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Atypical $\delta^{15}N$ variations at the southern boundary of the East Pacific oxygen minimum zone over the last 50 ka

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Abstract

We report a nitrogen isotope record (ODP Site 1233) from the southern Chile margin at 41°S. The site is located slightly south of the southern boundary of the Peru–Chile upwelling system and the associated oxygen minimum zone off Peru and northern Chile. We show that our nitrogen isotope record, from the time interval 0–50 calendar kiloyears before present (ka B.P.), bears an atypical pattern both in shape and timing when compared with records obtained from either the continental margin of the eastern Pacific or the Subantarctic Zone (SAZ) of the Southern Ocean. The $\delta^{15}N$ values at Site 1233 are relatively high throughout the record, varying between 9‰ and 13‰. The major features are a pronounced $\delta^{15}N$ increase at the beginning of the deglaciation, a maximum from 19 to 10 ka B.P.; thereafter a large decrease during the early Holocene, and millenial scale oscillations showing an Antarctic timing. We propose that the record results from an amalgam of low-latitude and high-latitude processes. Low-latitude processes, including a stronger advection signal of heavy nitrates from the denitrifying zones off Peru and northern Chile, would explain the timing of the deglaciation rise and the heaviest values found over this interval, excluding the Antarctic Cold Reversal period. The overall differences between site 1233 and records from Peru and northwest American margins suggest however that the origin of the $\delta^{15}N$ signal off Chile is largely controlled by hydrologic and climatic changes in the Southern Ocean. We propose that the interplay between nutrient demand in the SAZ and latitudinal shifts of hydrologic fronts controlled both the concentrations and the isotopic signature of the remaining nitrate delivered to the Chile margin. Then, the glacial surface waters of the southern Chile margin were likely lower in nitrate concentration and bear a higher $\delta^{15}N$ than during interglacial periods.

1. Introduction

The nitrogen cycle plays a central role in the biogeochemistry of the global ocean. As a limiting nutrient in the low-latitude ocean, the availability of nutrient N (mainly nitrate) controls biological productivity and consequently the flux of carbon and associated elements between the atmosphere, the ocean, and the sediments, and may play a fundamental role in modulating climate change. At the same time, in the high-latitude oceans, nitrate is not completely consumed in the surface ocean; its uptake is limited by some other factors, such as light or the micro-nutrient Fe. There are hypothesized roles for both of these vastly different nutrient regimes in the modulation of atmospheric CO_2 concentrations on glacial–interglacial time-scales (Sigman and Boyle, 2000; Pedersen and Bertrand, 2000).

Inventory changes associated with variation in the size of the main sink for nitrate have been proposed as a potential driver of CO_2 change because of nitrogen's fundamental role in controlling productivity in the low-latitude oceans. The premise is that any change in the absolute amount of nutrient N in the oceans should in turn affect the low-latitude biological pump's capacity to fix carbon at the sea surface and deliver it to the deep ocean. If there was a major reduction in the rate of nitrate loss from the oceans

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during glacial episodes, then the low-latitude ocean may have had a greater capacity to remove CO_2 from the surface ocean (Ganeshram et al., 1995; Altabet et al., 1995). At the same time, changes in the degree of major nutrient consumption in the high-latitude oceans have been put forth as a potential driver because at present the high latitudes are a source of CO_2 to the atmosphere. If more of the major nutrients, nitrate and phosphate, were consumed in the Southern Ocean surface during the last ice age, then a greater proportion of the CO_2 upwelled from the deep ocean would have returned to the deep ocean rather than escaping to the atmosphere (Sigman and Boyle, 2000, and references therein). As both regions are potentially contributors to this observed, enigmatic signal of changing CO_2, they have been targeted for multiple paleoceanographic studies (see references above).

Studies of temporal changes in the oceanic nitrogen cycle have been based on the use of nitrogen isotopes as measured from sedimentary organic matter. The major transformations of nitrate (e.g., denitrification, nitrification, and assimilation) have kinetic isotope fractionations associated with them such that the $^{15}N/^{14}N$ of the nitrate pool essentially records these processes. In each of these transformations of nitrogen, the lighter isotope preferentially undergoes reaction so that the substrate becomes enriched in the heavier isotope, ^{15}N, while the product is enriched in ^{14}N. The $^{15}N/^{14}N$ of the substrate pool increases with progressive consumption of the nitrate pool. The product, for our purposes, sedimentary organic matter, while depleted in ^{15}N relative to nitrate, is also becoming enriched, such that it tracks the $^{15}N/^{14}N$ increase of the nitrate pool with some offset. In the low-latitudes, consumption of nitrate is complete such that the fractionation associated with the uptake and assimilation of nitrate is not observed. In regions of annually complete nitrate consumption, changes in the $^{15}N/^{14}N$ measured from sediments are thought to reflect changes in the $^{15}N/^{14}N$ of nitrate due to some other transformation.

In sediment cores from oceanic upwelling regions, which also house the major regions of open ocean suboxia, changes in the sediment $^{15}N/^{14}N$ (as $\delta^{15}N$) are generally attributed variation in the extent of water column denitrification. Denitrification is the bacterial reduction of nitrate in the absence of oxygen. Nitrate becomes the terminal electron acceptor during the oxidation of organic matter. Denitrification occurs in suboxic sediments and water columns, where $[O_2]$ are $<5\,\mu M$. Water column denitrification accounts for roughly 20–50% of the nitrate removal from the oceans (Codispoti, 1995; Deutsch et al., 2004). There is a large isotopic fractionation associated with denitrification, such that the residual nitrate pool is significantly enriched in ^{15}N. The isotope enrichment effect is around 25‰ and is strongly expressed during water column denitrification. In these well-studied margin systems, the ^{15}N-enriched nitrate from the suboxic depth zone is upwelled, assimilated by phytoplankton and converted to organic N. The signature of denitrification is then delivered to the seafloor in sedimenting organic matter. Orbital and millennial scale variability observed in nitrogen isotope ($\delta^{15}N$) profiles from two of the three major regions of water column denitrification, the Eastern Tropical North Pacific (ETNP) and in the Arabian Sea, are assumed to reflect changes in the extent of denitrification and provide strong evidence of a link between the climate system and the oceanic nitrogen cycle (Ganeshram et al., 1995; Altabet et al., 1995, 2002; Kienast et al., 2002; Galbraith et al., 2004). The downcore $\delta^{15}N$ profiles from these regions show a similar pattern for the last 60 ka, with light values during glacial marine isotope stages 2, 3, and 4 and heavier values during interglacial MIS 1 and 5. A similar relationship between $\delta^{15}N$ and climate variation has been identified at a millennial time-scale as well (Altabet et al., 2002; Ivanochko et al., 2005; Pride et al., 1999; Emmer and Thunell, 2000; Hendy et al., 2004; Thunell and Kepple, 2004). The available records document abrupt shifts in phase with the Northern Hemisphere millennial-scale pattern with heavier $\delta^{15}N$ values during Greenland interstadials.

In the nitrate-rich polar regions, sedimentary $\delta^{15}N$ changes are thought to record changes in the degree of nitrate consumption, where higher $\delta^{15}N$ corresponds to more complete consumption of the surface nitrate pool (Altabet and François, 1994). The majority of sedimentary $\delta^{15}N$ records from the Southern Ocean (bulk sediment and diatom-bound $\delta^{15}N$) indicate that nitrate consumption was indeed greater during glacial times as is required by high-latitude explanations for glacial–interglacial CO_2 change (François et al., 1997; Robinson et al., 2004, 2005). One can make inferences related to a region's potential for supporting or refuting its hypothesized role in the climate system based on downcore $\delta^{15}N$ records of regional nitrogen cycle changes, either in the extent of denitrification or in the degree of consumption. However, these interpretations rest on the assumption that other nitrogen cycle processes that might influence sediment $\delta^{15}N$ are temporally constant. This includes the potential influence of an isotopically or geographically distinct nitrate source.

It has been demonstrated that a characteristic $\delta^{15}N$ signature of changes in the extent of denitrification is recorded in sediment records far from regions of active denitrification as a result of advection via subsurface currents (Kienast et al., 2002). In the ETNP, the California Undercurrent carries the signature of denitrification from the core of the ENTP oceanic suboxic zone as far as Oregon, while in the southeast Pacific, the Günther (or Peru–Chile) Undercurrent carries the signal from offshore Peru toward the Subantarctic as far south as 45–48°S (Silva and Neshyba, 1979). Here we present a nitrogen isotope record from the southeast Pacific off Southern Chile at 41°S. The site is located slightly south of the southern boundary of the Peru–Chile upwelling system beneath the northern edge of subantarctic surface water, at the origin of the Peru Chile Current (PCC) or Humboldt Current. We show that our nitrogen isotope record, from the time