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Expansion of pelagic denitrification during early Pleistocene cooling

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ABSTRACT

Bioavailable nitrogen is removed from the oceans in oxygen-deficient benthic and pelagic environments by denitrification. Future warming is predicted to reduce ocean oxygenation and to cause hypoxic regions to expand, potentially accelerating denitrification. A compilation of high-resolution sedimentary nitrogen isotope ($\delta^{15}N$) records from the eastern tropical Pacific, North Pacific, and the Arabian Sea, and a global multi-site survey are presented as evidence for weak pelagic denitrification at the end of the Pliocene warm period. Mean $\delta^{15}N$ values increased in the major oxygen minimum zones (OMZs) between 2.1 and 1.5 Ma. Pelagic denitrification strengthened during a period of long term global cooling, despite solubility driven increases in initial oxygen contents of Antarctic intermediate and Subantarctic mode waters ventilating the OMZs. This trend is opposite to the predicted mean trend for a cooling ocean as well as to the observed glacial–interglacial variation. Several alternatives to explain the shift are proposed, including a rise in net respiration, a progressive increase in the ventilation age of the deep ocean associated with million year scale, secular cooling, and a shoaling of the remotely ventilated thermocline to shallow depths corresponding to the zone of peak subsurface respiration. Given no evidence for a net increase in production, we assert that large-scale, climate-driven changes in ocean circulation regulate long timescale variations in the extent of pelagic denitrification. Additional data and modeling are required to fully explain the observations.

1. Introduction

Nitrogen (N) is an essential nutrient in the ocean and its biogeochemistry is intrinsically linked to those of carbon and oxygen. In many regions of the ocean, nitrogen is considered to be the limiting nutrient, providing a fundamental control on primary production and carbon fixation. A stable bioavailable nitrogen inventory relies on relative balance between nitrogen fixation and denitrification, the primary source and sink, respectively (DeVries et al., 2012). Nitrogen fixation results in the acquisition of new bioavailable nitrogen from the atmospheric N_2 pool. Denitrification is the bacterial reduction of nitrate in the near-absence of oxygen in the sediments and water column. The extent of denitrification is a function of oxygen availability, which is controlled by oxygen supply and consumption through respiration. Benthic denitrification is widespread throughout the ocean's shallow shelf and slope sediments, while pelagic denitrification is limited to regions of water column suboxia ($[O_2] < 10\ \mu M$). Open ocean pelagic denitrification primarily occurs in the eastern tropical Pacific Ocean and the Arabian Sea (Codispoti and Richards, 1976; Naqvi, 1991). These regions are oceanographically similar in that they receive nutrient-rich, relatively old ventilation age waters and experience large-scale wind driven upwelling and high export production (Ito and Deutsch, 2010). The combination of limited oxygen delivery, via the relatively old thermocline depth waters, and high local production are thought to be responsible for the intense oxygen depletion that results in large scale open ocean suboxia. Recent modeling and time-series studies suggest that suboxic zones are particularly sensitive to climate driven changes in ocean oxygenation (Deutsch et al., 2011).

In the OMZ regions, sedimentary nitrogen isotopes have been used to study recent denitrification histories with respect to glacial–interglacial climate change in hopes of better understanding potential fixed nitrogen inventory fluctuations and climate related linkages between the oceanic oxygen and nitrogen cycles (Altabet et al., 1999a; De Pol-Holz et al., 2007; Ganeshram et al., 2002; Pride et al., 1999). Denitrification strongly fractionates nitrogen's two stable isotopes, ^{14}N and ^{15}N, so that the N isotopic composition (as $\delta^{15}N$, where $[\delta^{15}N\,(‰) = (^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{std} - 1) \times 1000]$ and the standard is air) of the nitrate pool in regions of pelagic denitrification is elevated well above the oceanic

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mean (5‰; Sigman et al., 1999). This enriched nitrate is incorporated into phytoplankton biomass upon delivery to the euphotic zone and the organic nitrogen, bearing the isotopic signature of denitrification, is deposited on the seafloor as a record of the extent of suboxia. Orbital scale records of denitrification show a generalized pattern of weaker denitrification during glacials and cool stadial periods, and stronger denitrification during interglacials and warm interstadials (Altabet et al., 1995; De Pol-Holz et al., 2007; Galbraith et al., 2004; Ganeshram et al., 1995; Kienast et al., 2002; Pride et al., 1999; Robinson et al., 2007). One record, from the California margin (ODP Site 1012), demonstrates that this pattern of glacial–interglacial scale variability is consistent back to 5.0 Ma in the eastern tropical north Pacific OMZ (Liu et al., 2005, 2008). This long record also reveals a secular shift toward overall higher mean nitrogen isotope values around 2.1 Ma (Liu et al., 2008).

In fact, five geographically disparate records, including the California record (ODP Site 1012), two records from the eastern equatorial Pacific (ODP Sites 1239 and 1240 (SI Fig. 1)) and records from the Oman (ODP Site 724) and Namibian (ODP Site 1082; SI Fig. 1) margins, show a secular increase in sedimentary δ^{15}N values between 2.5 and 1.5 Ma (Fig. 2 and SI Fig. 1) (Etorneau et al., 2009, 2013; Liu et al., 2008; Muzaka et al., 1991). Each record is distinct and was interpreted in isolation. Here, we present a new, high resolution record from ODP Site 1242 on the Costa Rica margin, the first from within the tropical Pacific OMZ. We also present a multi-site survey of early Pleistocene (2.5–2.0 Ma) and late Pleistocene (0–1.0 Ma) mean δ^{15}N values. Together with the existing published records from ODP Sites 1012 and 724, a composite view of sedimentary N isotope data from within the OMZs, regions downstream of the OMZs, and regions nominally out of subsurface water contact with the OMZs is created in an effort to understand if there was a global expansion of suboxia in the shadow zones and to evaluate potential driving mechanisms.

2. Materials and methods

δ^{15}N data from ODP Sites 1240, 1239, 1082, 1084, 1058, 1012, 882, 806, and 724 were published previously (Etourneau et al., 2009; Galbraith et al., 2008; Liu et al., 2008; Muzaka et al., 1991; Poli et al., 2010; Rafter and Charles, 2012; Robinson and Meyers, 2002; Robinson et al., 2002). Samples from ODP Sites 1054, 1014, 929, 881, 806 and 758 were acidified, rinsed and dried. The carbonate-free residue was measured for total organic carbon (TOC) and total nitrogen (TN) contents and δ^{15}N with a CE Elantech elemental analyzer (EA) coupled to a Thermo DeltaPlus isotope ratio mass spectrometer (IRMS) at the University of Michigan School of Natural Resources and the Environment. Samples from ODP 1242 the late Pleistocene interval (0–40 ka) from ODP Site 1014 were measured for TN and δ^{15}N on untreated sediment with a Costech 4010 EA coupled to a Delta V IRMS at the University of Rhode Island. Accuracy and precision were better than ±0.3‰. General agreement between the acidified samples from the University of Michigan and unacidified samples from the University of Rhode Island labs was confirmed by comparison of same sample results from Sites 1012 and 1014.

Age estimates are based on biostratigraphic and paleomagnetic ages for Sites 929, 1054, 806, 881, 1014, 724, and 1242 and the timescale of Lourens et al. (2004) unless a more detailed age model has been previously published for all or part of the record (Sites 806, 882, 1082, 1084, 1012, 1239, and 1240) (Table 1; Curry et al., 1995; Etorneau et al., 2013, 2010; Fornaciari, 2000; Galbraith et al., 2008; Keigwin et al., 1998; Kroenke et al., 1991; Liu et al., 2008; Mix et al., 2003; Pierce et al., 1989; Poli et al., 2010; Prell et al., 1989; Rafter and Charles, 2012; Rea et al., 1993; Robinson and Meyers, 2002). A published age model for Site 1242, based on radiocarbon dates and δ^{18}O stratigraphy, exists for the last 40 ka (Benway et al., 2006).

For sites without continuous records, the age interval means are based on a minimum of 3–8 samples that span ∼40–100 ka (see Table 1 for exact number). For sites without at least a short continuous record (e.g. a glacial cycle), there is the potential for local glacial–interglacial scale variability in δ^{15}N to cause significant aliasing, however comparison of means based on 3–8 samples with glacial–interglacial records suggests that this is minimal, likely due to sample spacing. For example, the mean for 0–1.0 Ma measured on 3 samples from Pacific ODP Site 881 was 5.8 ± 0.8‰ while the mean from nearby Site 882, based on 444 samples is 5.5 ± 0.8‰ (Galbraith et al., 2008). Data from sites with fewer samples are less reliable but still informative. Statistical significance, based on $p < 0.01$, of the differences in the mean δ^{15}N values were evaluated using a t-test for samples with unequal variances (Welch, 1947).

SiZer (Significance of Zero Crossings of the Derivative) (Chaudhuri and Marron, 1999) was used to explore significant features of the high resolution δ^{15}N data from Sites 1012, 1242, and 724. SiZer looks for statistical significance of features across a range of timescales. SiZer assumes that the δ^{15}N values are independent random variables. At each point, a local linear kernel estimator is used to produce smooths of the time series. The kernel function used is a unimodal probability density function symmetric about zero and the degree of smoothing reflects the bandwidth or window size used for the local linear smoothing. A small bandwidth results in a smooth that is greatly impacted by sampling variability, to an unrealistic degree, while a large bandwidth may flatten important features of the time series. For each bandwidth and time, it is determined if the derivative of the smoothed curve is significantly different from zero at a 95% confidence interval. The SiZer analysis was performed using the SiZer Java applet from http://www.wagner.com.

3. Results and discussion

3.1. Increasing δ^{15}N values in the early Pleistocene

The multi-site survey and continuous bulk sedimentary δ^{15}N profiles together reveal an increase in δ^{15}N ranging between 0.9 and 3.7‰ in the Indo-Pacific and eastern South Atlantic during the early-mid Pleistocene (Figs. 1 and 2, Table 1) (Etourneau et al., 2009; Liu et al., 2008; Liu and Herbert, 2004; Muzaka et al., 1991). The SiZer analysis highlights the initiation of the long-term increase in δ^{15}N at each site, demonstrating the differences in timing between the California margin record and the two tropical OMZ records (Fig. 2). The largest increase in δ^{15}N initiates at 2.1 Ma offshore California (Liu et al., 2008). In the ETP and the Arabian Sea, a more gradual increase in δ^{15}N values occurs, beginning at 1.6 Ma and ending between 1.0 and 0.5 Ma (Fig. 2). The amplitude of the high frequency variability increased in the Pacific and Arabian Sea records as well. The three OMZ sites show subtle peaks around 0.3 Ma and decreases toward the present (Fig. 2). In the two Pacific sites, mean values from the last 100 ka are higher than values prior to the increase in the early Pleistocene. In the Arabian Sea, the decrease suggests a return to mean values seen around 2.0 Ma.

3.2. Interpreting the bulk δ^{15}N signal

The Pacific and the Arabian Sea sites are located beneath coastal upwelling systems that witness high export production as well as complete nutrient drawdown on an annual basis. The complete consumption of nitrate in these systems implies that sedimentary δ^{15}N values reflect the δ^{15}N value of subeuphotic zone nitrate (Altabet et al., 1999b). This is also true for most of the survey sites.