Reconciling down core anticorrelation of diatom carbon and nitrogen isotopic ratios from the Southern Ocean

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[1] Oceanic nutrient cycling in the Southern Ocean is supposed to have an important impact on glacial-interglacial atmospheric CO_2 changes and global climate. In order to characterize such nutrient cycling over the last two climatic cycles we investigated carbon and nitrogen isotopic ratios of diatom-bound organic matter ($\delta^{13}C_{diat}$ and $\delta^{15}N_{diat}$, respectively) in two cores retrieved form the Atlantic and Indian sectors of the Antarctic Ocean. The two cores show the same isotopic patterns. The $\delta^{13}C_{diat}$ values are depleted during glacial periods and enriched during interglacial periods, indicating lower productivity during cold times. The $\delta^{15}N_{diat}$ values are enriched during glacial periods and depleted during interglacial periods, arguing for greater nitrate utilization during cold times. Taken at face value, this apparent contradiction leads to opposite conclusions on the role of the Southern Ocean biological pump on the atmospheric CO_2 changes. However, the two sets of data can be reconciled by a "sea ice plus mixing rate scenario" that calls upon a balance between the effect of cutting off gas transfer at the ocean-atmosphere boundary and the effect of reducing vertical transport of nutrients through the pycnocline. *INDEX TERMS:* 4267 Oceanography: General: Paleoceanography; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; 4870 Oceanography: Biological and Chemical: Stable isotopes; *KEYWORDS:* Southern Ocean, paleoceanography, geochemistry, diatoms

1. Introduction

[2] Almost 15 years have passed by since the hypothesis that higher glacial levels of phytoplanktonic productivity in the Southern Ocean may have had a significant impact on lower glacial atmospheric CO_2 concentrations [*Sarmiento and Toggweiler*, 1984; *Knox and McElroy*, 1985; *Toggweiler and Sarmiento*, 1985; *Wenk and Siegenthaler*, 1985]. Such higher productivity may have been stimulated by greater inputs of dust-bearing iron [*Martin*, 1990] during glacial periods [*Petit et al.*, 1999]. Indeed, both incubation and large-scale ecosystem experiments demonstrate that iron fertilization promotes massive diatom blooms [*Martin and Fitzwater*, 1988; *Martin et al.*, 1994; *Coale et al.*, 1996]. However, studies of deep-sea sedimentary records from the Southern Ocean failed to demonstrate the expected increase in glacial productivity, with contradictory results according to the study area and the proxy used [*Charles and Fairbanks*, 1990; *Mortlock et al.*, 1991; *Anderson and Kumar*, 1995; *Kumar et al.*, 1995; *Singer and Shemesh*, 1995; *Bareille et al.*, 1998]. These discrepancies may be due to secondary processes such as opal dissolution and focusing that alter the surface signal. These secondary processes may also explain the observed decoupling between accumulation rates of biogenic opal and organic carbon [*Anderson et al.*, 1998; *Pondaven et al.*, 2000]. In order to overcome these problems, studies have been oriented to specific compound analysis such as the diatom-intrinsic organic matter. Because this organic matter is refractory to harsh acid attack [*Singer*, 1994; *Singer and Shemesh*, 1995; *Sigman et al.*, 1999], it has been postulated that it retains its original isotopic composition after diagenesis. Measurements of carbon and nitrogen isotopic ratios in diatom-bound organic matter have thus a great potential in characterizing the nutrient cycles in rich siliceous sediments. Unfortunately, time slice results (Holocene and Last Glacial Maximum) give a complex picture of the role of the high southern latitude biological pump on glacial-interglacial CO_2 changes. South of the modern Antarctic Polar Front, diatom carbon isotopes ($\delta^{13}C_{diat}$) argue for a possible glacial source of CO_2 [*Singer and Shemesh*, 1995; *Rosenthal et al.*, 2000], whereas the diatom nitrogen isotopes ($\delta^{15}N_{diat}$) argue for greater glacial nitrate utilization [*François et al.*, 1997]. Here we provide simultaneous down core records of $\delta^{13}C_{diat}$ and $\delta^{15}N_{diat}$ for the Atlantic and Indian sectors of the Antarctic Ocean that reflect nutrient cycling back to 240,000 years (240 ka). We then suggest that this apparent contradiction is due to changes in sea ice cover [*Stephens and Keeling*, 2000] and vertical mixing rates across the pycnocline [*Toggweiler*, 1999] that influenced the relative sizes of the nutrient pools.

2. Material and Methods

2.1. Stratigraphy

[3] Gravity core SO136-111 (56°40′S, 160°14′E, water depth of 3912 m) was retrieved from the Emerald Basin in the Indian sector south of the modern Antarctic Polar Front (Figure 1). Stratigraphy is based on bulk density and magnetic susceptibility (Figure 2) that clearly capture the glacial-interglacial cycles in which we are interested [*Shipboard Scientific Community*, 1998]. Wet bulk density and magnetic susceptibility are dependent on the relative composition of the sediments. The more detrital-bearing magnetite particles are present, the greater are density and magnetic signals. Close to the modern Antarctic Polar Front (APF), interglacial times are characterized by high biogenic silica burial and relatively low input of detrital sediment, leading to low wet bulk density and magnetic susceptibility values. On the opposite side, glacial times correspond to lower biogenic silica burial and greater detrital input (atmospheric dust and/or ice-rafted detritus), leading to high wet bulk density and magnetic susceptibility intervals. The bottom of core SO136-111 (9 m) extends back to marine isotopic stage 7.5 (~240 ka), and all glacial-interglacial cycles are clearly identified.

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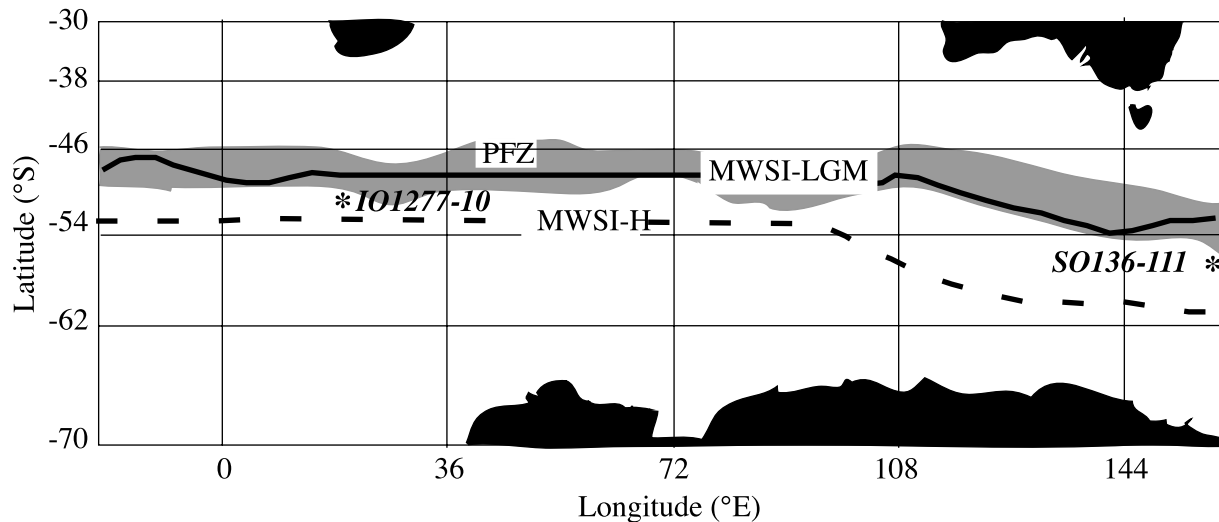
Figure 1. Core locations in relation to important Southern Ocean settings. PFZ, Polar Front Zone (from *Belkin and Gordon* [1996]), MWSI-H, maximum winter sea ice edge for the present time (from *Naval Oceanography Command Detachment* [1985]); MWSI-LGM, maximum winter sea ice edge for the Last Glacial Maximum (from *Crosta et al.* [1998a]).

[4] Gravity core IO1277-10 was retrieved at 52°02′S, 20°47′E, 2740 m depth in the Atlantic sector of the Southern Ocean. It is also located just south of the modern Antarctic Polar Front, thus representing the same oceanic regime (the permanent open ocean zone) as SO136-111 but for a different oceanic basin (Figure 1). Stratigraphy of core IO1277-10 is based on the relative abundance of *Eucampia antarctica*, which is a close proxy of $\delta^{18}O$ [*Burckle and Burak*, 1996]. Glacial periods are determined by high percentages of *E. antarctica*, while interglacial stages are represented by low percentages. Core IO1277-10 spans marine isotopic stages 1 and 2–3, with the Last Glacial Maximum (LGM) located at around 820 cm (Figure 3).

2.2. Isotope Analysis

[5] Diatom-bound organic matter was analyzed every 10 cm in core SO136-111 and every 20 cm in core IO1277-10 for carbon and nitrogen isotopic composition. The cleaning procedure to isolate diatom-bound organic matter follows the one described by *Singer and Shemesh* [1995]. We used stepwise physical washing and sieving in order to separate the diatom fraction from the bulk sediment. We then applied a perchloric/nitric oxidation to the diatom fraction <20 μm to remove the labile organic matter coating the diatom valves. The advantages of using the fraction <20 μm are that (1) it generally accounts for the largest amount of the whole diatom assemblage, (2) the glacial and interglacial assemblages are dominated by the same species *Fragilariopsis kerguelensis*, and (3) no radiolarians are present.

[6] Isotopic measurements of the acid-cleaned diatoms were performed on a Carlo Erba EA1110 elemental analyzer in line with a Finnigan MAT252 stable isotope ratio mass spectrometer. The $\delta^{13}C_{diat}$ and $\delta^{15}N_{diat}$ were simultaneously measured during sample combustion by peak jumping. At least two duplicates were measured for each sample. The mean standard deviations are 0.1‰ for the carbon isotopic ratio and 0.2‰ for the nitrogen isotopic ratio measurements. All results are reported in δ notation versus Peedee belemnite (PDB) for carbon (C) and versus air for nitrogen (N) and were continuously checked for internal consistency using several calibrated laboratory standards such as acetanilid, glycine, and cellulose.

[7] It has been recently suggested that $\delta^{15}N_{diat}$ values can be biased by nitric acid contamination during the cleaning procedure [*Sigman et al.*, 1999]. We, however, ruled out this possibility for the two following reasons. First, time digestion experiments of the diatom-bound organic matter in different acid solutions (HNO_3 + $HClO_4$ and $HCl + H_2O_2$) lead to $\delta^{15}N_{diat}$ values that are very similar. In both oxidation experiments the $\delta^{15}N_{diat}$ decreases by around 1‰ from the untreated value and reaches a plateau after 2 hours of oxidation that stills until the end of the experiment (Figure 4). The maximum discrepancy between the two sets of data is ~0.8‰ at 10 hours of oxidation. In the normal cleaning protocol we are using a 4 hour digestion time that corresponds to the plateau when $\delta^{15}N_{diat}$ values of the two experiments are identical. Second, such a contamination would occur at random and would generate $\delta^{15}N_{diat}$ records without any glacial-interglacial signal.

3. Results

3.1. Core SO136-111 (Indian Sector)

[8] The carbon isotopic ratio of sedimentary diatom-bound organic matter in core SO136-111 was 3–4‰ more depleted during glacial than during interglacial periods over the two last climatic cycles (Figure 5, thick line). Isotopic values vary from −25‰ during glacial times to −21‰ during interglacial times, in agreement with previous values on other cores from the Southern Ocean [*Shemesh et al.*, 1993; *Singer and Shemesh*, 1995; *Bentaleb and Fontugne*, 1998; *Rosenthal et al.*, 2000]. Maximum value during the Holocene is −23.5‰ with an ascending trend that shows that the upper top of the core may have been washed out during coring. The glacial-interglacial variations cannot be related to a diagenetic effect because the diatom-bound C and N are physically protected from early diagenesis by the frustule matrix [*Shemesh et al.*, 1993; *Sigman et al.*, 1999]. The $\delta^{13}C_{diat}$ record shows more variability during interglacial than during glacial periods in relation to the rapid succession of cold and warm events. Indeed, during isotopic stage 5, $\delta^{13}C_{diat}$ values are more depleted during cold interstadials than during warm substages but without reaching values as low as during real glacial stages (at 250, 300, and 350 cm). During isotopic stage 7, $\delta^{13}C_{diat}$ values decrease to
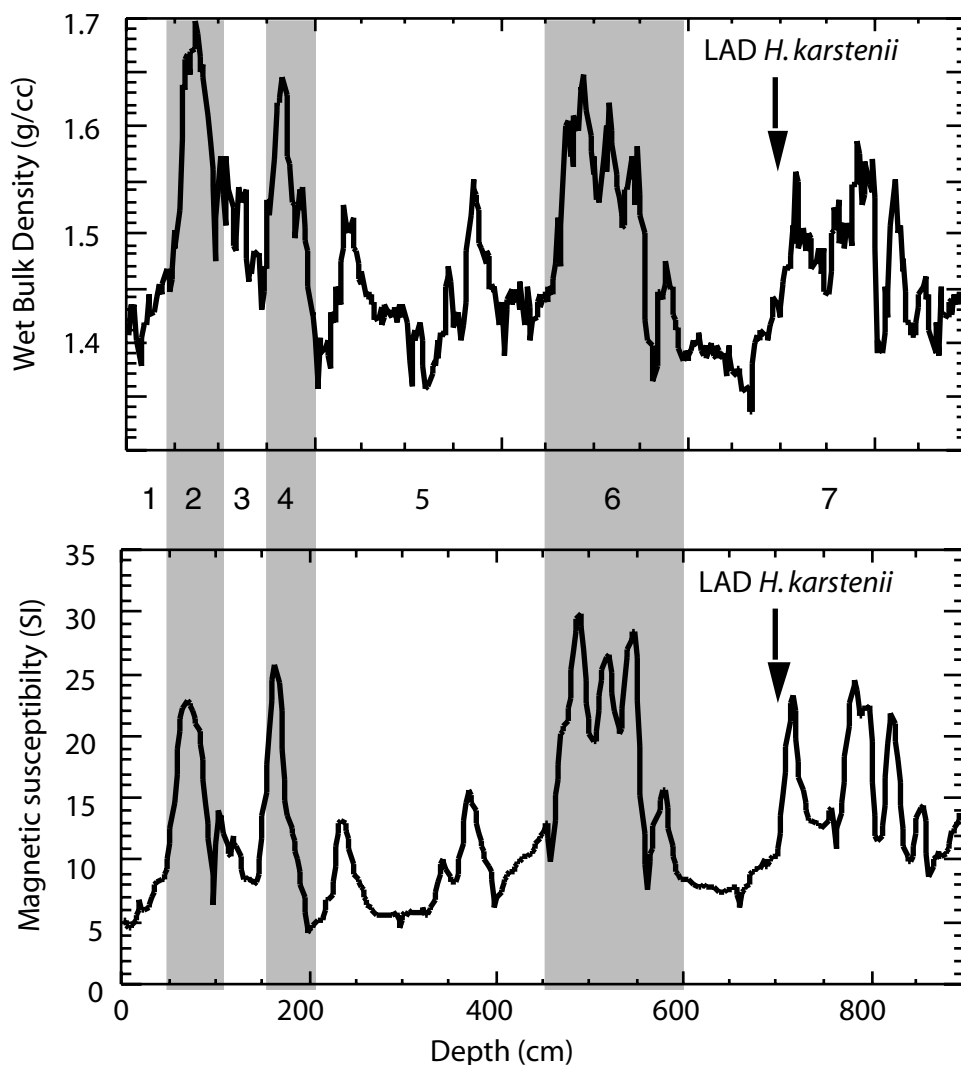
Figure 2. Stratigraphy of gravity core SO136-111 based on density (top plot) and magnetic susceptibility (bottom plot) measurements versus depth [*Shipboard Scientific Community*, 1998]. Shaded areas represent glacial isotopic stages.
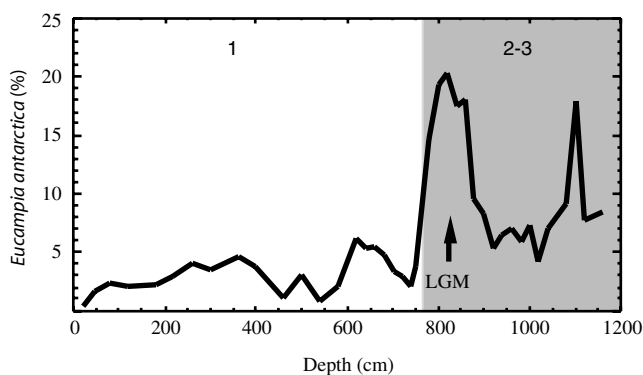

Figure 3. Stratigraphy of gravity core IO1277-10 based on the relative abundance of the diatom *Eucampia antarctica* versus depth. Shaded areas represent glacial isotopic stages. LGM, Last Glacial Maximum.

−24‰ at around 750 cm. At this depth, values are almost as depleted as during isotopic stages 2 and 6. This period of light values in the warm marine isotopic stage 7 represents the cold interstadial 7.4 defined by *Martinson et al.* [1987] and has been already identified by *Singer and Shemesh* [1995].

[9] The nitrogen isotopic ratio record of core SO136-111 is certainly the longest and most detailed record of $\delta^{15}N_{diat}$ currently in existence, extending back to isotopic stage 7.5. Values were 4‰ more enriched during glacial than during interglacial periods, being ~8‰ during cold periods and ~4‰ during maximum warm events (Figure 5, thin line). Our results indicate that this feature, already observed by *François et al.* [1997] and *Sigman et al.* [1999] in the Indian sector south of the Antarctic Ocean for the past 30 kyr, is a common phenomenon for the last two climatic cycles. Like the $\delta^{13}C_{diat}$ record, the $\delta^{15}N_{diat}$ record displays more variability during interglacial stages in relation with rapid climatic changes.

[10] The most striking feature in Figure 5 is that the two isotopic records are clearly anticorrelated over the two last climatic cycles, with enriched $\delta^{13}C_{diat}$ values synchronous with depleted $\delta^{15}N_{diat}$ values and depleted $\delta^{13}C_{diat}$ values in phase
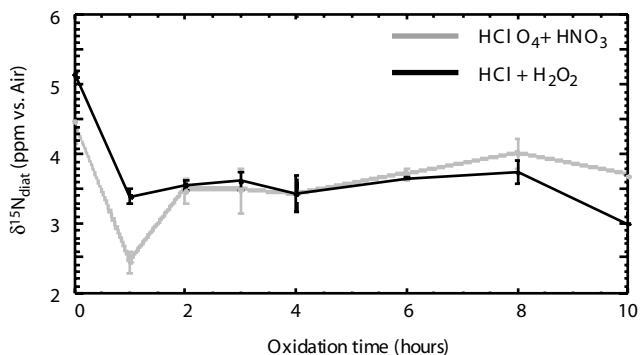
Figure 4. The effect of oxidation time on the nitrogen isotopic composition of diatom-bound organic matter using two different acid solutions. Standard deviations of the measurements are shown by the error bars, and solid lines connect the analysis means.

with enriched $\delta^{15}N_{diat}$ values. We calculated the correlation coefficient between the two records using the LinAge option of Analyseries software [*Paillard et al.*, 1993]. A high value of −0.82 indicates that the anticorrelation is not only encountered for the glacial-interglacial cycles but also even for the rapid climatic changes in all isotopic stages.

3.2. Core IO1277-10 (Atlantic Sector)

[11] The carbon isotopic ratio signal of core IO1277-10 follows the same pattern as the one observed in the SO136-111 core with depleted values during glacial periods and enriched values during interglacial periods (Figure 6, thick line). The amplitude is also around 3–4‰ from a value of −23.5‰ during the LGM to −19‰ during the Holocene. According to the nutrient proxies, it seems that the Holocene has been a relatively stable period in this region. Deeper than 900 cm, the $\delta^{13}C_{diat}$ exhibits a trend toward enriched values which certainly indicates that the bottom of the core reaches the marine isotopic stage 3.

[12] The nitrogen isotopic ratio record of core IO1277-10 is also similar to the SO136-111 core record. Values were around 6‰ during the LGM and 2.5‰ during the Holocene, indicating a 3.5‰ depletion of the $\delta^{15}N_{diat}$ over the last glacial-interglacial transition (Figure 6, thin line). In core IO1277-10 the $\delta^{15}N_{diat}$ and $\delta^{13}C_{diat}$ records are also remarkably anticorrelated with a correlation coefficient of −0.8.

[13] Carbon and nitrogen isotopic data of cores SO136-111 and IO1277-10 are electronically available at the NOAA-NGDC Paleoclimate Database.[1]

4. Discussion

[14] The difference in $\delta^{13}C_{diat}$ diatom-bound organic matter between glacial and interglacial periods ($\Delta_{G-IG}{}^{13}C_{diat}$) in both cores is about −4‰ (Figures 5 and 6, thick lines) and is in agreement with results from the western Atlantic sector of the Antarctic Ocean [*Rosenthal et al.*, 2000]. It means that this difference is representative for the whole region located between the sea ice edge and the APF, the so-called permanent open ocean zone [*Tréguer and Jacques*, 1992]. Several factors can account for these variations. *Rau et al.* [1989, 1992], *Jasper and Hayes* [1990], and *Bentaleb and Fontugne* [1998] have shown that photosynthetic

carbon demand, and hence primary production, and $[CO_{2(aq)}]$ are two essential factors that determine the $\delta^{13}C_{diat}$ of the primary photosynthetic organic matter. Other factors such as diatom growth rate, carbon source, and metabolic pathway [*Degens et al.*, 1968; *Macko et al.*, 1987; *Hinga et al.*, 1994] and diatom shape [*Popp et al.*, 1998] can also influence the isotopic composition of the organic matter. A recent study explored the range of possible variations in $[CO_{2(aq)}]$, growth rate, and diatom cell geometry under Antarctic surface water conditions [*Rosenthal et al.*, 2000]. They concluded a high sensitivity of carbon isotope fractionation to all three parameters. Here we try to decouple the effect of each parameter on the observed $\Delta_{G-IG}{}^{13}C_{diat}$.

[15] Glacial and interglacial diatom assemblages of cores SO136-111 and IO1277-10 are dominated by two open ocean species, *Fragilariopsis kerguelensis* and *Thalassiosira lentiginosa*, which represent >80% of the biogenic flora in the <20 μm fraction. It is therefore highly improbable that the average population's cell geometry has dominated the glacial-interglacial variations.

[16] If we now hypothesize that the glacial atmosphere was in equilibrium with the surface waters of the Southern Ocean, it is possible to separate the effects of $[CO_{2(aq)}]$ and carbon demand on the total $\Delta_{G-IG}{}^{13}C_{diat}$. Assuming a CO_2 atmospheric concentration of 190 ppm and a surface water cooling of 2°–3°C [*Pichon et al.*, 1992], *Rosenthal et al.* [2000] estimate a glacial ambient $[CO_{2(aq)}]$ equilibrium concentration of 11.7 μmol kg^{-1} of seawater in the Indo-Pacific sector of the Southern Ocean. Introducing this value in the equation developed by *Bentaleb and Fontugne* [1998] leads to an expected $\delta^{13}C_{org}$ value of −21.5‰ at equilibrium during glacial periods (at constant carbon demand). The measured $\delta^{13}C_{diat}$ values in core SO136–111 during glacial and interglacial periods are −24.5‰ and −20.5‰, respectively. The measured $\Delta_{G-IG}{}^{13}C_{diat}$ is therefore −4‰, from which 3‰ are due to a decrease in carbon demand and hence surface water productivity, and only 1‰ is attributed to the change in atmospheric CO_2. The same conclusion can be drawn from the core IO12770-10, with a $[CO_{2(aq)}]$ equilibrium concentration of 11.1 μmol kg^{-1} of seawater [*Rosenthal et al.*, 2000], leading to an expected $\delta^{13}C_{diat}$ equilibrium value of −21‰ during glacial periods, while the measured glacial $\delta^{13}C_{diat}$ value is −23.5‰. We reckon that the surface waters of the Southern Ocean may not have been regionally in equilibrium with the atmosphere [*Bentaleb and Fontugne*, 1998; *Rosenthal et al.*, 2000]. However, as a whole, the Southern Ocean is in equilibrium with the atmosphere [*Poisson et al.*, 1993]. Therefore the glacial state of chemical equilibrium between the ocean and the atmosphere may have played a secondary role in comparison of variations in primary production. We consider that $\delta^{13}C_{diat}$ signal in both cores mainly represents variations in phytoplankton carbon demand, coupled with variations in diatom growth rate. Indeed, a reduction of diatom growth rate would have emphasized the glacial depletion of Antarctic diatom $\delta^{13}C_{diat}$ due to lower carbon demand and greater isotopic fractionation. This is confirmed by independent studies showing that an important feature of the Southern Ocean on glacial-interglacial timescale is the northward shift of the "diatom ooze belt" [*Burckle*, 1984; *Bareille et al.*, 1998]. Our core sites, which are today under high surface water productivity, were under low surface water productivity during the last glacial period [*Charles et al.*, 1991; *Mortlock et al.*, 1991; *Kumar et al.*, 1993; *Anderson et al.*, 1998; *Bareille et al.*, 1998; *De la Rocha et al.*, 1998]. This indicates the predominant role of the primary production on the carbon isotopic ratio in diatom organic matter in this region over glacial to interglacial cycles.

[17] The $\delta^{15}N_{diat}$ record of core SO136-111 extends our knowledge of past nutrient supply to Antarctic surface waters and phytoplankton back to isotopic stage 7.5, at around 240 ka. The $\Delta_{G-IG}{}^{15}N_{diat}$ is around 4–5‰ between full glacial and interglacial conditions over the two last climatic cycles (Figure 5, thin line).
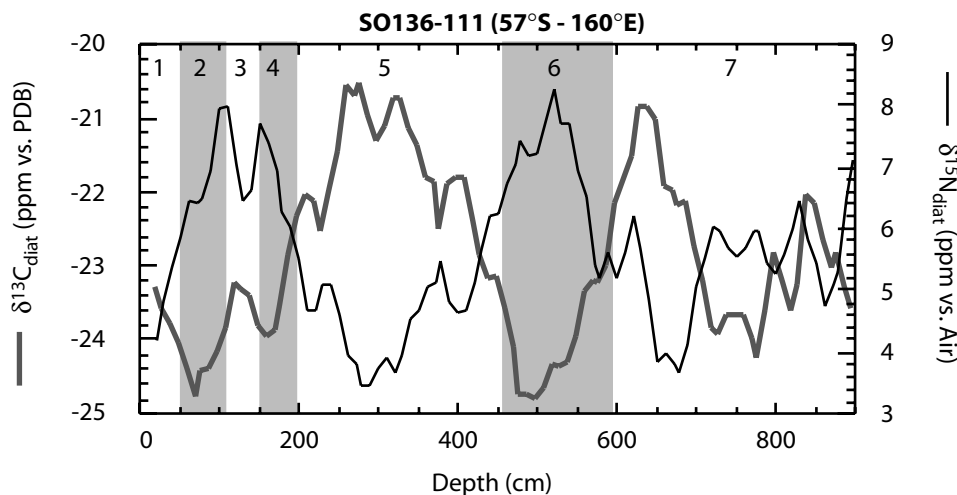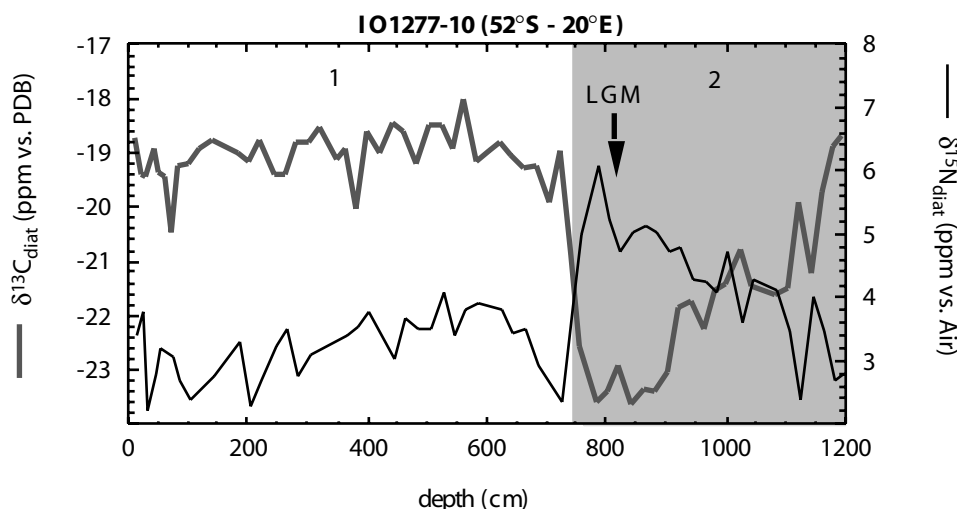
Figure 5. Records of carbon (thick line) and nitrogen (thin line) isotope records versus depth in core SO136-111. Data have been smoothed with a three-point running average. Shaded areas represent glacial isotopic stages.

François et al. [1992, 1997] related enriched values during the LGM relative to the Holocene to a greater utilization of surface nitrate by phytoplankton. Our record indicates that this feature has been valid for all glacial periods of the last 240,000 years. A greater NO_3^- relative utilization and accumulation by phytoplankton coupled with a lower productivity argue for a smaller pool of nutrients in the Antarctic surface waters during glacial periods. The smaller pool of nutrients has been attributed to increased surface waters stratification [*François et al.*, 1997; *Sigman and Boyle*, 2000]. Stratification is associated with a more vigorous sea ice cycle [*Crosta et al.*, 1998b] and episodic iceberg melting [*Labeyrie et al.*, 1986; *Shemesh et al.*, 1994, A. Shemesh et al., Comparison between records of Southern Ocean sediments and polar ice CO_2 during the last glacial-interglacial transition, submitted to *Paleoceanography*, 2001] that lowered the supply rates to the photic layer.
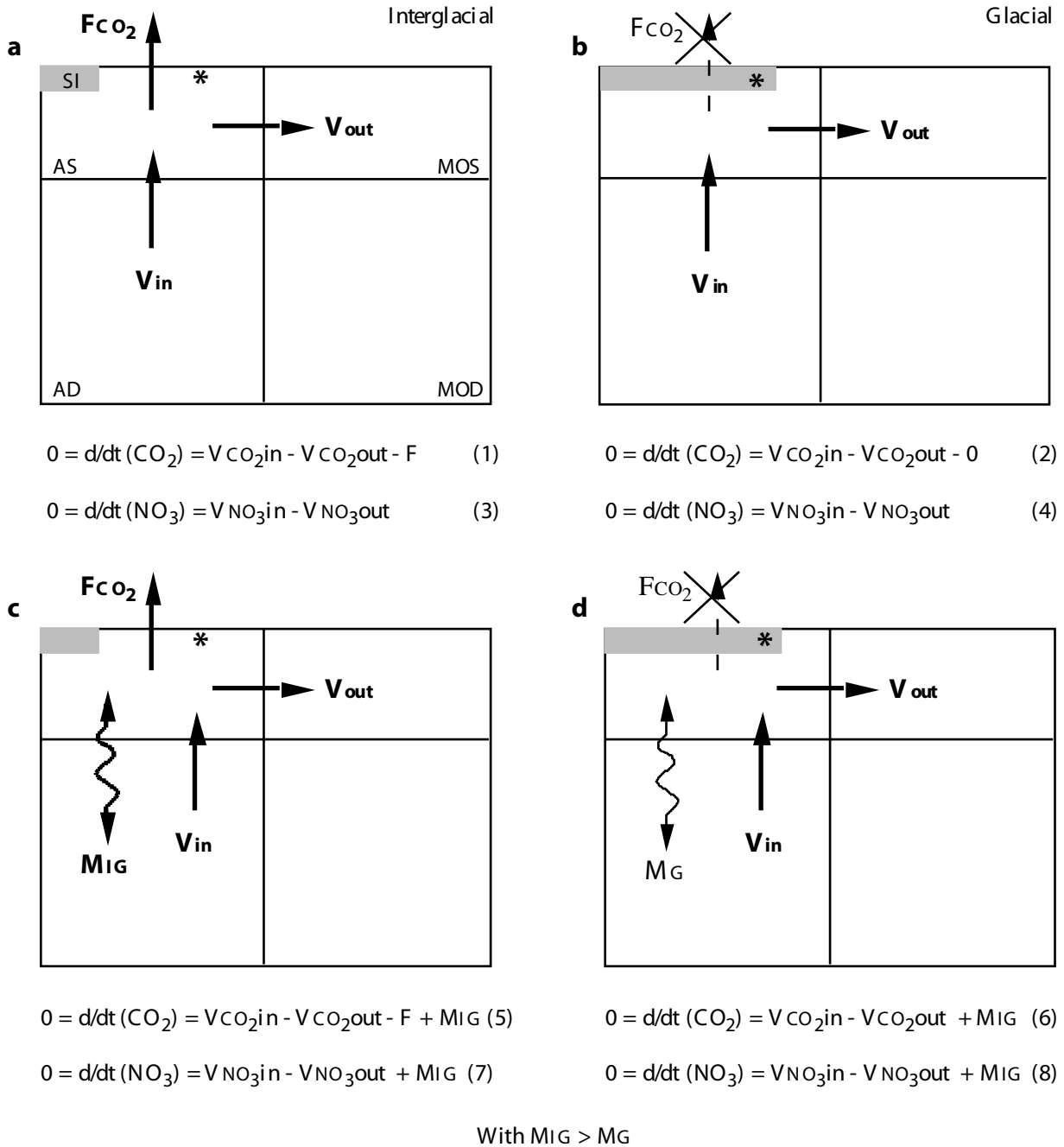
[18] As noted in section 3, the most striking feature in both cores is that carbon and nitrogen isotopic ratio records vary inversely. Taken at face value, these observations lead to different conclusions about the role of the Southern Ocean biological pump as an influence on atmospheric CO_2 changes. Depleted $\delta^{13}C_{diat}$ values

during glacial times argue for lower carbon demand south of the modern Polar Front, while enriched $\delta^{15}N_{diat}$ values indicate higher nitrate utilization. However, a qualitative scenario that combines changes in sea ice cover [*Stephens and Keeling*, 2000] and vertical mixing rates [*Toggweiler*, 1999] allows us to reconcile the glacial data for the permanent open ocean zone.

[19] Today, the incoming flux of CO_2 to the Antarctic surface layer (VCO_2in) is physically balanced by the northward flux leaving the surface layer (VCO_2out) and the degassing flux to the atmosphere (FCO_2), (Figure 7a, (1)). During glacial periods, sea ice was greatly expanded and was covering both core sites during ~2 months per year [*Crosta et al.*, 1998a]. Sea ice is known to act as an insulator at the ocean-atmosphere interface, hence blocking gas transfer to the atmosphere. The glacial FCO_2 was therefore reduced (Figure 7b, (2)), leading to increase the CO_2 concentrations under the sea ice and in the surrounding waters [*Stephens and Keeling*, 2000]. Such CO_2-enriched water masses were transported northward out of the polar box where they could eventually equilibrate with the atmosphere by releasing their excess CO_2. This scenario implies that diatoms were growing in

Figure 6. Records of carbon (thick line) and nitrogen (thin line) isotope records versus depth in core IO1277-10. Data have been smoothed with a three-point running average. Shaded areas represent glacial isotopic stages.

$$0 = d/dt\,(CO_2) = V_{CO_2}in - V_{CO_2}out - F \quad (1)$$

$$0 = d/dt\,(NO_3) = V_{NO_3}in - V_{NO_3}out \quad (3)$$

$$0 = d/dt\,(CO_2) = V_{CO_2}in - V_{CO_2}out - 0 \quad (2)$$

$$0 = d/dt\,(NO_3) = V_{NO_3}in - V_{NO_3}out \quad (4)$$

$$0 = d/dt\,(CO_2) = V_{CO_2}in - V_{CO_2}out - F + M_{IG} \quad (5)$$

$$0 = d/dt\,(NO_3) = V_{NO_3}in - V_{NO_3}out + M_{IG} \quad (7)$$

$$0 = d/dt\,(CO_2) = V_{CO_2}in - V_{CO_2}out + M_{IG} \quad (6)$$

$$0 = d/dt\,(NO_3) = V_{NO_3}in - V_{NO_3}out + M_{IG} \quad (8)$$

With $M_{IG} > M_G$

Figure 7. Conceptual models to explain the apparent contradiction between down core records of carbon and nitrogen isotope ratios. Sea ice scenario (Figures 7a and 7b), and sea ice plus mixing rate scenario (Figures 7c and 7d) for interglacial periods (Figures 7a and 7c) and glacial periods (Figures 7b and 7d). SI, sea ice; AS, Antarctic surface box; MOS, mean ocean surface box; AD, Antarctic deep box; MOD, mean ocean deep box; Vin, incoming flux of nutrient by permanent upwelling; M, incoming flux of nutrient by mixing processes through the pycnocline for the interglacial (M_{IG}) and the glacial (M_G) periods; Vout, outgoing flux of nutrient from the Antarctic surface box by northward transport; FCO_2, degassing flux of CO_2 at the ocean-atmosphere interface. The asterisk represents the position of the cores relative to the sea ice. Equations represent the mass balance of the nutrients in the Antarctic surface box.

CO_2-enriched surface waters. When coupled to lower glacial productivity, this scenario can explain the glacial $\delta^{13}C_{diat}$ depleted values relative to interglacial values. We then apply the same scenario in order to explain the observed $\delta^{15}N_{diat}$ down core records. Today, the incoming flux of nitrate to the Antarctic surface

layer (VNO_3in) is only balanced by the lateral outgoing flux (VNO_3out), (Figure 7a, (3)). Unlike CO_9, the loss of nitrate to the atmosphere is negligible. The greater sea ice extent during glacial periods had no effect on nitrate concentrations in subsurface waters. It means that diatoms were then growing on the same pool

of nitrate during glacial than interglacial periods (Figure 7b, (4)). When coupled to lower glacial productivity, this scenario should lead to glacial $\delta^{15}N_{diat}$ depleted values relative to interglacial values, which is not observed in the records. Hence the conclusions that we can draw using a "sea ice scenario" are in agreement with the observed $\delta^{13}C_{diat}$ down core records but at odds with the measured $\delta^{15}N_{diat}$ down core records.

[20] To explain the down core anticorrelation of carbon and nitrogen isotope ratios, we added a new parameter to the sea ice scenario, i.e., the vertical mixing rate between deep and surface Antarctic waters [*Toggweiler*, 1999]. In this scenario the present incoming flux of CO_2 to the Antarctic surface box is the sum of the upwelling component (VCO_2in) and a water-mixing component (MCO_2IG). It is balanced, like in the previous scenario, by the northward outgoing flux (VCO_2out) and the degassing flux (FCO_2), (Figure 7c, (5)). During glacial periods the FCO_2 is shut down by the larger sea ice extent, and the mixing rate is reduced because of greater water column stratification (Figure 7d, (6)). Carbon dioxide was accumulating in surface waters as long as the enrichment because cutting off the degassing flux exceeded the depletion caused by reducing the vertical mixing. In this case, diatoms were growing in glacial CO_2-enriched waters that may explain, when coupled to lower productivity, the observed glacial $\delta^{13}C_{diat}$ depleted values relative to interglacial values. The nitrate flux to the Antarctic surface waters (VNO_3in + MNO_3IG) is today balanced by the northward outgoing flux (Figure 7c, (7)). The difference during glacial times lays in a weaker mixing rate (MNO_3G < MNO_3IG) that reduced the nitrate pool in the surface layer (Figure 7d, (8)). A smaller and less renewed pool of nitrate, even coupled to lower productivity, may yield to glacial $\delta^{15}N_{diat}$ enriched values relative to interglacial values. The "sea ice + mixing rate scenario" is therefore in agreement with our results and can reconcile the down core anticorrelation of carbon and nitrogen isotope ratios south of the Antarctic Polar Front. When combined, a greater sea ice extent and a slower vertical mixing rate may also explain an important part of the atmospheric CO_2 reduction during glacial periods even if the productivity in Antarctic surface waters was lower. It is now important to document glacial-interglacial variations in carbon and nitrogen isotopic records in the Subantarctic Zone because it is there that the biological productivity has greatly increased during glacial times. Reconstruction of the nutrient cycling in this key region will allow us to test our scenario and to better understand the role of the Southern Ocean in atmospheric CO_2 variations.

5. Conclusions

[21] Carbon and nitrogen isotope measurements have been performed on an organic matter protected by the diatom silica matrix and therefore free of early diagenetic alteration. Down core records in two cores from the Atlantic and Indian sectors of the Antarctic Ocean are identical, indicating that the surface waters in the different Antarctic basins have evolved similarly on glacial-interglacial cycles. The $\delta^{13}C_{org}$ values were depleted during all glacial periods of the two last climatic cycles in comparison to interglacial times, while $\delta^{15}N_{org}$ values were enriched during glacial times relative to interglacial ones. These patterns are consistent with previous studies [*Singer and Shemesh*, 1995; *François et al.*, 1997; *Rosenthal et al.*, 2000] and are here presented for the first time on the same cores, extending our knowledge of nutrient cycling over the last 240 kyr. The apparent contradiction between $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ signals can be explained by a "sea ice plus mixing rate scenario" based on recent modeling studies [*Toggweiler*, 1999; *Stephens and Keeling*, 2000]. The scenario calls upon a balance between the effect of cutting off gas transfer at the ocean-atmosphere interface due to greater sea ice extent and the effect of reducing nutrient vertical transport through the pycnocline in relation to water column stratification and subsequent weaker mixing rate.

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