Easterly denitrification signal and nitrogen fixation feedback documented in the western Pacific sediments

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Received 14 October 2011; revised 14 November 2011; accepted 16 November 2011; published 24 December 2011.

A sedimentary δ¹⁵N record in the equatorial western Pacific (WP) shows glacial-interglacial variability from 6.2 to 11.2‰ during the last two climatic cycles, similar to the denitrification record in the eastern tropical Pacific (ETP). Contrastively, a record in the South China Sea (SCS) exhibits less changes from 4.4 to 6.4‰ and is quite alike previously published results in marginal seas in the WP. By ruling out several possible causes for the δ¹⁵N variability, the δ¹⁵N record in the equatorial WP is interpreted as the source nitrate δ¹⁵N signals advected from the ETP. Comparison of several δ¹⁵N records for the last 25 ka distributed in the WP brings out a pattern of northward decrease in δ¹⁵N values and variability from the equator to off Mindano and then to marginal seas, supposed to be caused by the northward increase of local N₂ fixation. Therefore, the less glacial-interglacial changes in some δ¹⁵N records in the WP could imply that the glacial decrease in subsurface δ¹⁵N due to less denitrification in source waters from the ETP would have been isotopically compensated by a synchronous decrease in local N₂ fixation.


1. Introduction

The balance between surface N₂ fixation and water column denitrification (WCD) can modulate the δ¹⁵N signal of the upper ocean. N₂ fixation introduces atmospheric N₂ (δ¹⁵N ~ 0) into the oceanic fixed-N pool with little isotopic fractionation; whereas WCD strongly discriminates against ¹⁵N, leaving higher δ¹⁵N in seawater [Altabet, 2006]. Photic zone nitrate δ¹⁵N signals can be documented in sedimentary organic matter (OM) produced in surface waters where N is completely utilized [Altabet, 2006]. δ¹⁵N records from WCD zones in the eastern tropical Pacific (ETP) have provided a pattern of enhanced WCD during interglacials and reduced WCD during glacialis [e.g., Ganeshram et al., 2000]. Moreover, water column studies reveal that the nitrate isotope signals of WCD can be transported out of the WCD zones, e.g., in the tropical central and western Pacific (WP), by ocean circulations [Kienast et al., 2008; Sigman et al., 2009]. And sedimentary δ¹⁵N records similar to those from WCD zones have been observed in higher latitudes outside the WCD zones [Kienast et al., 2002; Martinez et al., 2006; Galbraith et al., 2008], suggesting a wide impact of WCD variability during the late Quaternary. However, there is still a lack of firm sedimentary record in WP showing signals from the WCD zones. For example, most δ¹⁵N records in the WP, e.g., the South China Sea (SCS), the Sulu Sea (SS), and the Okinawa Trough (OT), exhibit much less or even unchanged temporal variability (<2‰) [Kienast, 2000; Horikawa et al., 2006; Kao et al., 2008]. The invariant δ¹⁵N records (<5‰) in the SCS have been even interpreted as representing a constant mean oceanic δ¹⁵N during the late Quaternary [Kienast, 2000], and hence a minor impact of WCD zones.

The WP is an oligotrophic region where N₂ fixation supplies significant N to support primary production. Were local N₂ fixation temporally coupled with easterly advected WCD signals, N₂ fixation could have produced the isotopically light N to offset the isotopic signals from WCD zones [Galbraith et al., 2004]. We expect that this presumption can reconcile those less variant δ¹⁵N records in the WP. Additionally, because N₂ fixation in the WP is minimum near the equator relative to high-latitude sites [Hashihama et al., 2009; Shiozaki et al., 2010; Some et al., 2010], the western equatorial Pacific (WEP) is the most likely region to document the easterly WCD signals from ETP. In this paper, δ¹⁵N records from two sediment cores, one in the WEP and the other in the southern SCS, are reported. As will be shown, the two records exhibit quite different glacial-interglacial patterns, which could give us better understanding of the spatial and temporal changes of oceanic δ¹⁵N in the WP.

2. Oceanographic Settings

The WEP is a crossroad where several major ocean currents terminate and originate [Fine et al., 1994] (Figure 1). The westward North and South Equatorial Currents (NEC and SEC, respectively) bifurcate at ~15° latitudes, and the equatorward branches are the Mindanao Current (MC) in the north, the seasonal reverse New Guinea Coastal Current (NGCC) and the permanent New Guinea Coastal Undercurrent (NGUC) in the south. Most part of NGUC crosses the equator east of 135°E and feeds the eastward Equatorial Undercurrent (EUC) [Zenk et al., 2005]. Some part of MC feeds the North Equatorial Counter Current (NECC) and the other part is lost to the Indonesian throughflow (ITF). The cyclonic circulation composed of the NEC, MC, and NECC produces the cyclonic Mindanao Dome (MDD) centering at 7°N, 130°E. MDD is intensified during the Asian winter monsoon [Masumoto and Yamagata, 1991].

The northern branch of NEC eventually forms the main part of the Kuroshio Current (KC), which is the main nutrient source to the marginal seas in the WP, e.g., the East China Sea, the SCS, and the SS. The SCS is connected to the WP via the Luzon Strait (sill depth ~2000 m) in the northeast,
through which inflow of North Pacific Intermediate Water and KC brings nutrients from the eastern Pacific to the SCS and SS.

3. Samples and Experiments

[6] Core MD01-2386 (1°57.8′N, 129°47.6′E, 2816 water depth) was retrieved in 2001 at the northern shelf margin of the Halmahera Sea; and core MD01-2392 (9°51.1′N, 110°12.6′E, 1966 water depth) in the southwest SCS (Figure 1). The age model of MD86 is based on five radiocarbon dates over the past 18 ka [Jiang et al., 2004] and δ18O curve of planktonic foraminiferal Globigerinoides ruber. The age model of MD92 is based on aligning G. ruber δ18O record with that in a nearby core MD97-2151, independently corroborated by 14C dates and a few biostratigraphic, geomagnetic and tephrochronologic markers [Xie et al., 2007] (Figure 2).

[7] Sedimentary δ15N was analyzed on freeze-dried, homogenized bulk samples. Total organic carbon (TOC), total nitrogen (TN) and δ13C_TOC were analyzed on decarbonate samples treated with 1M HCl. The measurements were performed on a CE EA1112 C/N/S analyzer coupled to a DELTAplusXL mass spectrometer. The analytical precision is ±0.3‰ for δ15N and ±0.2‰ for δ13C. Biogenic silica (BSI) in MD86 was extracted, according to Mortlock and Froelich [1989], with 2 M Na2CO3 at 85°C for 5 h and analyzed by molybdate blue spectrometry.

4. Results and Discussion

[8] Downcore δ15N record in MD86 shows significant glacial-interglacial variability from 6.2 to 11.2‰ during the last two climate cycles. The lower values occur during cold periods and higher values during warm periods (Figure 2d). By comparison, δ15N in MD92 exhibits less changed lower values between 4.4 and 6.4‰ (Figure 2b). TN ranges from 0.05 to 0.14% in MD86 and from 0.05 to 0.11% in MD92. TN correlates linearly with TOC in both cores (r² = 0.91 in MD86 and 0.70 in MD92), with positive intercepts of TN of 0.016 and 0.003, respectively, suggesting minute but fixed inorganic N backgrounds in bulk N. Therefore, downcore δ15N variations are predominantly controlled by organic N.

[9] Values of δ15N_TOC (−22.1 to −19.8‰) and TOC/TN ratio (6.0 to 10.0) in both cores lie in the typical ranges for marine OM, and exhibit no trends or variability associated with climatic cycles. These values suggest minimum influence of terrigenous OM that can confound the bulk δ15N signature as an indicator of phytoplankton-utilized δ15N. Thus, sedimentary δ15N in this study is, indeed, reflective of the δ15N of the nitrate-fueling phytoplankton production.

4.1. Possible Causes for the Downcore δ15N Variability at Site MD86

[10] Previously published δ15N records at sites 3bPC, 5bPC, and SC-8 in the WEP (Figure 1) have been interpreted as the changes in size and location of MDD, assuming incomplete nitrate utilization (INU) of the upwelled nitrate and progressive uptake of the nitrate pool along flow path [Nakatsuka et al., 1995]. However, in the MDD the upwelled waters are present up to 75 m water depth, not reaching the surface [Udarbe-Walker and Villanoy, 2001]; and surface nitrate is undetectable even close to the dome center [Kienast et al., 2008]. Low particulate δ15N observed in the westernmost WEP (< 4‰) is related to isotopically light N input [Yoshikawa et al., 2005], i.e., N2 fixation [Kienast et al., 2008], rather than with INU. Therefore, changes in MDD and INU are unlikely responsible for the δ15N variability observed in MD86.

[11] Nowadays the well oxygenated water at site MD86 (DO >3 mg L−1 through the water column) [Bassinot and Baltzer, 2002] prevents local denitrification. This scenario could have held true in the past because its oceanographic

Figure 1. Study area and sediment cores. Red circles are study cores in this work, and stars are previously studied ones. Light gray areas are emerging lands during the Last Glacial Maximum. Arrows sketch the major currents presented in the text. MDN: Mindanao.

Figure 2. Downcore data of foram δ18O in (a) MD01-2392 and (c) MD01-2386, and δ15N in (b) MD92 and (d) MD86, and (e) TOC and (f) BSi in MD86. OIS: Oxygen Isotope Stage.
setting is open with a sharp bathymetric feature (Figure 1), suggesting minimum influence of sea level changes on local circulations. The absence of local denitrification, together with the much reduced WCD zones during the glacial that could have emanated to the WP discussed below, would have diminished the importance of N₂ fixation for the glacial lower δ¹⁵N values, because glacial δ¹⁵N in MD86 is not only much higher than that from N₂ fixation, but also slightly higher than that in the WCD zones.

[12] A decrease in the vertical supply of ¹⁵N-enriched nitrate to the photic zone due to deepening of thermocline has been proposed as a cause for the late Holocene δ¹⁵N decline observed off Mindanao [Kienast et al., 2008]. In MD86, tracers of productivity (TOC, BSi) exhibit higher values during the glacial periods (Figures 2e and 2f), implying shallower thermocline, which is also indicated by the larger foram δ¹⁸O and δ¹³C differences between the subsurface Pulleniatina obliquiloculata and surface G. riber at the site [Jiang et al., 2004]. This occurrence could have been caused by the intensified MDD and vertical mixing related with the enhanced East Asian winter monsoon during the glacials. The coincident lower δ¹⁵N values and shallower thermocline in MD86 during the glacials, however, contradict the application of thermocline shift as the cause of δ¹⁵N variations.

[13] Our δ¹⁵N record in MD86 is grossly similar to those from WCD zones, as shown by δ¹⁵N curve at ODP 893a in the Santa Barbara Basin [Emmer and Thunell, 2000] (Figure 3), implying a link between them. Presently, subsurface water in the WP is characterized by low Nₐ (Nₐ = N - 16 x P + 2.9 mmol) and higher than the oceanic “mean” values for nitrate δ¹⁵N (6–8‰), indicating the long distance advection of nitrate from WCD zones [Kienast et al., 2008]. Core-top δ¹⁵N of 7.9‰ in MD86 is well within the range of subsurface δ¹⁵N, suggesting the fidelity of sedimentary δ¹⁵N at the site to document subsurface δ¹⁵N. Therefore, it is conceivable that δ¹⁵N signals of WCD zones during climatic cycles could have been transported to the WP via subsurface and documented faithfully in MD86. The higher values and larger amplitudes than WCD signals at the site likely result from progressive uptake of the nitrate pool, the production of sinking OM, and its transportation and regeneration back to nitrate along the flow path [Sigman et al., 2009]. Together with the WCD signals found in the Pacific high latitudes [Kienast et al., 2002; Martínez et al., 2006; Galbraith et al., 2008], the results in MD86 suggest basin-wide subsurface δ¹⁵N changes in concert with the variations of WCD zones during climatic cycles, implying a great impact of changes in WCD zones [Ganeshram et al., 2000].

4.2. Spatial Pattern of δ¹⁵N Record in the WP

[14] Contrary to the results in MD86, the less changed δ¹⁵N in MD92 repeats the published records distributed throughout the SCS [Kienast, 2000], except one in a drift deposit receiving allochthonous OM input [Kienast et al., 2005]. In addition, sedimentary δ¹⁵N from nearby seas, e.g., in cores MD04 in the OT and SUP8 in the SS (Figure 1), also show low values and small amplitudes (3.2–6.2‰ range) [Horikawa et al., 2006; Kao et al., 2008] (Figure 3).

[15] However, in the open WEP the few reported δ¹⁵N records display heavy values and large amplitudes. For example, the records close to the MDD center (MD67 in Figure 3) show elevated values (6–7‰) during 10–7 ka, followed by a >3‰ decrease during 7–3 ka [Kienast et al., 2008]; and the records at sites 3bPC, 5bPC, and SC-11 exhibit glacial-interglacial variability between 9–12‰ or 11–15‰ [Nakatsuka et al., 1995]. The systematically heavy values at the latter three sites are attributed to the zonal transport of surface nitrate from ETP [Nakatsuka et al., 1995]. Comparatively, our record at site MD86 shows lower values than those of Nakatsuka et al. [1995], which might be due to the westernmost location of the site, where the influence of lateral advection of surface nitrate from ETP is minimal [Yoshikawa et al., 2006].

[16] We notice a spatial pattern of δ¹⁵N records showing northward decrease in absolute values and variability for the last 25 ka from the equator to off Mindanao and then to the OT, the SCS and the SS (Figure 3). Interestingly, this pattern co-occurs with the spatial pattern of the northward increase in N₂ fixation in the WP, with a minimum near the equator and “hot spots” in the KC and marginal seas due to the northward increase of dust deposition from the Asian continent [Wong et al., 2002; Hashihama et al., 2009; Someset al., 2010; Shiozaki et al., 2010]. In the absence of N₂ fixation, sedimentary δ¹⁵N records in the WP would have paralleled those in WCD zones [Galbraith et al., 2004], as shown in MD86 where N₂ fixation is minimum. Therefore, we speculate that the WCD signals would have been greatly masked by local N₂ fixation in off Mindanao, SCS, SS, and OT because of the opposing δ¹⁵N signals of N₂ fixation and WCD. Thus the less changed δ¹⁵N during climatic cycles in these WP records would imply that the glacial decrease in subsurface nitrate δ¹⁵N due to less WCD zones would have been isotopically compensated by a decrease in local N₂ fixation. This occurrence is quite similar to what has been proposed in the Caribbean Sea [Ren et al., 2009]. Nevertheless, more records associated with N₂ fixation in the WP are necessary to confirm this supposition.

[17] Acknowledgments. This work is granted by Chinese NSF (40876028) and the National Basic Research Program (2009CB421206). Zhimin Jian at Tongji Univ. provides foram δ³⁴S data in MD01-2386.


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