Southern Ocean control on the extent of denitrification in the southeast Pacific over the last 70 ka

Rebecca S. Robinsona,*, Alan Mixb, Philippe Martinezc

aPrinceton Environmental Institute and Department of Geosciences, Princeton University, Princeton, NJ, USA
bCollege of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR, USA
cDépartement de Géologie et Océanographie, Université Bordeaux I, UMR CNRS 5805 EPOC, avenue des facultés, 33405 Talence cedex, France

Received 18 October 2005; received in revised form 24 July 2006; accepted 2 August 2006

Abstract

Temporal changes in oceanic denitrification, the bacterial reduction of nitrate under suboxic conditions, highlight the potential importance of N inventory changes and the production of N2O on the climate system. At the same time, the cause of the globally observed variation in denitrification remains unclear. High-resolution benthic foraminiferal oxygen isotope and bulk sediment nitrogen isotope records from ODP Site 1234 on the Chile Margin record integrated denitrification changes within the Peru–Chile Upwelling system over the last ~70 ka. Denitrification changes in the southeast Pacific are coherent with Antarctic climate changes recorded by the Byrd ice core δ18O record, and lead northern hemisphere climate events. The southern-hemisphere character of the Chile margin δ15N record suggests that episodes of reduced denitrification in the SE Pacific represent times when more oxygen was supplied as the result of changes in the ventilation and preformed nutrient content of Subantarctic Mode Water (SAMW), which forms in the Subantarctic zone of the Southern Ocean and feeds into the low-latitude thermocline.

Temporal changes in the global inventory of fixed N caused by denitrification could generate changes in the strength of the biological pump large enough to contribute significantly to the glacial–interglacial variations in atmospheric CO2 (Knox and McElroy, 1984; Ganeshram et al., 1995, 2000; Petit et al., 1999; Altabet et al., 2002). N2O, another by-product of denitrification, is also a powerful greenhouse gas and large-scale changes in its production rate could potentially impact global climate. At present, the most important oceanic regions for water column denitrification are in the Eastern Tropical North and South Pacific (ETNP and ETSP, respectively) and the Arabian Sea (AS). Water column suboxia in these regions is the combined result of advection of oxygen-poor subsurface water and large-scale upwelling, which fuels the significant export of organics that further consume subsurface O2 upon remineralization.

Denitrification imparts an isotopic signature upon the standing nitrate pool. As nitrate is consumed during denitrification, the residual NO3 pool becomes significantly enriched in 15N, and the high δ15N signature (δ15N = (15N/14N_{sample}/15N/14N_{reference}−1) where the

1. Introduction

1.1. Changes in oceanic nitrate inventory

Bioavailable, or fixed nitrogen, is essential to life and is thought to be a limiting nutrient for productivity in the oceans. The primary sources of nutrient-N, dominantly nitrate (NO3), to oceans are riverine input, atmospheric deposition, and nitrogen fixation. The largest sink, denitrification occurs in suboxic (<5μM O2) sediment and water columns where NO3, rather than O2, is utilized as the primary electron acceptor for the oxidation of organic matter. Denitrification within shallow suboxic sediments is responsible for approximately 50–80% of the total nitrate removal from the ocean, with the remainder consumed in suboxic water columns (Brandes and Devol, 2002; Deutsch et al., 2004).
 universal reference is N₂ in air) of the subsurface denitrification zone is transmitted to the surface ocean through upwelling. In the euphotic zone, the ¹⁵N-enriched NO₃⁻ is assimilated by phytoplankton and a portion of this organic matter is subsequently delivered to the seafloor in the sinking organic matter. The generally high sedimentation rates on these organic-rich margins result in excellent preservation of the isotopic signal in the bulk sediment (Altabet et al., 1999b; Pride et al., 1999; Kienast et al., 2002).

Downcore records of sedimentary δ¹⁵N from locations proximal to the water column denitrification regions of the Arabian Sea, the ETNP, and the Peru margin show a generally consistent pattern of lower δ¹⁵N during glacial and northern hemisphere (NH) stadial times and higher δ¹⁵N during interglacial and NH interstadials over the last 50–150 ka. These δ¹⁵N changes have been interpreted as the result of significant variation in the extent of water column denitrification (Altabet et al., 1995; Ganeshram et al., 1999; Kienast et al., 2002). It appears that there has been a roughly synchronous, global variation in denitrification, where the loss of nitrate is least during glacial/cool periods and greatest during interglacial/warm episodes (Galbraith et al., 2004). A problem in interpreting the δ¹⁵N changes in these geographically disparate records as synchronous reflects the difficulty of dating sediments in which respiratory dissolution of carbonates hampers the construction of precise age models based on foraminiferal radiocarbon ages and oxygen isotope stratigraphies. This problem is particularly acute on the Peru margin. More recent work on Termination 1 in southern-hemisphere (SH) sediment cores from Peru and Chile suggest that denitrification changes in the southeast Pacific precede those from NH records (Higginson et al., 2003; Higginson and Altabet, 2004; De Pol-Holz et al., 2006; Higginson et al., in prep.).

Assuming approximate global synchrony of δ¹⁵N variations, Galbraith et al. (2004) suggested that physically driven changes potentially associated with glacial cooling, i.e. lower temperatures and increased wind speeds, could increase the oxygen supply to the thermocline enough to diminish the extent of suboxia in regions of denitrification. Alternatively, an increase in subsurface oxygen content could be achieved by reduced export production (in response to reduced upwelling rates, micronutrient depletion, or other causes), which would in turn reduce oxygen demand associated with subsurface oxidation of organic matter (Altabet et al., 1995, 2002; Ganeshram et al., 1995; Robinson et al., 2005); however, reduced denitrification would potentially serve as a negative feedback mechanism, over time increasing nutrient supplies that drive production.

Monsoon-related fluctuations in the intensity of upwelling and export productivity have been implicated in the generation of water column denitrification variability in the Arabian Sea. This inference was based upon covariance of chlorine as a measure of export, and δ¹⁵N (Altabet et al., 2002). However, a similar pattern of change in sedimentary δ¹⁵N is present in records from the Mexican and California margins, but δ¹⁵N does not vary in phase with inferred changes in export productivity. In this case, the export of organics and thus changes in local subsurface oxygen demand cannot be implicated as the cause of changing denitrification rates (Kienast et al., 2002; Hendy et al., 2004). In this region the delivery of oxygen to the subsurface of the ETNP via the equatorial undercurrent (EUC) is hypothesized as the dominant control on subsurface oxygen concentration and the regional extent of denitrification (Kienast et al., 2002). Because the EUC feeds both the northward and southward flowing poleward undercurrents, this hypothesis predicts a temporal pattern of denitrification that is hemispherically synchronous around the equator (Tsuchiya and Talley, 1998; Kienast et al., 2002). Here we present new data on δ¹⁵N with firm stratigraphic constraints that provide a robust comparison between the ETNP and the ETSP, as a test of the hypothesis that variations in the EUC drives changes in denitrification throughout the eastern Pacific Ocean.

1.2. Southeast Pacific

The Peru–Chile Current originates in the subpolar convergence and flows northward along the west coast of South America (Fig. 1a). This region supports one of the most productive eastern boundary current upwelling systems on Earth with an exceptionally intense oxygen minimum zone (OMZ) off Peru (Codispoti and Packard, 1980; Lipschutz et al., 1990). The region of active water column denitrification, lies around 7–20°S within the core of the OMZ in the SE Pacific (Fig. 1b).

The Peru–Chile (or Guenther) Undercurrent (PCU) flows poleward beneath the surface current between 100 and 300 m depth from its origin at the equator through the Peru upwelling region to as far south as 48°S (Wooster and Gilmartin, 1961; Silva and Neshyba, 1979; Lukas, 1986; Strub et al., 1998). The PCU originates in the region of water column denitrification and as a result carries oxygen-poor, ¹⁵N-enriched NO₃⁻ bearing water to the south along the margin (Liu, 1979). Upwelling delivers the ¹⁵N-enriched NO₃⁻ to the surface for assimilation by phytoplankton and delivery to the seafloor through organic matter export.

Paleoceanographic records from the Peru upwelling system are scarce, partially due to the difficulties in dating the organic carbon-rich, carbonate-poor materials. Because the PCU transports subsurface waters from the OMZ off Peru southward, the Chile margin represents an ideal location for studying integrated denitrification in the SE Pacific. Along the Chile margin to the north of the Subtropical Front (~40°S), NO₃⁻ is roughly completely consumed on an annual basis such that the sinking particulate N bears the isotopic signature of the source NO₃⁻ (Figs. 1a and 2). The isotopic signature of denitrification is apparent in surface sediment samples along the
margin; there is a trend of decreasing $\delta^{15}$N away from the region of active denitrification (Fig. 2). This scenario is analogous to the California Undercurrent system where the ETNP denitrification signal is robustly and synchronously recorded outside the region of active water column denitrification off California and perhaps as far north as Oregon (Liu and Kaplan, 1989; Emmer and Thunell, 2000; Kienast et al., 2002; Hendy et al., 2004).

ODP Site 1234 from the Chile Margin ($36^\circ 13.15^\prime$S, $73^\circ 40.90^\prime$W, 1015 m water depth) provides both a high-resolution $\delta^{15}$N record, which we interpret in terms of variation in regional denitrification, and a $^{14}$C-dated a benthic foraminiferal oxygen isotope stratigraphy from the southeast Pacific (Fig. 1). We compare the eastern Pacific $\delta^{15}$N data to the Byrd and GISP2 ice core $\delta^{18}$O records of climate change on Antarctica and Greenland, using the synchronized ice-core chronology of Blunier and Brook (2001). A record of nutrient utilization from the central Pacific Subantarctic zone (Robinson et al., 2005) helps to constrain the bio-physical controls on the preformed oxygen and nutrient supply to the eastern Pacific. Finally, we examine the inter-hemispheric differences in timing of $\delta^{15}$N variations in Site 1234 from the SE Pacific with its counterpart from the NE Pacific ($34^\circ$N, ODP Site 1017E, Fig. 1b; (Hendy et al., 2004)) to specifically address the hypothesized role of the EUC in driving denitrification changes in both hemispheres (Kienast et al., 2002).

### 2. Materials and methods

#### 2.1. Total nitrogen (TN), total organic carbon (TOC), and $\delta^{15}$N

Bulk sediment samples were freeze-dried and representative sub-samples were powdered for elemental and isotopic analyses. TN and $\delta^{15}$N were measured on 25–30 mg bulk sediment samples while TOC was measured on samples decarbonated with sulfurous acid in silver tins following Verardo et al. (1990). TN and TOC were measured on a Carlo Erba (NC2500) elemental analyzer equipped with a Costech “zero-blank” autosampler, coupled to a ThermoFinnigan DeltaPlusXL isotope ratio mass spectrometer at the College of Oceanic and Atmospheric Sciences, Oregon State University. The isotope ratios of the local reference gases were calibrated by analyzing primary standards procured from the US National Institute of Standards and Technology (NIST).
The primary standard used was NIST 8548 ammonium sulfate, \((\text{NH}_4)_2\text{SO}_4\), which is assumed to have \(\delta^{15}\text{N} = 20.30\%\) with respect to \(\text{N}_2\) in air (Hut, 1987). Reproducibility, based on multiple analyses of NIST 8548 and a bulk Chile margin sediment sample \((n \geq 10)\) was better than \(\pm 0.2\%\).

2.2. Oxygen isotope analyses and age model

Benthic foraminifera (\textit{Uvigerina peregrina}) samples (~100 µg CaCO\(_3\)) were analyzed for oxygen and carbon isotope ratios at the College of Oceanic and Atmospheric Sciences, Oregon State University, using a Finnigan/MAT 252 mass spectrometer and a Kiel-III online acid digestion system. These data are reported in detail elsewhere (Mix et al., in prep.). Foraminiferal samples were ultrasonically cleaned, but otherwise not pre-treated before analysis. This system automatically reacts calcite samples in individual sample vials with 100% H\(_3\)PO\(_4\), in vacuo at 70°C, and cryogenically pumps the evolved CO\(_2\) to the dual micro-inlet of the mass spectrometer. Instrumental corrections to isotope values follow Mook and Grootes (1973). Average internal precision on carbonate analyses is \(+0.02\%\) and \(+0.01\%\) on \(\delta^{18}\text{O}\) and \(\delta^{13}\text{C}\), respectively. External precision of replicate analyses of a local carbonate standard (known as Wiley marble) run daily on this system in the same size range as the samples and over the same time interval, was \(+0.06\%\) for \(\delta^{18}\text{O}\) and \(+0.02\%\) for \(\delta^{13}\text{C}\) (+1 standard deviation, \(n = 722\)).

The age model, reported in detail elsewhere by Mix et al. (in prep.), for the time interval 0–31,000 years is based on 11 radiocarbon dates on mixed species of benthic foraminifera, with calendar corrections following Fairbanks et al. (2005) (Fig. 3). The modern seafloor reservoir age at Site 1234 is assumed to be 1268 years, based on water column data from GEOSCE'S Sites 322 and 324 at equivalent \(T = 3.7\) °C, \(S = 34.40, s_t = 27.4\). At these sites, \(\delta^{14}\text{C}\) is \(-143\%\) and \(-149\%\), respectively, for an average of \(-146\%\) = 1268 years. Ages for the interval >31,000 years reflect visual correlation of the Site 1234 \(\delta^{18}\text{O}\) record to the deep Atlantic benthic \(\delta^{18}\text{O}\) record of MD95204 which was tuned to the layer-counted GISP2 chronology based on planktonic foraminiferal \(\delta^{18}\text{O}\) (Shackleton et al., 2000). In addition, three tie points were made to the Byrd ice core \(\delta^{18}\text{O}\) record (Blunier and Brook, 2001), at events that were not well constrained by correlation to MD95204 (Fig. 3).

Secondary verification of the age model comes from the inferred ages of two magnetic excursions found in Site 1234 at 18.5 and 23 mcd (Mix et al., 2003), neither of which was
used as an age control point. The age model for Site 1234 implies that these magnetic excursions occurred at 34.2 and 41.0 ka, respectively. These ages compare well with known ages for the Mono Lake (Wagner et al., 2000) and the Laschamp (Laj et al., 2000) magnetic events, both of which were calibrated to the GISP2 ice core chronology.

Based on this age model, sediment accumulation rates at Site 1234 range from 20 to 150 cm/ka. These relatively rapid sedimentation rates reflect input of fine-grained terrigenous sediment eroded from the Andes and Coast Range, and transported to the ocean by major rivers such as the Bio Bio, which debouches near Concepción. Rapid burial likely contributes to the preservation of foraminifer and minimizes the potential age offsets between organic materials (which carry the $^{15}\text{N}$ signature) and foraminifera (which provide stratigraphic and chronologic constraints).

On organic-rich margins, lateral advection and redistribution of the organic fraction can result in age offsets between these fractions of as much as a few thousand years (Mollenhauer et al., 2005). For example, $^{14}\text{C}$ dates from the total organic and alkenone sedimentary fractions in a Chilean margin study site, within a depocenter at ~41 $^\circ$ S, were roughly 1 ka older than their corresponding foraminiferal $^{14}\text{C}$ ages (Mollenhauer et al., 2005). ODP Site 1234 has roughly similar sediment composition in that both sites are dominated by terrigenous materials (Mix et al., 2003). Given the high sedimentation rates, we assume that age differences between foraminifera and organic materials are likely to be <1 ka. We have made no adjustments in the ages of the organic fraction relative to the foraminiferal data, but if anything the effect would be to make the $^{15}\text{N}$ record slightly older.

3. Results

Weight percent TN and TOC were relatively high during interglacial marine isotope stage (MIS) 5 and the Holocene and low during MISs 2–4 (Fig. 3). C/N is 8–10 with little variation from 20 to 50 ka, but with a slight increase in the amplitude of variation from 0 to 20 ka. Sedimentary $^{15}\text{N}$ has a distinctly different pattern of variation with higher amplitude and higher frequency fluctuations than TN, TOC, or C/N throughout the record. The foraminiferal $^{18}\text{O}$ and the sedimentary $^{15}\text{N}$ records approximately co-occur, although the $^{15}\text{N}$ transitions are more rapid than their $^{18}\text{O}$ counterparts such that, at times, $^{15}\text{N}$ leads $^{18}\text{O}$ (Fig. 3). Changes in sedimentary $^{15}\text{N}$ at Site 1234 are generally consistent with the patterns of variation observed in other denitrification regions in that episodes of lower $^{15}\text{N}$ co-occur with lower $^{18}\text{O}$. This pattern is taken as evidence for weaker denitrification during glacial and stadial episodes and stronger denitrification during interglacial and interstadial intervals (Altabet et al., 1999a, 2002; Ganeshram et al., 2000, 2002; Kienast et al., 2002; Hendy et al., 2004).

4. Discussion

4.1. Potential influences on sediment $^{15}\text{N}$

Downcore $^{15}\text{N}$ records are potentially influenced by many factors including the input of land-derived organic material, changes in the degree of nitrate consumption and preservation, and changes in the source of nitrate and/or its isotopic composition. The Chile margin receives significant inputs of terrigenous material, mostly siliciclastics. During glacial episodes inputs from land were greater along the margin (Lamy et al., 1998, 1999, 2004). Although siliciclastic inputs were greater there was likely little input of terrestrial organic material to Site 1234. Sediment C/N varies little from typical values of 8–9, approximately the ratio expected from marine algae that have undergone some degree of burial diagenesis (Meyers, 1997), throughout the oldest part of the record. Slight, single point variations in the last 20 ka are not consistent with any $^{15}\text{N}$ or TN changes and insignificant with respect to larger, more systematic changes. Schubert et al. (2000) made a similar interpretation based on organic carbon isotope results from a nearby, but more landward core location offshore Concepción, Chile. There is little significant influence of land-derived organics in this area of the margin.

Present conditions at Site 1234, with essentially complete consumption of nitrate on an annual basis and a proximal upwelling cell sourced from the PCU indicate that sedimentary $^{15}\text{N}$ should record the $^{15}\text{N}$ of the nitrate delivered to the surface with little or no diagenetic influence or effects associated with partial nutrient consumption. The $^{15}\text{N}$ of NO$_3^-$ from 150 m depth at 33 $^\circ$ S fits this expectation (Fig. 2), falling within the range of observed surface sediment $^{15}\text{N}$ at 33 $^\circ$ S (sediment data from Hebbeln et al., 2000), and suggesting that the surface sediment is a faithful recorder of the water column nitrate with little or no isotopic offset due to alteration during sinking or sedimentation. We assume these basic conditions of high sediment flux leading to excellent preservation of the isotopic signal as it is transmitted from the surface ocean to the seafloor, and annually complete consumption of nutrients, were likely met throughout the relatively short 70 ka span of the presented record.

Three potential sources of nitrate contribute to the waters of the Chile margin overlying Site 1234, the (1) northern and (2) southern-sourced subsurface water masses as well as (3) nitrate-bearing Subantarctic surface water. Each has a distinct and possibly variable isotopic composition. The two sources of subsurface water upwelled along the central Chile margin are the PCU, originating in the Equatorial region near the heart of the denitrification zone off Peru, and Subantarctic Mode Water (SAMW) from the Subantarctic Zone of Southern Ocean.

The $^{15}\text{N}$ of nitrate within the PCU decreases southward from the center of the Peru Upwelling near 10 $^\circ$ S, as
described by a latitudinal transect of surface sediment $\delta^{15}$N (Hebbeln et al., 2000) (Fig. 2). The southward decrease in $\delta^{15}$N indicates mixing between the PCU and waters sourced from the Southern Ocean that, at present, have nitrate $\delta^{15}$N of 5–7‰ (Sigman et al., 2000). The Site 1234 core top sedimentary $\delta^{15}$N, 10‰, also falls along the core-top trend of the Hebbeln et al. (2000). Surface sediment $\delta^{15}$N values of around 10‰ in this region demonstrate the dominance of the PCU on modern sedimentary $\delta^{15}$N at Site 1234.

One hypothesis to explain the observed intervals of lower $\delta^{15}$N at Site 1234 is that these events represent times when the PCU was significantly diluted by the southern sourced water, with its lower $\delta^{15}$N signature, rather than a change in the $\delta^{15}$N of nitrate in either the PCU or SAMW. Little is known about the potential causes of temporal variability in the southward flux of PCU. It was traditionally thought that the poleward undercurrents associated with Eastern Boundary current upwelling systems are forced by upwelling favorable winds, but there is no evidence for a relationship between the strength of the PCU and upwelling or wind stress fields (Huyer et al., 1991). Variability in the strength of the PCU specifically may be related to sea-level variation due to disturbances in the equatorial regions (Pizarro et al., 2002). Although variability is documented, there is no evidence for a total shutdown of the PCU along the Chilean margin in the modern (Huyer et al., 1991; Pizarro et al., 2002). A nearly complete long-term cessation of PCU transport would be required to achieve the observed LGM $\delta^{15}$N values of ~7‰ at Site 1234, in the range of values expected from the southern sourced water masses, assuming no change in the $\delta^{15}$N of nitrate supplied on either end. This is an unrealistically large reduction in the strength of a current that can be identified today as far south as 48°S. In addition, sedimentary $\delta^{15}$N records from within the region of active denitrification offshore Peru document similar timing and magnitude of change in $\delta^{15}$N to that of Site 1234 across Termination I (Higginson et al., 2003; Altabet et al., 2004; Higginson and Altabet, 2004). This suggests that there was constant water mass communication between these two regions, and that $\delta^{15}$N variations at Site 1234 reflect changes in the source waters that are transported southward by the PCU. Thus, we reject the notion that the $\delta^{15}$N record at Site 1234 reflects changes of water transport within the PCU.

A second hypothesis to explain $\delta^{15}$N at Site 1234 is that variations reflect changes in the relative influence of upwelled denitrified water and Subantarctic surface waters. At present, the Subtropical Front lies near 40°S along the Chile Margin, where [NO$_3$] is roughly 4–6 μM annually. The position of the Subtropical Front may have shifted northward with the westerly wind belt during glacial times (Lamy et al., 2002, 2004; Heusser et al., 2006). If surface conditions shifted northward by 4–5° of latitude during the glacial interval (Lamy et al., 2002, 2004; Kaiser et al., 2005), Site 1234 may have received a significant input of potentially isotopically distinct NO$_3^-$ that could fundamentally alter the sedimentary $\delta^{15}$N signal.

Several lines of evidence argue against a strong Subantarctic surface influence on $\delta^{15}$N. Radiolarians at Site 1233 demonstrate that Subantarctic faunas did not reach this far north, even at the peak of the last ice age (Pisias et al., 2006). Subantarctic influence on $\delta^{15}$N of nitrate, depends upon both the isotopic composition and the total concentration of NO$_3^-$ introduced by surface flow (which nitrate-poor) relative to upwelling from the PCU (which is relatively nitrate rich at ~35 μM). Moreover, nitrate content of the Subantarctic surface waters was likely reduced by 30% during the last ice age (Robinson et al., 2005). This would push the northern boundary of nitrate-bearing surface waters southward in spite of the hypothesized northward physical migration of the fronts in the Subantarctic region, nitrate $\delta^{15}$N increases with increasing nutrient consumption such that it is at its highest toward the northern edge of the Southern Ocean, with values as high as 14‰ (Sigman et al., 1999), so a low-$\delta^{15}$N end member for southern surface waters being advected equatorward in the Peru–Chile Current is unlikely. Comparison of the ODP Sites 1234 and 1233, which is located at 41°S within the modern transition between the subtropical and subpolar South Pacific ocean (Fig. 1a) illustrates the relative importance of these two water masses along the southern Chilean coast (Fig. 4). Site 1233 bears a high-resolution, well-dated sedimentary $\delta^{15}$N record (Lamy et al., 2004; Kaiser et al., 2005; Martinez et al., 2006) that reflects an amalgam of nitrate advected from the Subantarctic combined with time variable input of NO$_3^-$ delivered by the poleward flowing PCU (Fig. 4) (Martinez et al., 2006). The $\delta^{15}$N profiles at Sites 1234 and 1233 are quite different indicating that throughout much of the last 50 ka these sites witnessed a distinctly different $\delta^{15}$NO$_3^-$ at the surface. The age models for both Sites 1233 and 1234 are very well constrained. Both are based on multiple $^{14}$C ages in the upper ~30 ka and tuning of high-resolution oxygen isotope records below (Lamy et al., 2004; Kaiser et al., 2005; Martinez et al., 2006). The 4–5 ka offsets in the timing of the peaks are real. For example, there is a large peak at Site 1233 during the LGM, when $\delta^{15}$N at Site 1234 is at a minimum. Following the LGM, $\delta^{15}$N increased upon deglaciation at Site 1234 and the early Holocene peak occurs synchronously with the second significant peak in the 1233 record. The ~15 ka peak visible in both records is also present in records further to the north and is likely the early Holocene maximum in denitrification visible in multiple $\delta^{15}$N records along the margin (Higginson and Altabet, 2004; De Pol-Holz et al., 2006) while the peak at the LGM at Site 1233 has also been shown in the Subantarctic Pacific $\delta^{15}$N record from core E11-2 (Robinson et al., 2005). On this basis of comparison we reject the hypothesis that the Subantarctic surface was a significant contributor of nutrients and the $\delta^{15}$N signature at Site 1234.
The sedimentary $\delta^{15}$N record at Site 1234 is dominantly controlled by the regional variation in water column denitrification in the suboxic zone offshore Peru and northern Chile. Although suboxic bottom water conditions are found in the Concepción Bay region of the Chile margin (Farias et al., 2004), it is restricted to a small area, so the isotope $\delta^{15}$N record at Site 1234 is not likely driven by changes in local denitrification rates. The core location is outside of Concepción Bay on the upper slope where the waters are not suboxic but the overlying surface is influenced by the upwelling of nutrient-rich PCU water. Site 1234 is likely recording changes in the $\delta^{15}$N of nitrate advected southward along the margin within the PCU from the region of open ocean water column denitrification to the north. We next explore three optional hypotheses for variations in $\delta^{15}$N of these low-latitude source waters.

4.2. Regional paleoproductivity

Looking for a causal relationship between changes in the export of organic carbon and the extent of denitrification is not straightforward. Local variations in export production do not necessarily co-vary with those associated with the advected denitrification signal. Rather, export production to the north, within the primary region of active denitrification, must be evaluated in order to make this comparison.

Estimates of export productivity from benthic foraminiferal transfer functions and inorganic geochemical proxies from within the Eastern Equatorial Pacific and the Peru Upwelling region indicate that productivity is lowest during MIS 2 and 4 and elevated in the warm or stadial intervals (Loubere, 1999, 2000; Loubere et al., 2003, 2004). This indeed is the pattern that one might expect from local productivity-driven variations in denitrification, when the flux of organics and thus oxygen demand in the subsurface is greatest. However, estimates of paleoproduction in the region remain controversial (Lyle et al., 2002; Payton et al., 2004). The benthic foraminiferal indices suggest higher export productivity during MIS 2 from a core slightly to the south of the main Peru upwelling (Loubere et al., 2003), as well as from the northern Chile margin (Mohtadi et al., 2004). More recently, work comparing sedimentary $\delta^{15}$N and Th-normalized export fluxes on the Peru margin suggests that paleoproduction did not vary synchronously with the $\delta^{15}$N and therefore cannot be the local driver of the inferred changes in denitrification (De Pol-Holz et al., 2006). Because regional proxy estimates of paleoproduction remain equivocal it is not possible to uniquely assess the potential role of local/ regional organic carbon flux on the extent of suboxia in the eastern south Pacific.

4.3. Physical controls on oxygen supply

Climatically driven increases in the supply of oxygen through enhanced ventilation rates and cooling of the high-latitude surface ocean could contribute significantly to a higher subsurface $[O_2]$ during glacials and suppress suboxia and consequently reduce water column denitrification (Galbraith et al., 2004; Meissner et al., 2005). Modeling experiments simulating the glacial oxygen supply resulting from purely physical changes suggest that denitrification rates may have been as much as 50% lower globally during the LGM (Meissner et al., 2005).

The suboxic water column in the SE Pacific has a direct connection to the high-latitude surface through the EUC–PCU system. The PCU has its origin in the lower thermocline of the EUC (Wooster and Gilmartin, 1961). This subsurface water mass, which resides between 75 and
300 m depth in the EUC east of 150°W is known as the 13°C thermostad (Tsuchiya, 1981; Tsuchiya et al., 1989). Radiocarbon data tracks the source of the 13°C water to the northern edge of the Antarctic Circumpolar Current within the Southern Ocean where SAMW is formed in the SW Pacific (Tsuchiya, 1981; Toggweiler et al., 1991). SAMW is formed during deep winter mixing followed by the onset of a stratified surface layer in the spring. Some amount of diapycnal mixing along its flow path likely warms it from ~8°C at its origin in the Subantarctic to 13°C in the EUC. This component of the EUC is characterized by its low temperature, high salinity, and high oxygen content. In the eastern Pacific the oxygen is consumed rapidly likely as a result of the significant export associated with the equatorial divergence and slow regional recirculation (Wyrtki, 1962).

On the basis that the proposed physical changes in oxygen supply were regulated by climate change in the region of thermocline ventilation, we compare the Byrd ice core record of Antarctic climate with the Site 1234 δ15N profile (Fig. 5). Intervals of higher δ15N (more denitrification) and low benthic δ18O (warmer and/or lower salinity water masses) during MIS 2–3 correspond to Antarctic warm events A1–A4 and another broad warm interval on Antarctica around 25 ka (Fig. 5). The high-amplitude deglacial shift to elevated δ15N that dominates the Holocene was initiated

![Fig. 5. Last 70 ka of (a) GISP2 δ18O, (b) Byrd δ18O, (c) Site 1234 δ15N, (d) Site 1017E δ15N (Hendy et al., 2004), (e) RC23-27 δ15N (Altabet et al., 2002), (f) diatom-bound δ15N E11-2 Pacific SAZ (scale inverted) (Robinson et al., 2005). MISs are bounded by solid black lines and identified across the top of the figure. The Younger Dryas and the Bolling-Allerod are shaded and labeled. The dashed gray line marks the absolute minimum in the eastern Pacific denitrification records (1234 and 1017E) and in nutrient supply as inferred from the Subantarctic diatom-bound δ15N from E11-2. The shaded gray bars labeled A1–A4 highlight the Antarctic warm events during the last glacial period as well as peaks in denitrification along the Chile margin.](image-url)
around 18.5 ka, slightly after the Antarctic temperature rise, but well before the NH shift around 14 ka. The Chile denitrification record shows characteristically SH timing of millennial-scale events that precede analogous events in the NH. Changes on the Chile margin were a response to the highest amplitude Antarctic warming events of MIS 2–4. The general observation that warmer intervals on Antarctica correspond to episodes of enhanced denitrification in the SE Pacific during the last glacial period is consistent with the proposed physical mechanisms for modulating suboxia within the Peru–Chile upwelling system (Galbraith et al., 2004; Meissner et al., 2005).

4.4. High-latitude biological controls on preformed properties

SAMW, the source of the 13 °C thermoclad, plays an important role in low-latitude ocean biogeochemical cycles due to its strong influence on the nutrient content of the low-latitude thermocline (Toggweiler et al., 1991; Sarmiento et al., 2004). The nitrate and phosphate bearing surface waters in the Subantarctic region are subducted to form SAMW and then spread throughout the low-latitude thermocline, with the exception of the North Pacific (Sarmiento et al., 2004). This water mass fuels low-latitude ecosystems through the upward transport of the nutrient-rich thermocline water into the sunlit surface layer. If the nutrient content of this water varies during SAMW formation (the preformed nutrient content) then so may downstream oxygen demand.

Foraminiferal Cd/Ca, diatom-bound δ13C, and diatom-bound δ15N measurements at sites in the Southern Ocean (Rosenthal et al., 2000; Robinson et al., 2005) point to elevated nutrient consumption in the ice age Subantarctic. Increased consumption in the Subantarctic surface would lower the total nutrient content of the low-latitude thermocline through a reduction in the preformed nutrient content of SAMW. The general shape of the diatom-bound δ15N record of nutrient consumption from core E11-2 in the central south Pacific negatively co-varies with the eastern Pacific δ15N records (Fig. 5). Glacial nutrient consumption in the Subantarctic was elevated relative to the Holocene with a pronounced peak during the last glacial maximum and a sharp decrease during deglaciation to low values in the early Holocene (Fig. 5). This first-order pattern of glacial–interglacial change, shown here at Site E11-2 from the central Pacific, is a widespread feature present in records from the Indian and Atlantic sectors of the SAZ (Robinson et al., 2005).

Records from the Subantarctic predict that the preformed nutrient content of the thermocline was lower during the last ice age than in the Holocene, that it was at a minimum during the LGM, and then rose sharply during the deglaciation. This prediction fits with the overall observed variation in denitrification, and with the presence of anomalously low δ13C in planktic foraminifera of the EEP during deglaciation (Spero and Lea, 2002; Mix, 2006).

Taken together, the EEP export production data and the high-latitude nutrient consumption record suggest that the nutrient content of the EUC and thus the regional oxygen demand was likely lowered during glacial times and argues a role for ocean biology, both in the high-latitude surface and the low-latitude subsurface, in dictating the extent of suboxia and consequently denitrification in the eastern Pacific. The early deglacial shifts in nutrient consumption and low-latitude denitrification also correspond to major changes in Southern Ocean sea ice extent, as evidenced in sediment ice rafted detritus and ice core non-sea-salt Na+ records (Kanfoush et al., 2000, 2002; Wolff et al., 2003). Changes in sea ice extent were likely a response to physical changes and a driver of biological ones.

4.5. Inter-hemispheric asynchrony in denitrification

Comparison of the Site 1234 δ15N record with Site 1017E from offshore California at 34°N (Hendy et al., 2004) and RC23-27 from the Arabian Sea (Altabet et al., 2004) allows for evaluation of regional or hemispheric differences in the downcore records of δ15N from the three major regions of water column denitrification. The extremely high-amplitude variation from 40 to 60 ka in the Arabian Sea is not present in the eastern Pacific. Instead, both Pacific records show the highest amplitude change to be associated with Termination I.

The Chile and California sites both record co-variation between δ15N and δ18O suggesting that denitrification is greater when the regional climate is warming. Both sites are located outside of the eastern tropical Pacific’s region of water column denitrification but within upwelling systems under the influence of poleward undercurrents that transmit tropical signals to the north and south. These δ15N records, of roughly similar resolution with good age control, are ideally suited for an evaluation of the potential role of EUC on the generation of suboxic conditions in the eastern tropical Pacific. Based on the current chronologies, timing of millennial-scale δ15N changes in the Site 1234 is different from those of the NH. The incidences of increased denitrification associated with Antarctic warm events during MIS 2–4 at Site 1234 all lead their NH counterparts in a way analogous to the leads of the Byrd ice core δ18O record relative to that of GISP2 (Fig. 5) (Blunier et al., 1998; Blunier and Brook, 2001).

The SE Pacific δ15N record also leads the Arabian Sea regions during the radiocarbon-dated interval of Termination I transition (Higginson et al., 2003; Altabet et al., 2004). Within this interval, a δ15N minimum is shared by both Site 1234 and 1017E at 18.5 ka and is followed by a sharp step-wise increase to a maximum at ~15.5 ka. The increase is more rapid at Site 1234 so that the early Holocene maximum leads its counterpart in the NE Pacific by approximately 1000 years. The second Holocene maxima, at around 10 ka, is also slightly earlier at Site 1234. The overall pattern of δ15N change during Termination I, in both the NH and SH Pacific sites, with an increase
beginning around 18 ka, is characteristic of SH climate records (Clark et al., 2004; Kiefer and Kienast, 2005). The Byrd ice core \( \delta^{18}O \) begins to rise around 22 ka, and after a small decrease around 19 ka, continues its rise into the Holocene. In contrast to the Pacific records, the deglacial rise in \( \delta^{15}N \) in the Arabian Sea mimics the timing of deglacial warming in the GISP2 ice core record, near 15–16 ka.

Overall, denitrification in the eastern Pacific, as recorded by the Chile margin sediments, appears to be responding to SH climate changes. Our preferred explanation for the timing comes from the subsurface hydrography in the SE Pacific and the potential bio-physical changes in the region of SAMW formation. SAMW feeds into the 13 °C thermostad of the EUC which then flows into the PCC to become the primary source of the upwelled water along the Peru margin that fuels the high export of organic matter and consequently the suboxia in the subsurface (Toggweiler et al., 1991; Spero and Lea, 2002; Sarmiento et al., 2004). Moreover, the EEP, the principal locus of oxygen drawdown in the EUC, also receives much of its nutrients from this same source through the nutrient-rich tongue of SEC.

Our observations suggest that the SE Pacific is tightly linked to the Southern Ocean. The last ice age was a time of intense, year-round stratification of the Antarctic Zone of the Southern Ocean (Francois et al., 1997; Sigman et al., 2004). We hypothesize a partial breakdown of stratification occurring during Antarctic warm events associated with increased supply of nutrient-rich water to the Antarctic surface due to deep mixing. Such a pulse of nutrients would make its way into the Subantarctic Zone and SAMW, ultimately leading to greater export production, oxygen demand, and consequently an increase in denitrification within the Peru Upwelling.

The NH records of denitrification from the northeast Pacific and the Arabian Sea mimic the timing of climate events in Greenland, with the exception of the deglacial transition at Site 1017E, which changes essentially synchronously with Site 1234. Although the lead by the SH record suggests there are hemispheric controls on the timing of the variation in denitrification, the overall link between hemispheric warming and hemispheric denitrification still points to a mechanistic link, perhaps high-latitude stratification and nutrient status changes. In the North Pacific, as in the Southern Ocean, glacial episodes are characterized by lower export productivity inferred to be the result of enhanced stratification upon cooling (Jaccard et al., 2005).

The suboxic water column along the eastern north Pacific margin occupies a significantly larger depth interval than its SH counterpart. As such, its extent is controlled in part by oxygen supplied through the EUC-CU and in part by North Pacific Intermediate Water (NPIW), which resides in the depth interval below the CU. NPIW is sourced in the northwest Pacific and thus represents a potential connection between the extent of denitrification in the ETNP and the bio-physical changes in the Subarctic North Pacific; a link that would have strictly NH timing. That Site 1017 record displays a characteristically SH transition across Termination 1 suggests that mechanisms of biogeochemical ocean adjustment associated with a major deglaciation are fundamentally different from the regional adjustments associated with shorter timescale oscillations.

5. Conclusions

The coherent timing of Antarctic climate change and the SH low-latitude denitrification record from ODP Site 1234 suggests a key role for the high-latitude Southern Ocean in regulating the biogeochemical cycling along the Peru–Chile margin. This contrasts with the NH-character of the denitrification records from the northeast Pacific and Arabian Sea. The source of subsurface oxygen and nutrients to the SE Pacific region is SAMW, which forms at the southern edge of the Subantarctic. The overall pattern of high-latitude nutrient status changes in the Subantarctic suggests that the preformed nutrient content of the low-latitude thermocline likely played a key role in governing subsurface oxygen demand and consequently the degree of suboxia and denitrification in the SE Pacific. In particular, the minimum in denitrification associated with the LGM is not coincident with the Antarctic or Greenland temperature minima but rather with the apparent maximum in nutrient consumption in the SAZ or changes in sea ice extent (Kanfoush et al., 2000, 2002; Wolff et al., 2003; Robinson et al., 2005). At the same time, the similarity between millennial-scale variation in \( \delta^{15}N \) on the Chile margin and \( \delta^{18}O \) in the Byrd ice core, particularly during MIS 3, may reflect regional physical changes associated with cooling and enhanced windiness (Galbraith et al., 2004; Meissner et al., 2005). In sum, variation in denitrification in the southeast Pacific may be forced remotely through an interaction between Southern Ocean climate change, physical oceanography, and polar biology.

Acknowledgments

This work was supported by USSSP and a PEI Huber Fellowship to RSR and grants from USSSP and NSF-0319016 to ACM. The water samples were provided by R. de Pol Holz. Thanks to shipboard scientific party of Leg 202. Special thanks to D. Graham and W. Rugh for their assistance in the laboratory and to D. Sigman and E. Galbraith for discussion and suggestions.

References


Kienast, S.S., Calvert, S.E., Pedersen, T.F., 2002. Nitrogen isotope and productivity variations along the northeast Pacific margin over the last 120 kyr: surface and subsurface paleoceanography. Paleoceanography 17 (4).


Lamy, F., Hebbeln, D., Wefer, G., 1998. Late quaternary precessional cycles of terrigenous sediment input off the Norte Chico, Chile (27.5 degrees S) and palaeoclimate implications. Palaeogeography, Palaeoclimatology and Palaeoecology 141 (3-4), 233–251.

Lamy, F., Hebbeln, D., Wefer, G., 1999. High-resolution marine record of climatic change in mid-latitude Chile during the last 28,000 years based on terrigenous sediment parameters. Quaternary Research 51 (1), 83–93.


