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# Increase in water column denitrification during the deglaciation controlled by oxygen demand in the eastern equatorial Pacific

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Received: 17 April 2009 – Accepted: 4 May 2009 – Published: 19 May 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Here we present organic export production and isotopic nitrogen results over the last 30 000 years from one core localized off Costa Rica (ODP Site 1242) on the leading edge of the oxygen minimum zone of the Eastern Tropical North Pacific. Marine export production reveals glacial-interglacial variations with low organic matter (total organic carbon and total nitrogen) contents during warm intervals, twice more during cold episodes and double peaked maximum during the deglaciation, between ~15.5–18.5 and 11–13 ka BP. When this new export production record is compared with four nearby cores localized within the Eastern Pacific along the Equatorial divergence, a good agreement between all the cores is observed, with the major feature being a maximum of export during the early deglaciation. As for export production, water-column denitrification represented by sedimentary  $\delta^{15}\text{N}$  records along the Eastern tropical North and South Pacific between 15° N and 36° S is coherent as well over the last deglaciation period. The whole isotopic nitrogen profiles indicate that denitrification increased abruptly at 19 ka BP to a maximum during the early deglaciation, confirming a typical Antarctic timing. It is proposed that the increase in export production and then in subsurface oxygen demand lead to an intensification of water-column denitrification within the oxygen minimum zones in the easternmost Pacific at the time of the last deglaciation. The triggering mechanism would have been primarily linked to an increase in preformed nutrients contents feeding the Equatorial Undercurrent driven by the resumption of overturning in the Southern Ocean and the return of nutrients from the deep ocean to the sea-surface. An increase in equatorial wind-driven upwelling of sub-surface nutrient-rich waters could have played the role of an amplifier.

## 1 Introduction

The extent of intermediate water suboxia and open ocean denitrification varies significantly with climate with a positive feedback between the production of  $\text{N}_2\text{O}$ , a strong

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greenhouse gas, during denitrification and warming. Increased oxygenation of intermediate waters during glacial intervals has been attributed to both enhanced oxygen supply during water mass formation (ventilation) and decreased oxygen demand due to lower export production in the subsurface (Galbraith et al., 2004; Ganeshram et al., 1995, 2000; Altabet et al., 1995; Altabet et al., 2002). Higher glacial wind speeds and lower temperatures increase modeled horizontal oxygen supply to the oxygen minimum zones (OMZ) (Meissner et al., 2005). Co-located records of export productivity and the extent of denitrification indicate that oxygen demand due to local export is not responsible for the observed changes in suboxia and denitrification along the eastern Pacific margins. However, export in regions outside of suboxic zones, provided they are upstream in terms of ocean circulation, may have played an important role in drawing down subsurface oxygen concentrations. Net oxygen demand on such a large scale, is related to the preformed nutrient content of the low latitude thermocline. If low latitude export productivity is higher overall, then suboxia at the terminus of intermediate water flow paths will intensify. Glacial-interglacial changes in the preformed nutrients are hypothesized to drive changes in both Equatorial export productivity and water column suboxia and denitrification in the eastern Pacific (Brunelle et al., 2007; Loubere, 2002; Loubere et al., 2007; Robinson et al., 2007; Sarmiento et al., 2004; Toggweiler et al., 1991). Recent modeling efforts suggest that an increase in preformed nutrients, associated with intensified Southern Ocean overturning circulation during Antarctic Warm Periods, explains mid-stadial increases in N<sub>2</sub>O concentrations observed in ice core records (Schmittner et al., 2007).

Sediments from within the Eastern Tropical Pacific (ETP) directly record changes in preformed nutrient concentrations and suboxia. The ETP houses both the equatorial upwelling system as well as two large regions of open ocean suboxia underlying the eastern boundary current upwelling systems centered off Peru and Mexico. Nutrients subducted in the thermocline in the Subantarctic Zone of the Southern Ocean as Subantarctic Mode Water (SAMW) are the dominant fuel for productivity in the low latitude oceans, with the exception of the North Pacific (Sarmiento et al., 2004). Variations in

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performed nutrient content of SAMW are likely felt in a direct way in the EEP, because SAMW feeds into the Equatorial Undercurrent (EUC) that then shoals eastward across the Pacific. Upwelling delivers EUC waters to the surface in the equatorial cold tongue. Throughout the equatorial cold tongue, radiocarbon-poor surface waters indicate their distal origins as SAMW (Toggweiler et al., 1991).

Localized oxygen demand in eastern equatorial Pacific (EEP) is thought to drawdown  $O_2$  in the EUC waters that enter the poleward undercurrents (Lukas, 1986). Glacial-interglacial sedimentary nitrogen isotope records from the SE and NE Pacific margins indicate that the extent of water column denitrification was quite low during the last glacial period and increased significantly upon deglaciation (Altabet et al., 1995; Altabet et al., 2002; De Pol-Holz et al., 2006; Galbraith, 2006; Ganeshram et al., 2002; Ganeshram et al., 2000; Robinson et al., 2007). We hypothesize that the deglacial maximum in suboxia and water column denitrification is related to the increase in oxygen demand in the EEP and this in turn results from an increase in the performed nutrient content of SAMW (Loubere, 2002; Loubere et al., 2007; Spero and Lea, 2002; Robinson et al., 2005; Robinson et al., 2007).

## 2 Material and methods

In this study, we compare regional trends in export productivity in the EEP with ETP margin records of water column denitrification, with the addition of new export and nitrogen isotope data from ODP Site 1242, located on the Costa Rica margin, underlying the leading edge of the suboxic OMZ. Site 1242 is located at  $7^{\circ}51.352' N$ ,  $83^{\circ}36.418' W$  in a shallow basin at 1364 m water depth within the structurally complex intersection between Cocos Ridge and the Mesoamerican trench (Fig. 1). The site is in a graben on the crest of the Cocos Ridge. The sediments consist of lithologically homogenous hemipelagic olive-brown clayey silts, with minor amounts of well-preserved biogenic components (Mix et al., 2003). Geochemical analyses presented here at Site 1242 were measured every 4 cm in the upper 4.5 m, i.e. every 0.3 kyr on average.

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The age model, from Benway et al. (2006), is based on a  $\delta^{18}\text{O}$  record on benthic foraminifers compared with both benthic  $\delta^{18}\text{O}$  and radiocarbon dates from a co-located core (ME0005A-43JC). Sedimentation rates over the studied interval range between 4 and 15  $\text{cm ka}^{-1}$ . Nitrogen isotope ratios ( $\delta^{15}\text{N}$ , ‰) and total nitrogen contents (TN, wt%) were determined on dried, ground bulk sediment, using a Carlo-Erba CN analyser 2500 interfaced directly to a Micromass-Isoprime spectrometer using ~20–30 mg aliquots of homogenized bulk sediment. The precision of the isotopic analyses based on replicates of international standards and samples is better than  $\pm 0.2\%$ . Nitrogen isotopic values are reported in delta ( $\delta$ ) notation where:  $\delta^{15}\text{N} = ((^{15}\text{N}/^{14}\text{N}_{\text{sample}} / ^{15}\text{N}/^{14}\text{N}_{\text{standard}}) - 1) \times 1000$ , and the standard is atmospheric  $\text{N}_2$ . Organic carbon (TOC, wt%) measurements were carried out using a LECO C-S 125 analyser after treatment of the sediment with hydrochloric acid to remove calcium carbonate, where precision were better than  $\pm 5\%$ .

A comparison of TOC and TN at site 1242 suggests that a small amount of the nitrogen may come from an inorganic source (certainly mostly ammonium), as indicated by the positive intercept of TN when plotting TOC against TN ( $\text{TN} = 0.0747 \text{ TOC} + 0.075$ ;  $r^2 = 0.909$ ; not shown). Ammonium is generally fixed within clay lattices (Müller, 1977). However, due to the large amount of TOC in core 1242, the isotopic composition of total nitrogen mostly reflects that of organic matter rather than inorganic N which constitutes only a small fraction of total N in these sediments.

At present, Site 1242 is located under the warm, relatively low-salinity waters of the intertropical convergence in the Panama Basin. Biological productivity is relatively low compared to other continental margin settings (Pennington et al., 2006). Off Costa Rica, nitrates are completely consumed annually in the surface waters overlying site 1242 indicating that the N isotope record at this site should reflect the N isotopic composition of the upwelled water. In this region, subsurface  $\text{O}_2$  concentrations at ~150–200 m average 5–6  $\mu\text{M}$  on an annual basis with some seasonal variations according to hydrostation data from the World Ocean Atlas database (<http://www.nodc.noaa.gov/>). The threshold oxygen level below which suboxia and then denitrification can take place

is not absolutely determined and some authors proposed based on field observations that it ranges between 2 and 10 mM (see Codispoti et al., 2005). Oxygen concentration within the OMZ (between 300 and 700 m) over Site 1242, fall into this range. Water column denitrification imparts a strong isotopic signature on the sub-surface nitrate pool due to the faster reaction rate of the lighter isotope,  $^{14}\text{N}$ , during nitrate reduction. The remaining nitrate pool is enriched in  $^{15}\text{N}$ . The extent of denitrification is reflected in the isotopic composition of nitrate that is upwelled and that signal is transferred to the organic matter produced during photosynthesis and eventually buried on the seafloor. Sitting on the leading edge of the OMZ, Site 1242 should provide a minimum estimate of the denitrification changes, without overprinting by regional productivity features.

### 3 Discussion and conclusion

#### 3.1 Export productivity and denitrification in the Eastern Equatorial Pacific

At site 1242, total organic carbon (TOC) contents are high all along the time interval 0–30 ka BP, varying between 2.2 and 3.8 wt%. Total nitrogen (TN) contents follow the same pattern than the TOC profile, and vary between 0.24 and 0.38 wt%. Both records present glacial-interglacial variations with low organic matter contents during warm intervals, twice more during cold episodes and double peaked maximum during the deglaciation, between  $\sim 15.5$ –18.5 and 11–13 ka BP. A significant contribution of terrestrial organic matter is excluded at this site. The C/N ratio is too low (ranging between 9 and 10.5) and is rather indicative of marine organic matter (Meyers, 1997). The sedimentary organic matter variability at site 1242 more likely reflects changes in local export production and/or in dilution by one of the major sedimentary components (silicoclastic and biogenic carbonate material). A rough estimation of past export organic carbon fluxes changes using conventional mass accumulation rates calculation method (sedimentation rates  $\times$  dry bulk density  $\times$  TOC%) give a record quite similar in terms of temporal variability than the TOC and TN concentrations. The first mech-

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anism controlling the export and then the burial of the organic matter seems to be the exportation from the sea surface.

However, mass accumulation rates of sedimentary components should be interpreted with caution because of the potential influence of lateral sediment redistribution during syn- and post-depositional processes on the seafloor (Francois et al., 2004). In addition, deriving from a single core a regional interpretation may be challenging given the large regional variability of the productivity response to climate that characterize some oceanic regions (Bertrand et al., 1996). Then, we also compare our own results with TOC and TN concentration from 4 nearby sites between 90° W and the Costa Rica margin (TR163-22, ODP Site 1240, ME0005-24JC, P7GC; see Figs. 1 and 2). All these cores show good agreement with Site 1242 off Costa Rica across the glacial-interglacial transition between themselves (Pedersen et al., 1991; Farrell et al., 1995; Kienast et al., 2006; Robinson et al., submitted), and more importantly with <sup>230</sup>Th-normalized organic carbon flux estimates from ME0005A-24JC (Kienast et al., 2006; Fig. 2) and from site 1240 (Pichevin et al., 2007) which are more reliable estimation of marine primary export production (François et al., 2004). Since this method of normalization estimates absolute vertical organic fluxes for each measurement, a larger export during the deglaciation with a peak centered at ~15 ka BP in the EEP is clearly evident, all the more that sedimentary focusing was certainly greater during the Holocene in this region (Kienast et al., 2006). Therefore, a combination of the different records from the EEP all together indicate that export production from across the EEP display a regionally coherent pattern of change over the last 30 ky, with higher overall export during the glacial interval, a maximum during the deglaciation, especially during the early deglaciation, and low export in the Holocene.

The extent of water column denitrification, as represented by sedimentary  $\delta^{15}\text{N}$  in ETP margin sediments, appears to have been regionally coherent as well. Along the margin of the Americas, between 15° N and 36° S from southern Mexico to southern Chile, denitrification was weak during the last ice age and increased abruptly at 18–19 ka BP to a maximum at ~15 ka, with a slight decrease around 13–14 ka (Fig. 3;

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Site 1242 off Costa Rica: this study; Core GeoB 7139-2: De Pol-Holz et al., 2006; Core ME5A-11PC: Hendy and Pedersen, 2006, and see also Thunell and Kepple, 2004). Off Peru at sites W7706, the deglacial  $\delta^{15}\text{N}$  peak (not shown in Fig. 3) is older and occurred at  $\sim 16$  ka. The age-model of all the cores is based on a combination of radiocarbon and oxygen isotope on benthic foraminifera, except off Peru where it is based on alkenones  $^{14}\text{C}$  measurements because of the paucity or the absence of carbonate tests (Higginson and Altabet., 2004). Yet, it has been demonstrated that the radiocarbon age given by alkenones were older (1 to 4.5 ka) than the age given by foraminifera tests (Mollenhauer et al., 2003). We can then admit that the denitrification peak off Peru was synchronized with the other sites. In both the Chilean and the Costa Rica records,  $\delta^{15}\text{N}$  and thus local denitrification remains relatively steady with elevated values throughout the last 10 ka, whereas the records off Peru and Southern Mexico (Gulf of Tehuantepec) indicate a decrease during this time interval (Higginson and Altabet, 2004; Hendy and Pedersen, 2006). Such a Holocene  $\delta^{15}\text{N}$  decrease toward glacial values is not specific of the southern Mexican margin but has already been observed in other records within or proximal to denitrifying areas (Higginson and Altabet, 2004; Pride et al., 1999; Martinez et al., 2006). This feature could result from an overprinting of the denitrification signal by local changes in nutrient utilization by phytoplankton at the sea-surface during photosynthesis related to upwelling activity and/or in by variable local hydrologic conditions influence.

### 3.2 Enhanced nutrient supply during the deglaciation

The deglacial peaks in export production the in EEP are coincident with the peaks in denitrification inferred from the nitrogen isotope records. This observation fits with the hypothesized increase in subsurface oxygen demand leading to an intensification of the oxygen minimum zone in the easternmost Pacific. In order for the increase in export in the EEP to be causally related to the increase in water column denitrification on the margin there must have been a net increase in oxygen demand along the flow path of SAMW, not merely a local one. The EEP is directly connected to SAMW, the

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primary source of nutrients to the low latitudes, via the EUC. However, the increase in export could be the result of either intensified upwelling or enhanced nutrient content of EUC waters.

The good covariance between higher marine export production and decreased alkenones- or Mg/Ca-based sea-surface reconstructions at sites ME5A-24JC (Kienast et al., 2006) and 1242 (Klinkhammer et al., 2009) respectively in the EEP and the ETP would lend support to the hypothesis of increased wind-driven upwelling activity during the deglaciation (Kienast et al., 2006; Bush and Philander, 1998), although not so clear for the Holocene period. There are however some other studies which did not describe such a cooling associated with the deglaciation in this area of the EEP but rather an Antarctic-type deglacial pattern starting at ~19 ka BP (Koutavas et al., 2002; Lea et al., 2006; see also Kiefer and Kienast, 2005 for a synthesis). Since lower SST in the EEP may also result from colder source waters in the Austral Ocean without invoking large changes in upwelling activity, the understanding of the relationships between SST and productivity is then not straightforward.

There is strong evidence for enhanced nutrient content of subsurface EUC waters. Records of planktonic foraminifera  $\delta^{13}\text{C}$  and a residual  $\delta^{15}\text{N}$ , washed of the regional denitrification overprinting, suggest that the upwelling of relatively nutrient-rich water in EEP led to deglacial increases in export (Spero and Lea, 2002; Pena et al., 2008; Robinson et al., 2009). Such an increase in nutrient supply would have the larger effect on low latitude export and subsurface oxygen demand required to drive the change in the strength of the OMZ (Fig. 3). The increase in preformed nutrients (low  $\delta^{13}\text{C}$  values at Site 1240; Fig. 3) during the deglaciation was likely driven by the resumption of overturning and the return of nutrients (and  $\text{CO}_2$ ) from the deep ocean to the surface ocean-atmosphere system (Spero and Lea, 2002; Pena et al., 2008; Robinson et al., 2009). Evidence for the release of sequestered deep waters comes from radiocarbon of intermediate and deep ocean benthic foraminifera (Marchitto et al., 2007; Schmittner et al., 2007) (Fig. 3).

Longer timescale records of  $\delta^{15}\text{N}$  along the NE Pacific margin indicate that glacial-

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interglacial variations in the extent of denitrification have persisted for the last several million years, where cooler climate periods are associated with weak or negligible denitrification (Liu et al., 2008; Altabet et al., 1999). In the Equatorial Pacific, Pena et al.'s 500 ka BP  $\delta^{13}\text{C}$  record of planktonic foraminifera indicates that preformed nutrients peaked during each of the 4 glacial terminations (Pena et al., 2008). This pulse of nutrients likely caused the peaks in export and oxygen demand that led to rapid intensification of suboxia during glacial terminations in general. However, export records indicate that this elevated input of nutrients was not sustained. This suggests an additional factor at work. Two alternative mechanisms to maintain suboxia through the interglacials exist: 1) a change in ventilation associated with the bimodal climate variability and the physical controls on oxygen supply (Meissner et al., 2005) or 2) Local fluctuations in export and oxygen demand. If indeed there was a step-like decrease in ventilation associated with the termination of the glacial period, one would then expect sedimentary  $\delta^{15}\text{N}$  to be elevated relative to glacial values throughout the interglacial periods, as seen in the records from Chile and Costa Rica shown here. However, records from the Peru margin or from the Gulf of Tehuantepec off Southern Mexico show decreases to near glacial low values in the late Holocene (Higginson and Altabet, 2004; Hendy et al., 2006; Chazen et al., 2008). These records are from near shelf sediments and so may reflect local conditions rather than the broader regional situation.

*Acknowledgements.* We are grateful to Alan Mix, Ralf Tiedemann, Peter Blum, the Shipboard Scientific party, captain and crew of ODP Leg 202. We thank J. Firth, P. Rumford and B. Horan for their great help in sampling ODP Site 1242 at College Station, Texas. This research used samples provided by the Ocean Drilling Program (ODP). The ODP is sponsored by NSF and participating countries under management of Joint Oceanographic Institutions (JOI), Inc. We thank Olivia Bertran and Isabelle Billy for assistance in the lab, and Elfi Mollier-Vogel for her help in drawing Fig. 1. We thank Alan Mix and Markus Kienast for stimulating and constructive discussions.

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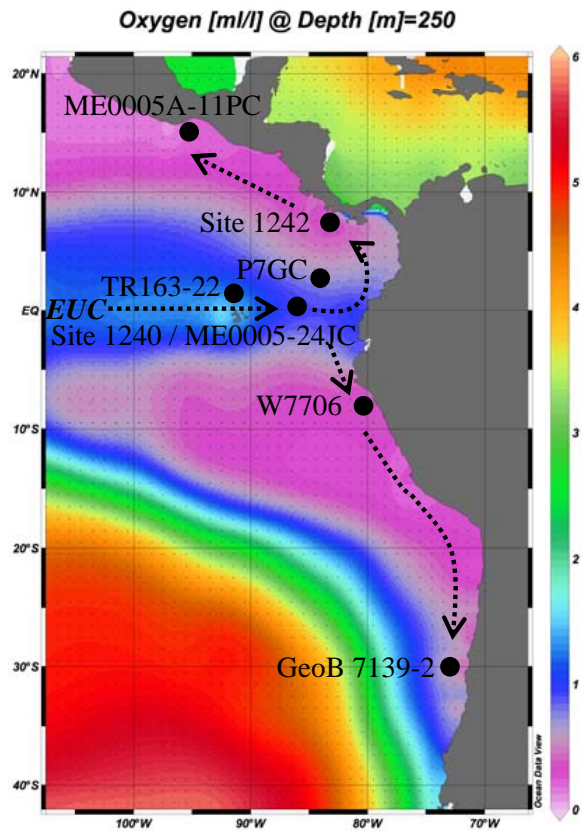
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**Fig. 1.** Sub-surface dissolved oxygen concentrations at 250 m depth (Garcia et al., 2006). Locations of ODP Site 1242 (this study) as well as additional sites (TR163-22, ODP Site 1240, ME0005-24JC, P7GC W7706, GeoB 7139-2) discussed in the text are marked with a black dot. Sub-surface current EUC (Equatorial Undercurrent) is also indicated by an arrow.

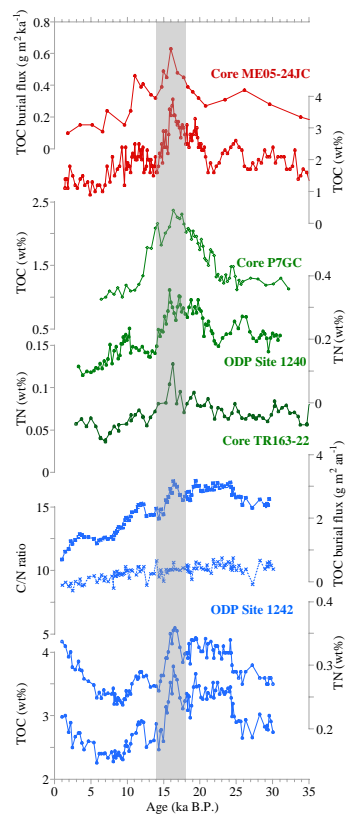
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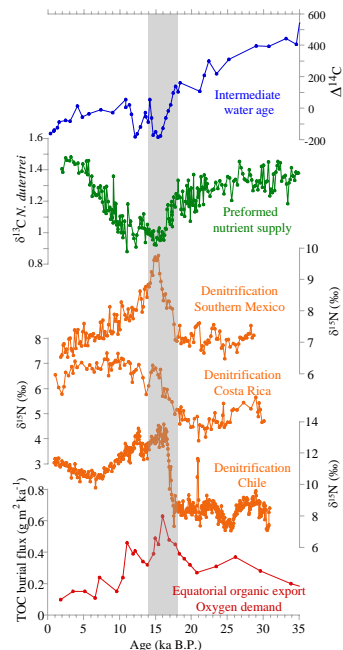
**Fig. 2.** Downcore profiles of TOC (wt%) and TN (wt%) contents, of C/N ratio, and of burial fluxes of TOC (in  $\text{g m}^{-2} \text{ka}^{-1}$ ) at ODP Site 1242 (in blue). Downcore profiles of TOC (wt%), TN (wt%), and TOC burial fluxes for additional sites (in green and blue) referred in the text and localized in Fig. 1. The shaded area highlights the interval of organic export maximum in the Eastern Equatorial Pacific during the deglaciation.

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**Fig. 3.** Downcore profiles of organic export flux representative of the EEP as represented by  $^{230}\text{Th}$  normalized TOC flux at Site ME005A-24JC (from Kienast et al., 2006), of  $\delta^{15}\text{N}$  representative of water-column denitrification off Costa Rica (ODP Site 1242, this study), off Chile (Core GeoB7139-2 from De Pol-Holz et al., 2006), off Southern Mexico in the Gulf of Tehuantepec (Core ME0005A-11PC from Hendy and Pedersen, 2006), of planktonic foraminiferal  $\delta^{13}\text{C}$  (*N. dutertrei* from Site 1240; Pena et al., 2008), and of radiocarbon composition of benthic foraminifera from offshore Baja California in the northeast Pacific (from Marchitto et al., 2007). The shaded area highlights the interval of the deglaciation characterized by higher export production synchronous with higher water-column denitrification, driven by higher nutrient supply in the EEP and an increase in the influx of old and nutrient-rich bottom waters toward the surface.

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