) [Pichon *et al.*, 1992].

[13] The bulk sediment records differ significantly from the diatom-bound $\delta^{15}\text{N}$ records. Moreover, the bulk records from E11-2 and MD84-527 are similar to one another, with relatively elevated $\delta^{15}\text{N}$ during the deglaciation and the glacial maximum and lower values earlier in the glacial and during the Holocene in MD84-527. Comparison with the Th-normalized opal flux record from MD84-527 (roughly equivalent to total flux in this opal-dominated core) shows that high bulk sediment $\delta^{15}\text{N}$ occurs during periods of low sediment flux [Francois *et al.*, 1993]. This was initially interpreted as indicating stratification during the LGM and deglaciation, such that productivity decreased because of a reduced supply of nutrients [Francois *et al.*, 1993]. However, here we observe that larger differences between bulk and diatom-bound $\delta^{15}\text{N}$ occur when Th-normalized opal flux is lower (Figure 4). This comparison indicates that much of the variation in bulk sedimentary $\delta^{15}\text{N}$ in these cores can be explained as the result of varying diagenetic alteration. There was apparently more isotopic alteration when the opal flux to the seafloor was low. This is consistent with sediment trap data from the modern subantarctic, which indicate an anomalously high $\delta^{15}\text{N}$ for the wintertime low-flux sinking material, suggesting that a reduced summertime flux would lead to a higher annually integrated sinking flux $\delta^{15}\text{N}$ [Lourey *et al.*, 2003].

3.2. Full Glacial Cycle in the Pacific Subantarctic Zone

[14] The E11-2 diatom-bound $\delta^{15}\text{N}$ record extends back nearly a complete glacial cycle to ~ 110 ka in marine isotope stage (MIS) 5 (Figure 3). As a first-order observation, the diatom-bound $\delta^{15}\text{N}$ and planktonic $\delta^{18}\text{O}$ curves are quite similar; diatom-bound $\delta^{15}\text{N}$ shifts with $\delta^{18}\text{O}$ into the glacial and returns to interglacial values late in MIS 5. However, during the glacial, diatom-bound $\delta^{15}\text{N}$ increases to nearly LGM values in the $\delta^{18}\text{O}$ trough of MIS 3, while there is no specific peak in diatom-bound $\delta^{15}\text{N}$ to parallel the increase in $\delta^{18}\text{O}$ in MIS 4.

4. Interpretation and Discussion

4.1. Cause of Elevated Diatom-Bound $\delta^{15}\text{N}$ in the Glacial Subantarctic Zone

[15] In the first paleoceanographic studies of the Southern Ocean, key observations from the glacial age SAZ were explained as the result of an equatorward shift in Southern Ocean characteristics. For instance, sedimentary opal accumulation was greater during the LGM in the subantarctic but reduced in the Antarctic, which was interpreted as a northward shift in Southern Ocean productivity [Charles *et al.*, 1991; Mortlock *et al.*, 1991]. An explanation can be posed for the SAZ diatom-bound $\delta^{15}\text{N}$ data that similarly involves an equatorward migration of AZ and PFZ conditions into the SAZ.

[16] While few measurements have been made, the existing core top data for diatom bound $\delta^{15}\text{N}$ appear to indicate an unexpected decrease of 1–2‰ as one goes from the AZ (core top $\delta^{15}\text{N} \sim 3\text{--}4.5\%$) to the southern edge of the SAZ

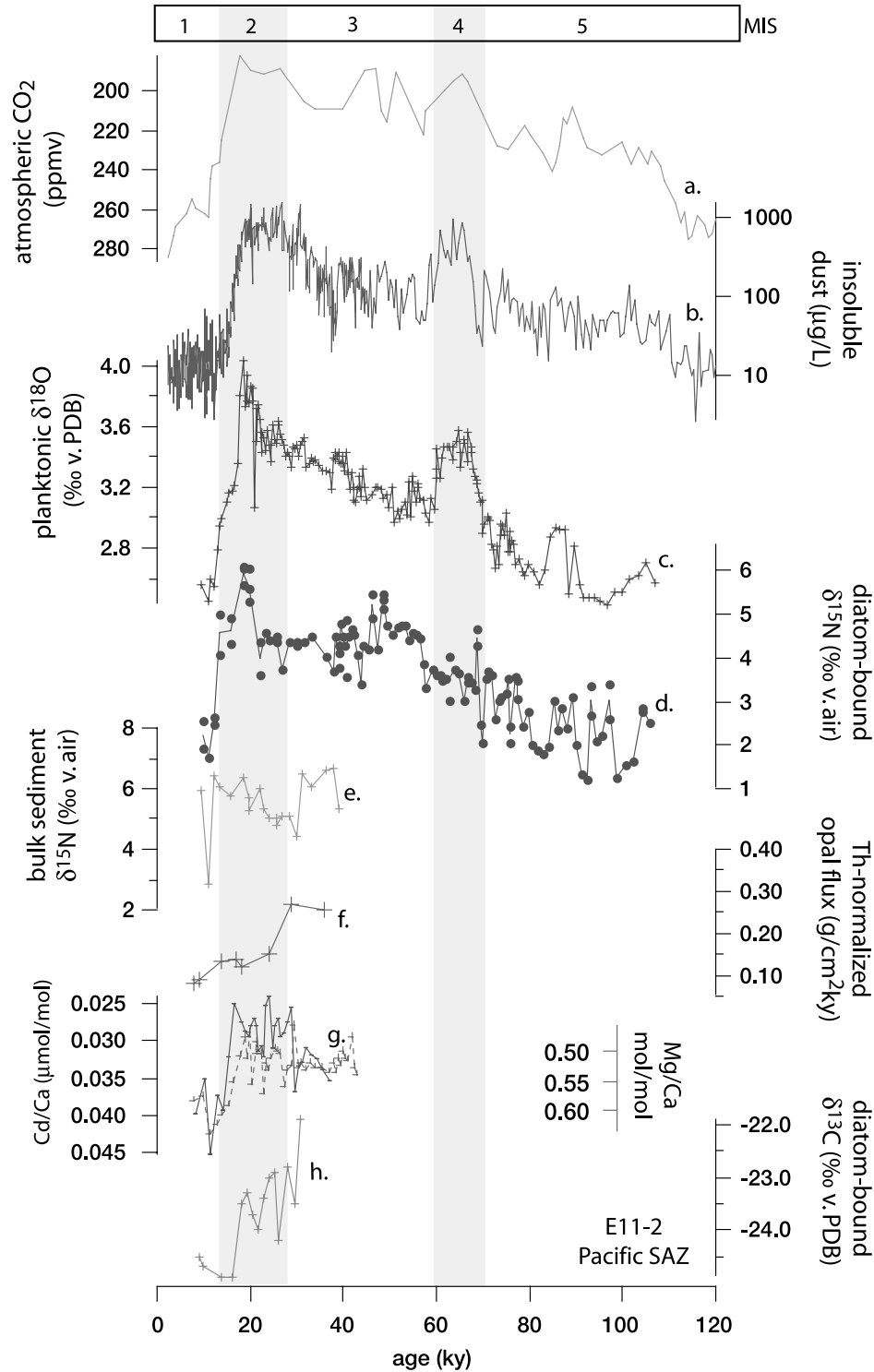


Figure 3. Ice core profiles of (a) atmospheric CO₂ from Vostok ice core [Petit et al., 1999] and (b) EPICA ice core insoluble dust concentration [Delmonte et al., 2004] for the last glacial cycle. These global climate signals are compared with (c) foraminiferal δ¹⁸O [Ninnemann and Charles, 1997], (d) diatom-bound δ¹⁵N, (e) bulk sediment δ¹⁵N, (f) Th-normalized opal burial rate, (g) foraminiferal Cd/Ca and Mg/Ca (dashed line), and (h) diatom-bound δ¹³C_{org} [Rosenthal et al., 2000] from Pacific subantarctic sediment core E11-2. The δ¹⁸O, Cd/Ca, and Mg/Ca were measured on the planktonic foraminifera *N. pachyderma* (sin.). See color version of this figure in the HTML.

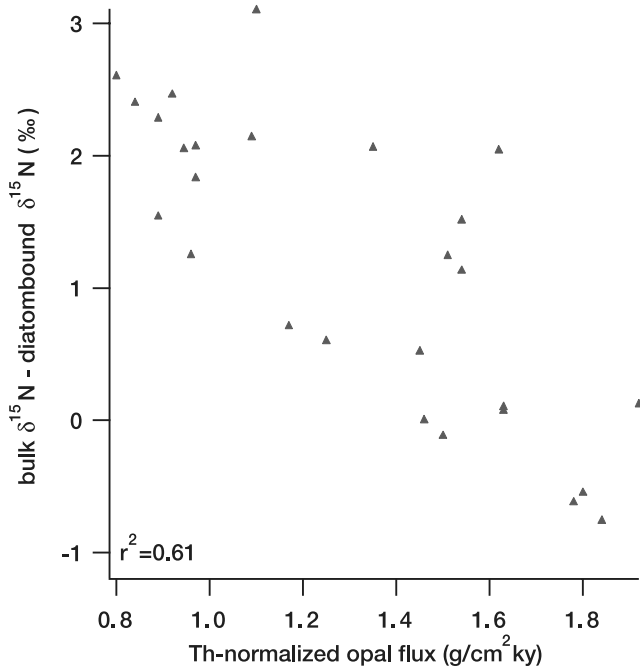


Figure 4. Th-normalized opal flux versus the difference between diatom-bound $\delta^{15}\text{N}$ and bulk sedimentary $\delta^{15}\text{N}$ measured in the same samples from MD84-527. The degree of difference between the two $\delta^{15}\text{N}$ measures increases with decreasing opal flux, suggesting that bulk sedimentary N is subject to greater isotopic alteration during periods of slower sedimentation. See color version of this figure in the HTML.

(2–3.5‰; this study), with higher values as one goes further north in the SAZ [Robinson *et al.*, 2004]. The observed AZ-to-SAZ $\delta^{15}\text{N}$ decrease is opposite to the trend that would be expected to result from the northward increase in nitrate utilization. One possible explanation is a higher isotope effect (greater isotopic fractionation) associated with nitrate assimilation in the SAZ than in the AZ. An unexpectedly weak northward increase in the $\delta^{15}\text{N}$ of sediment trap materials has been observed in transects across the APF [Altabet and Francois, 2001; Lourey *et al.*, 2003]. There is tentative evidence that this weaker-than-expected increase is due to a higher isotope effect for nitrate assimilation in the SAZ and PFZ than in the AZ that undergoes seasonal ice cover (P. J. DiFiore *et al.*, manuscript in preparation, 2005). We are currently investigating the implications of a meridional gradient in the isotope effect with regard to how they relate to current models of the controls on isotope fractionation during nitrate assimilation [Needoba and Harrison, 2004; Needoba *et al.*, 2004]. However, it is not clear whether a higher SAZ isotope effect for nitrate assimilation can explain an actual northward decrease in diatom-bound $\delta^{15}\text{N}$. Alternatively, it is possible that an AZ-to-SAZ difference exists in the isotopic relationship between diatom microfossil-bound N and the bulk biomass N of the diatom. To resolve these issues will require

a major ground-truthing study involving sediment trap materials.

[17] The apparent elevation of core top diatom bound $\delta^{15}\text{N}$ in the AZ relative to the SAZ raises the possibility that migration of AZ conditions into the SAZ during glacial times caused the glacial increase in SAZ $\delta^{15}\text{N}$. There are, however, arguments against this interpretation. One might posit that a northward migration of environmental conditions, such as the observed decrease in sea surface temperature [Mashiotta *et al.*, 1999], would be associated with a shift in phytoplankton populations. Yet documented diatom assemblage changes are largely associated with the equatorward expansion of sea ice, which was restricted to the region south of the Subantarctic Front (i.e., the PFZ and AZ) [Crosta *et al.*, 1998]. Within the SAZ, the assemblage changes are small, amounting to ~10–15% in the total assemblage accounting [Burckle, 1984; Crosta *et al.*, 1998; Pichon *et al.*, 1992]. As such, there is no clear evidence of a major glacial/interglacial change in diatom assemblage within the SAZ and specifically at E11-2 [Burckle, 1984] or MD84-527 [Pichon *et al.*, 1992]. In addition, given the high opal flux in the PFZ and the southern boundary of the Antarctic Circumpolar Current [Nelson *et al.*, 2001; Sigmon *et al.*, 2002], if the diatom $\delta^{15}\text{N}$ changes were due to the intrusion of PFZ and AZ conditions into the SAZ, then one would expect an increase in diatom-bound $\delta^{15}\text{N}$ to occur in tandem with an increase in opal flux at any given site. This is not the case (Figures 2 and 3). Rather, the major decrease in opal flux occurs prior to the LGM during MIS 3, when diatom-bound $\delta^{15}\text{N}$ is stable. Diatom-bound $\delta^{15}\text{N}$ decreases upon deglaciation, when opal flux changed little (as in E11-2) or increased sharply (as in MD84-527). The abundance of foraminifera and CaCO_3 through interglacial and glacial intervals in both cores also argues against a LGM shift to AZ-like conditions, under which little CaCO_3 is produced and/or preserved. Finally, the similarity of the diatom-bound $\delta^{15}\text{N}$ records in the two cores, despite different sedimentation histories, suggests that diatom-bound $\delta^{15}\text{N}$ is recording a more homogeneous feature of the glacial SAZ than the migration of a frontal system.

[18] The most straightforward explanation for this apparently circumpolar isotopic change is that the regional consumption of nitrate is changing in concert with climate. According to this view, there was greater drawdown of nutrients during glacials than interglacials, with the greatest intensification of consumption occurring during the LGM, when climatic conditions were most different from present. The degree of glacial nitrate drawdown can be estimated by assuming isotope dynamics appropriate for progressive consumption of a closed nitrate pool (i.e., the “Rayleigh model” [Mariotti *et al.*, 1981]). In the context of this model, there are two end-member cases that can be considered, one in which diatom-bound N follows the instantaneous product, which would apply in a system where lateral supply of nitrate dominates, and the other in which diatom-bound N follows the accumulated product, which would apply best in environments where nutrients are supplied vertically and consumed locally. The data in hand indicate that the SAZ represents an intermediate system; there is some vertical

supply and local consumption as well as lateral advection of nutrients [Lourey *et al.*, 2003; Sigman *et al.*, 1999b]. Using the “instantaneous” product equation [Mariotti *et al.*, 1981] and an isotope effect for nitrate assimilation of 5–8‰ [Altabet and Francois, 2001; Lourey *et al.*, 2003; Sigman *et al.*, 1999b], we calculate that, during the peak glacial conditions at E11-2, subantarctic nitrate consumption increased by 35–55% (i.e., yielding a subantarctic nitrate concentration of 10–7.5 μM , respectively). A more conservative estimate of a 15–25% increase in nitrate drawdown arises from the MD84-527 record, which shows only a 2.5‰ shift. Using the accumulated product case, a starting nitrate concentration of 25 μM with a $\delta^{15}\text{N}$ of 7‰ [Sigman *et al.*, 1999b], and isotope effect range of 8–5‰, we calculate that the 4‰ shift at E11-2 represents an increase from $\sim 30\%$ at present to $\sim 85\text{--}100\%$ during the glacial. At MD84-527, where nitrate drawdown is greater today, the 2.5‰ increase translates to a change from $\sim 60\%$ at present to $\sim 85\text{--}100\%$ during the glacial, similar to estimates from E11-2.

4.2. Supporting Proxy Records

[19] Other proxy records bolster the case for a change in nutrient status. Cd/Ca of foraminiferal calcite has been used as a proxy for changes in oceanic $[\text{PO}_4^{3-}]$ [Boyle, 1988]. The Cd/Ca of tests of the planktonic species *N. pachyderma* (sin.) from core E11-2 is 0.015 $\mu\text{mol/mol}$ lower in glacial age sediment than in the Holocene (Figure 3g), suggesting that the $[\text{PO}_4^{3-}]$ of subantarctic surface waters was $\sim 35\%$ lower during the last ice age [Mashiotta, 1997], in good agreement with the instantaneous product estimate derived using diatom-bound $\delta^{15}\text{N}$ data (i.e., supporting the lower range of nitrate drawdown estimates from the N isotopes). Moreover, the $\delta^{13}\text{C}$ of photosynthate, as indicated from diatom-bound organic matter, suggests that the aqueous CO_2 concentration was low and/or algal growth rates were higher during the last ice age, as would be expected if a greater proportion of the major nutrient supply was consumed by phytoplankton [Rosenthal *et al.*, 2000] (Figure 3h). The same sense of change has been observed for these tracers in other subantarctic records, some of which come from the Atlantic and Indian sectors [Mashiotta, 1997; Rosenthal *et al.*, 1997].

[20] Our estimation of nutrient drawdown from the Cd/Ca data does not take into account an inferred temperature effect on the distribution coefficient of Cd/Ca between seawater and biogenic CaCO_3 [Rickaby and Elderfield, 1999]. However, the deglacial warming inferred from Mg/Ca in E11-2 [Mashiotta *et al.*, 1999] leads the Cd/Ca increase (Cd/Ca and Mg/Ca having been measured from the same picked foraminifera (Figure 3g)), which may indicate that the glacial-interglacial Cd/Ca shift is not an artifact of temperature. The temperature dependant partition coefficient (D_{Cd}) proposed by Rickaby and Elderfield [1999] was inferred from *Globigerina bulloides* picked from surface sediments collected along a meridional transect in the North Atlantic. D_{Cd} determined from culture experiments using *G. bulloides* at 22°C was 1.9 [Mashiotta *et al.*, 1997], while the temperature dependant equation for D_{Cd} of [Rickaby and Elderfield, 1999] ($D_{\text{Cd}} = 0.637\text{exp}$

0.15T) at 22°C gives a D_{Cd} of 17. This discrepancy suggests that the temperature dependence of D_{Cd} has been overestimated or that variability in D_{Cd} is not exclusively temperature driven. No comparable studies have been conducted on the D_{Cd} for *N. pachyderma*, but subantarctic records of Cd/Ca in this species and *G. bulloides* show the same sense of change.

4.3. Cause of Nutrient Drawdown in the Glacial Subantarctic

[21] Iron, silicate, and light are each plausible controls on the degree of nitrate consumption in the SAZ. Incubation experiments in subantarctic waters do not show a fertilization effect on net primary production for silicate additions devoid of iron [Hutchins *et al.*, 2001], so the evidence reported here for more complete nitrate consumption during glacial times cannot be explained solely by an increase in silicate supply. At the same time, silicate supply to the SAZ may have been higher during the last ice age as a result of decreased demand in the AZ, either in response to (1) increased light limitation in the AZ [Anderson *et al.*, 2002] or (2) Fe fertilization and an associated decrease in the ratio of Si to NO_3^- uptake [Brzezinski *et al.*, 2002].

[22] The relative importance of iron and light in the modern SAZ is more difficult to assess. Incubation results would suggest that, given unchanging light conditions, iron enrichment would lead to greater nutrient drawdown [Boyd *et al.*, 2001]. We do not know whether improving light conditions, without changes in iron, would substantially increase the amount of nitrate drawdown. Even with more rapid growth due to enhanced light, SAZ phytoplankton might still run out of iron in the course of the growing season before nitrate was reduced below modern levels. Thus we are left with three plausible explanations for the observed increase in SAZ nitrate utilization: (1) iron enrichment, (2) improved light conditions, and (3) enhanced availability of both iron and light. It is our sense that explanations 1 and 3 are most likely. While iron enrichment could be achieved by a higher iron:major nutrient in the water being supplied to the subantarctic surface, a greater aeolian supply of iron is a more straightforward explanation. Moreover, it is consistent with data and model results suggesting that the aeolian supply of iron to the subantarctic surface was much greater during glacial times [Kumar *et al.*, 1995; Mahowald *et al.*, 1999]. Light conditions might have been improved by shoaling the mixed layer, perhaps because of surface freshening. Diatom assemblage data suggest that wintertime sea ice extended to near the PFZ during the LGM [Crosta *et al.*, 1998]; melting during the summer, encouraged by the sharp SST gradient in the PFZ, is a conceivable source of fresh water.

[23] Increased iron supply can potentially explain another feature of our Indian and Pacific records. Taken together, the diatom-bound $\delta^{15}\text{N}$ and Th-normalized opal flux records imply that the highest degrees of nitrate consumption occur without an associated maximum in opal deposition. At the same time, there is evidence for enriched organic carbon [Dezileau *et al.*, 2003] and authigenic uranium [Chase *et al.*, 2001; Dezileau *et al.*, 2002; Francois *et al.*, 1997] deposition in the SAZ

during the LGM. This “decoupling” of the opal flux and nitrogen isotope records may result from a change in Si/N and Si/C uptake ratios under iron replete conditions [Brzezinski *et al.*, 2002; Dezileau *et al.*, 2003; Hutchins and Bruland, 1998; Takeda, 1998].

[24] A decrease in the Si-to-major nutrient uptake ratio as a response to enhanced Fe deposition has previously been proposed for the AZ [Brzezinski *et al.*, 2002]. This would lead to an increase in the supply of silicate to the SAZ and, as noted above, may explain the increase in opal deposition observed in some regions of the SAZ [Charles *et al.*, 1991]. It is possible that during glacial times the SAZ might have absorbed all of the excess silicate from the AZ, preventing any significant amount of silicate from being incorporated into Subantarctic Mode Water (SAMW) and reaching low-latitude biota. At the same time, if the distal AZ was responding to increased Fe supply, then it seems more likely that the SAZ responded similarly. The data reported here seem consistent with an LGM decrease in the Si-to-major nutrient uptake ratio of SAZ Phytoplankton. We must recognize the caveat that it is not clear to what degree the glacial N isotopic enrichment we measure in our two cores is due to local productivity or nutrient consumption elsewhere in the SAZ and the zonal transport of ^{15}N -enriched surface nitrate to the core sites. However, similarities between our two widely spaced records argue for a SAZ-wide phenomenon. Such a decrease in the Si-to-major nutrient uptake ratio might enhance the AZ-derived silicate excess, or at least would not consume it, allowing the excess to be passed on to low-latitude biota through newly formed SAMW.

[25] Thus the tentative picture that arises is intermediate between the two end-member scenarios for the “silicic acid leakage” hypothesis considered by Matsumoto *et al.* [2002b], one in which the silicate excess drives higher productivity in the SAZ (with a small change in the $\text{CaCO}_3/C_{\text{org}}$ of export production) and the other in which the silicate excess is allowed to change the Ca/C_{org} ratio of low-latitude export production. While there are data that indicate a higher opal flux in the Atlantic sector [Charles *et al.*, 1991], our data suggest an increase in SAZ nitrate consumption without a corresponding increase in opal flux. Thus it seems plausible that silicate consumption did not increase in step with nitrate consumption in the SAZ, which would work to increase in the $\text{SiO}_4^{4-}/\text{NO}_3^-$ ratio of the water supplied to the low-latitude thermocline.

[26] The extended 110 kyr record of diatom-bound $\delta^{15}\text{N}$ at the Pacific SAZ site E11-2 affords us the opportunity to compare the SAZ diatom-bound $\delta^{15}\text{N}$ record to both local and global records of climate change, including $\delta^{18}\text{O}$ of planktonic foraminifera at E11-2 and dust accumulation and atmospheric CO_2 concentration from Antarctic ice cores over most of the last glacial cycle (Figure 3). The diatom-bound $\delta^{15}\text{N}$ record shares the characteristic sawtooth shape of the general climate records. The gradual $\sim 4\%$ increase in diatom-bound $\delta^{15}\text{N}$ during the studied interval occurred during a period over which CO_2 decreased by half of its full amplitude of glacial-interglacial change. Although we do not have the complete cycle in the E11-2 diatom-bound $\delta^{15}\text{N}$ record, the lowest values at its base are similar to those during the early Holocene and, from the MD84-527 record,

we can infer that there is little systematic change during the Holocene. Thus it seems that increased glacial nutrient consumption corresponds to only the latter half of the full glacial decrease in atmospheric CO_2 content. The EPICA ice core record shows overall elevated dust content throughout the glacial interval considered, with prominent maxima around the LGM and MIS 4 [Delmonte *et al.*, 2004]. The diatom-bound $\delta^{15}\text{N}$ record shows its strongest maximum in nitrate consumption during the LGM, as one would expect if iron fertilization were controlling the degree of nutrient consumption. However, there is not a clear response during MIS 4; diatom-bound $\delta^{15}\text{N}$ is higher than during the early Holocene, but there is not a distinct peak associated with this period. Although Antarctic ice cores are probably not an ideal indicator of SAZ dust deposition, the lack of pervasive correlation encourages us to look to other possible influences on nutrient consumption in the SAZ surface. Given that iron, light, and silicate supply all have a potential influence on SAZ nitrate utilization, it is perhaps to be expected that we do not observe a simple link between diatom $\delta^{15}\text{N}$ and dust deposition alone. For example, the observed increase in nutrient consumption during MIS 3 might indicate enhanced light availability due to a more stratified surface layer associated with slightly warmer conditions.

4.4. Glacial-Interglacial CO_2 Change

[27] The SAZ represents the gateway between the high-latitude surface ocean, with its connection to the deep sea, and the warmer, temperate, subtropical and tropical surface ocean and thermocline. The westerly winds blowing between 30° and 60°S drive an overturning, with deep water rising into the Antarctic surface, flowing into the subantarctic, and then sinking into the shallow subsurface to ventilate the low-latitude thermocline. In the modern ocean, nutrients are constantly being lost from the lower latitudes by the rain of organic detritus into the abyss. These nutrients are resupplied to the upper ocean mostly from the new mid-depth waters that form in the SAZ [Sarmiento *et al.*, 2004]. Thus the nutrient supply to the subtropical and tropical surface ocean depends largely on the incomplete consumption of nutrients by algae in the subantarctic surface: If subantarctic nutrients are efficiently depleted, then there will be only a meager supply of nutrients downstream to the low-latitude thermocline and surface ocean. Thus nutrient drawdown in the glacial SAZ would have reduced atmospheric CO_2 by two related mechanisms. First, it would have sequestered additional CO_2 in the ocean interior by exporting organic matter into the subsurface. Second, assuming that the drop in low-latitude productivity associated with thermocline nutrient depletion translates to a decrease in low-latitude biogenic calcium carbonate production, it would have increased ocean alkalinity by causing a transient reduction in the burial rate of calcium carbonate [Matsumoto *et al.*, 2002b; Sigman *et al.*, 1998].

[28] We use a modified version of the carbon cycle and ocean productivity simulation (CYCLOPS) box model [Keir, 1988; Sigman *et al.*, 1998] to evaluate the importance of these two effects in the context of our SAZ data (see Appendix A for model details). If only the CO_2 sequestration is included in the model (i.e., the open system dynamics

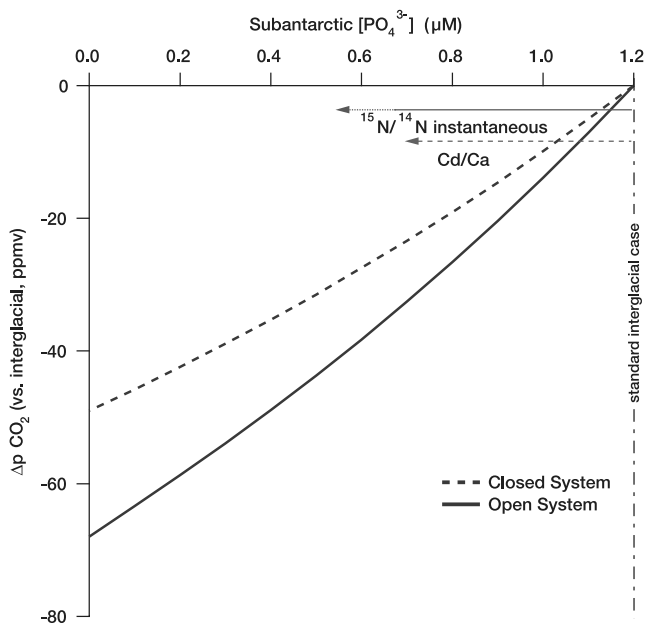


Figure 5. Response of atmospheric CO_2 in the carbon cycle and ocean productivity simulation (CYCLOPS) model [Keir, 1988; Sigman *et al.*, 1998, 2003] to the biological consumption of the major nutrients in the subantarctic, represented here by Phosphate. The model was modified with the addition of a surface subantarctic box located between the Antarctic and the low-latitude intermediate-depth boxes (see Appendix A for revised circulation). In the closed system experiments (dashed line), CaCO_3 rain is dissolved completely in the subsurface, and there is no river input of dissolved inorganic carbon (DIC) or alkalinity (ALK). The open system (solid line) includes river input of DIC and ALK and the marine burial of biogenic CaCO_3 , processes that change the whole ocean reservoir of DIC and ALK [Sigman *et al.*, 1998]. Proxy data estimates of the degree of glacial subantarctic nutrient drawdown are indicated with the arrows along the upper axis. The Cd/Ca data suggest a 35% decrease in concentration from modern subantarctic conditions (dashed arrow). The $^{15}\text{N}/^{14}\text{N}$ data, in the context of the “instantaneous” product equation of Rayleigh fractionation [Mariotti *et al.*, 1981], assuming an isotope effect of 5–8‰, yield a glacial Subantarctic nitrate concentration between 7.5 and 10 μM (or phosphate concentrations of 0.55 and 0.66 μM , respectively.) See color version of this figure in the HTML.

of CaCO_3 are excluded [Sigman *et al.*, 1998]), a complete drawdown of nutrients in the subantarctic would reduce atmospheric CO_2 by 47 ppm (Figure 5, dashed line), which is less than that caused by a comparable nutrient drawdown in the Antarctic [Sigman *et al.*, 1999a]. This is to be expected, given that SAMW formation ventilates the thermocline, which represents only a small fraction of the ocean interior and thus can hold relatively little excess CO_2 [Sigman and Haug, 2003].

[29] However, because subantarctic surface nutrient content determines the nutrient supply to the low-latitude ocean

[Sarmiento *et al.*, 2004], a subantarctic nutrient drawdown causes a sizable additional CO_2 decrease through its effect on whole ocean alkalinity (20 ppm for a complete nutrient drawdown; Figure 5, solid line). As SAZ nutrient utilization is increased, low-latitude productivity decreases in response to the reduction in thermocline nutrient supply, which reduces the flux of CaCO_3 out of the low-latitude surface ocean. Along with the increase in (CaCO_3 -free) SAZ export production, this causes a transient dissolution event in the deep sea, with deep ocean $[\text{CO}_3^{2-}]$ eventually being restored by the resulting buildup of whole ocean alkalinity (i.e., a transient excess in river input over seafloor burial), which also lowers atmospheric CO_2 [Broecker and Peng, 1987]. In addition, the permanent decrease in low-latitude CaCO_3 flux to the seafloor (proceeding from the standard interglacial case to complete SAZ nutrient consumption) requires a 700 m deepening of the steady state lysocline, which is also accomplished by an increase in ocean alkalinity [Sigman *et al.*, 1998]. A decrease in the $\text{CaCO}_3/\text{C}_{\text{org}}$ ratio of low-latitude export production would also be called for if there were indeed an increase in the $\text{SiO}_4^{4-}/\text{NO}_3^-$ ratio of the nutrient supply to the low latitudes (see above) [Brzezinski *et al.*, 2002; Matsumoto *et al.*, 2002b]. However, this is not addressed by our model experiment.

[30] In net, a 50 to 100% drawdown in subantarctic nutrients lowers atmospheric CO_2 by 39 to 67 ppm, respectively (Figure 5, solid line). The lower estimates of nutrient drawdown based on the diatom-bound $\delta^{15}\text{N}$ and Cd/Ca data suggest a 40 ppm change (Figure 5), approximately what one would estimate from comparison of the relative timing of the CO_2 decline and diatom-bound $\delta^{15}\text{N}$ increase from E11-2, assuming that this was the sole driver of the CO_2 decrease over this time interval (Figure 4). Aspects of the model tend to make this calculated CO_2 drawdown an upper bound in the context of box models (see Appendix A). Nevertheless, this degree of drawdown would significantly augment Antarctic mechanisms for reducing atmospheric CO_2 (e.g., Antarctic stratification [Francois *et al.*, 1997; Robinson *et al.*, 2004]), making a glacial drawdown of 80–100 ppm more readily achievable. More generally, the CO_2 effects of polar nutrient drawdown are currently debated [Archer *et al.*, 2003; Toggweiler *et al.*, 2003], so our understanding of the role of subantarctic nutrient drawdown in glacial/interglacial CO_2 change is likely to evolve.

4.5. Linkages to the Low Latitudes

[31] There is extensive evidence for thermocline-depth nutrient depletion during the last ice age, in the Atlantic [Marchitto *et al.*, 1998], the North Indian Ocean [Boyle, 1992; Boyle *et al.*, 1995; Kallel *et al.*, 1988], and the Pacific [Herguera *et al.*, 1992; Keigwin, 1998; Matsumoto *et al.*, 2002a]. In addition, proxy evidence suggests that export productivity within several important low-latitude upwelling systems was reduced during the last ice age [Ganeshram *et al.*, 1995; Keigwin and Jones, 1990; Kienast *et al.*, 2002; Pride *et al.*, 1999]. Finally, the three major regions of water column denitrification, the eastern tropical north Pacific, eastern tropical south Pacific, and the Arabian Sea, all record lowered rates of water column denitrification during glacial times [Altabet *et al.*, 1995, 2002; Ganeshram *et al.*,

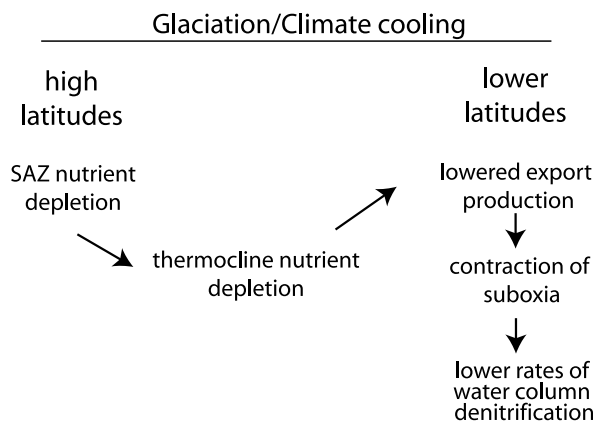


Figure 6. A simple schematic of high- to low-latitude linkages. A significant increase in nutrient drawdown in the glacial SAZ would have caused a drop in the supply of nutrients to the low-latitude thermocline, which may be related to (1) reductions in export production, (2) decreased subsurface O_2 consumption and, consequently, (3) lower rates of water column denitrification beneath the major low-latitude upwelling systems, as observed in multiple sedimentary archives [Altabet et al., 1995, 2002; Galbraith et al., 2004; Ganeshram et al., 1995, 2000; Pride et al., 1999].

2000; Galbraith et al., 2004; Ganeshram et al., 1995]. The global character of these regional records has not been adequately explained.

[32] Higher nutrient utilization in SAZ surface waters would have caused thermocline nutrient depletion in the lower latitudes by reducing the supply of nutrients introduced to the thermocline through Subantarctic Mode Water formation. This would reduce the overall fertility of the lower-latitude surface ocean, which, in turn, would cause a decline in the delivery of reduced C to the subsurface. With less C to be oxidized, the O_2 consumption rate in the thermocline would have been reduced, causing a net increase in intermediate depth $[O_2]$ (Figure 6).

[33] The coastal upwelling regions may have been particularly affected by these changes. The high nutrient content and suboxia in the subsurface of these regions is largely due to “nutrient trapping” [Toggweiler, 1995], the capacity for which is greatly reduced as the preformed nutrient content of thermocline water decreases [Sigman et al., 2003]. Thus a SAZ-driven decrease in thermocline nutrient content may explain the dramatic weakening in productivity, O_2 deficiency, and denitrification in coastal upwelling systems that is observed during the last glacial maximum (Figure 6) [Altabet et al., 1995, 2002; Galbraith et al., 2004; Ganeshram et al., 1995, 2000; Pride et al., 1999].

5. Conclusions

[34] The diatom-bound $\delta^{15}N$ records from the Indian and Pacific sectors of the subantarctic presented here show a coherent connection to glacial/interglacial climate change. While the absolute controls on diatom-bound $\delta^{15}N$ are

unknown and questions remain about the potential impact of equatorward migration of AZ conditions into the SAZ during glacial times, there is evidence suggesting the influence of such changes would be minimal at the studied sites. Thus the observed shift to higher $\delta^{15}N$ values during the glacial is interpreted as a signal of higher nitrate consumption within the SAZ.

[35] Given this interpretation of these first diatom-bound N isotope measurements from the SAZ, the proxies for nutrient status in this region, long taken as a point of confusion, are now aligned and thus make a compelling case for the hypothesis of greater nutrient consumption during the last ice age. Fe fertilization by atmospheric dust deposition is the simplest mechanism to explain the inferred increase in nutrient consumption, but changes in light conditions, possibly because of the addition of fresh water during seasonal ice melting, cannot be ruled out. Regardless of the cause, enhanced nutrient consumption would have worked to lower the concentration of atmospheric CO_2 . This enhanced degree of nutrient consumption would also have lowered the preformed nutrient content of the low-latitude thermocline, providing an explanation for the observation of coincident changes in water column denitrification in geographically disparate regions of the low-latitude ocean.

[36] The diatom-bound $\delta^{15}N$ records reported here suggest an important role for paleoceanographic reconstructions from the SAZ in understanding both high- and low-latitude biogeochemical cycles in the past [e.g., Sarmiento et al., 2004]. However, despite the apparent convergence of the different paleoceanographic proxies in indicating higher nitrate consumption in the glacial age SAZ, there are major uncertainties for each of these proxies, so their interpretation will remain tentative until more attention is given to ground truthing. A paleoceanographic approach to overcoming uncertainties might involve studying sediment records from sites that are more distant from the Southern Ocean fronts.

Appendix A

[37] We adapted the CYCLOPS ocean box model [Keir, 1988; Sigman et al., 1998, 2003] for simulations of Subantarctic/Polar Frontal Zone nutrient drawdown (Figure A1). In the model, this box is downstream of the Antarctic surface in the wind-driven overturning circulation and feeds water into the low-latitude intermediate box, intending to represent the formation of both Subantarctic Mode Water and Antarctic Intermediate Water. The addition of this box has no impact on the overall circulation in the model, with deep water formation in the North Atlantic ultimately feeding the upwelling in the Antarctic, which is then returned through intermediate water formation, some upwelling into the low-latitude surface, and the flow of both surface and intermediate water back to the North Atlantic deep water formation region.

[38] Phosphate is the only nutrient carried in the model. In the interglacial standard case, the $[PO_4^{3-}]$ of the Subantarctic/Polar Frontal Zone surface box is set to $1.2 \mu M$, taken from modern observations of this latitude band. Because this is lower than the prescribed $[PO_4^{3-}]$ of the Antarctic

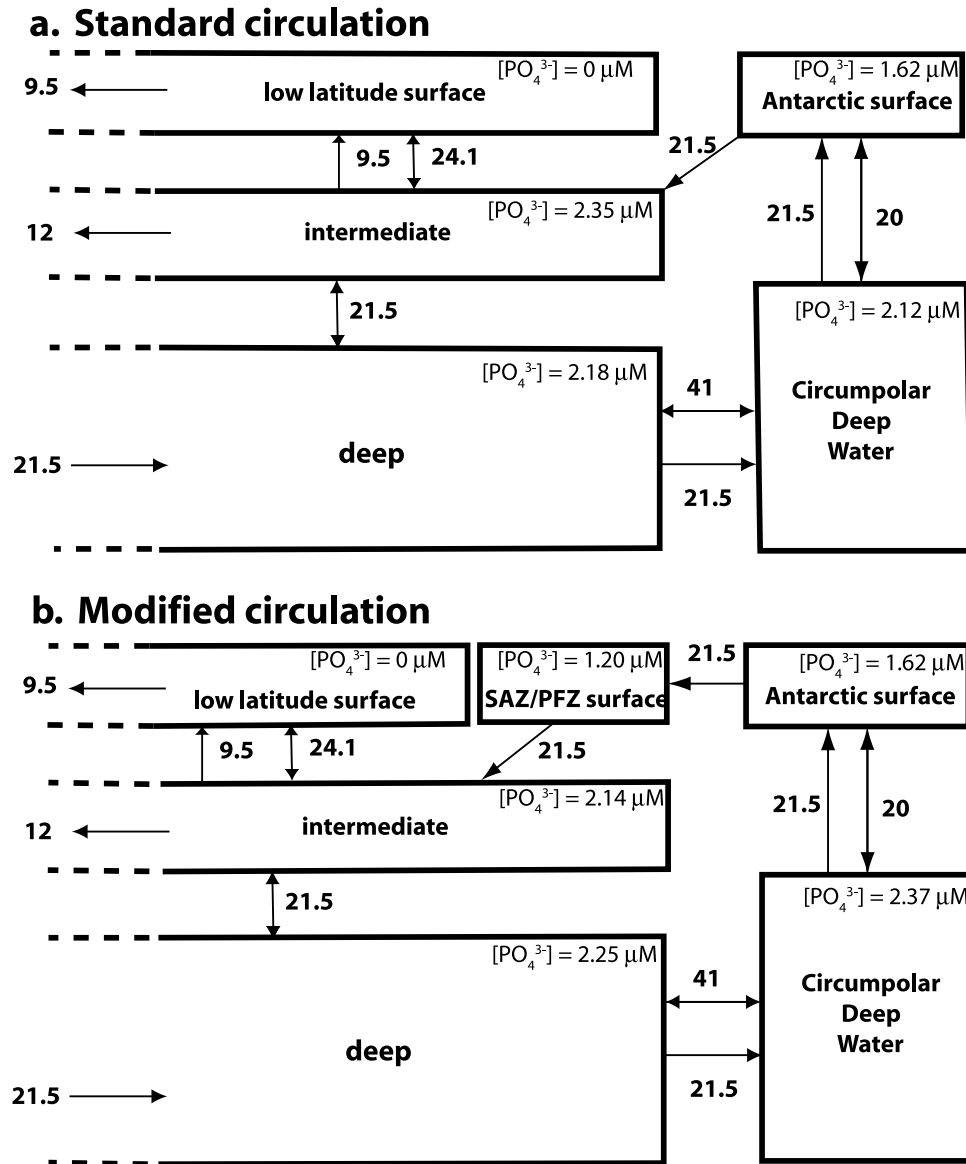


Figure A1. Summarized architecture of the geochemical box model used above, comparing the (a) previously published version of CYCLOPS [Keir, 1988] and (b) modified version used here. In the standard model, one large Southern Ocean (Antarctic) surface box supplies water and nutrients to the low-latitude thermocline and intermediate depth. In the modified version, Antarctic surface waters flow into a Subantarctic Zone/Polar Frontal Zone (SAZ/PFZ) box, with the mid-depth ventilation occurring in this box. Ocean basins are represented in this diagram as globally binned surface and intermediate and deep regimes. Fluxes are shown in sverdrups ($10^6 \text{ m}^3 \text{ s}^{-1}$). Single arrows denote advection, and double-ended arrows signify exchange. Phosphate concentration is prescribed for the surface boxes (through automatic adjustment of export production) and determined by the model for the subsurface boxes.

surface ($1.62 \mu\text{M}$), this model adaptation in itself causes a decrease in atmospheric CO_2 of roughly 25 ppm. Nevertheless, the additional CO_2 decrease observed in the SAZ/PFZ nutrient drawdown experiment (Figure 5) should give a fair representation of box model CO_2 sensitivities to this biogeochemical change. Like the Antarctic, the SAZ/PFZ export production includes organic carbon only, with no calcium carbonate flux. Also like the Antarctic, the SAZ/

PFZ export production is remineralized solely in Circumpolar Deep Water, based on the notion that this region sits at the polar margin of the thermocline. As with other aspects described below, these parameter choices lead to an upper limit estimate of the CO_2 effect from SAZ/PFZ nutrient drawdown. The details of the closed system and open system cases for calcium carbonate dynamics have been described previously [Sigman *et al.*, 1998]; the open system

case includes the published parameterization for the effect of sedimentary respiration on calcite undersaturation in sediment pore waters.

[39] This basic scheme neglects several aspects of the real Subantarctic Zone. First, the subantarctic surface exchanges water with the subtropics [McNeil et al., 2001; Speer et al., 2000]. Thus SAZ nutrient concentration cannot solely be described by drawdown from an Antarctic surface nutrient source. For the purposes of this study, which focuses on the more poleward SAZ (the region that is important in mode water formation [McCartney, 1977]), our simplification is defensible. Second, the Antarctic surface and its interface with the Polar Frontal Zone may contribute a significant amount of the water to Antarctic Intermediate Water formation, whereas the cores in this study are both north of the Subantarctic Front. We feel justified in having all waters fed from the box in which we carry out nutrient drawdown partially because a core from within the Polar Frontal Zone in the Indian sector appears to show the

same sense of isotopic change noted in our subantarctic cores (R. Robinson, unpublished data, 2004). Nevertheless, this also contributes to making our calculation an upper limit on the importance of our measured nutrient drawdown on atmospheric CO₂, at least in the context of box models. The more fundamental uncertainty involves the very different sensitivity of box models and ocean general circulation models to low- versus high-latitude carbon cycle changes and the debate regarding its cause [Archer et al., 2000; Matsumoto et al., 2002b; Toggweiler et al., 2003].

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