

Interactive comment on “Increase in water column denitrification during the deglaciation controlled by oxygen demand in the eastern equatorial Pacific” by P. Martinez and R. S. Robinson

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Reply to REVIEWER 2

We acknowledge Reviewer 1 for his/her comments on our manuscript.

General comment 1 of Reviewer 2 If the equatorial oxygen demand was the only forcing behind denitrification changes in the oxygen minimum zones of the eastern North and South Pacific, one would expect very similar changes in the $d_{15}N$ records shown in the manuscript (off Chile, off Costa Rica and off Mexico). Just consider what is shown in Figure 3. The transition from low glacial values to the deglacial maximum in core ME0005A-11PC (off Southern Mexico) starts at 18ka BP. The core off Chile starts at

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17.5ka BP and the ODP Site 1242 (off Costa Rica) very slowly at (arguably) 20ka BP. The new data (off Costa Rica) doesn't show a deglacial maximum as the other sites (it reaches its maximum as a double peak centered at 10ka BP). To me, the 2.5 kyr difference between the onsets of denitrification is rather large as to consider them synchronous (even with the age model limitations). Moreover, The ODP 1242 Site $d_{15}N$ does not show a reduction towards the Holocene as the other records. The deglacial rate of change in the $d_{15}N$ records is also very different. While the Chile core shows a very dramatic increase (1kyr), the Mexico site is a bit slower (2kyr) and the Costa Rica site is very gradual (5ka, if one considers the local maximum at 15ka BP to be the deglacial maximum). How the authors explain these differences if they consider the oxygen demand as the single driving mechanism? I need a better argument than just referring the records as being 'in good agreement'.

We do not agree with this comment. We could see that the deglacial transition from low glacial $d_{15}N$ values to higher $d_{15}N$ values is rather slow at site 1242 compared to the two other sites. First, we think that this could be partly due to age model limitations, since we did not tuned some records against others, and then since each core has its own age model. At site 1242, the stratigraphy is based on a $d_{18}O$ on benthic foraminifers compared with both benthic $d_{18}O$ and 6 radiocarbon dates from a collocated core (see Benway et al., 2006), and only 1 AMS 14C between 15 and 20 kyr. Besides, we do not agree when the Reviewer 2 write that the "2.5 kyr difference between the onsets of denitrification is rather large as to consider them synchronous". The two cores off Southern Mexico and Chile (Hendy and Pedersen, 2006; De Pol-Holz et al., 2006) present clearly synchronous deglacial increase at about 18 kyr, or possibly 17.5 kyr, this difference being certainly the result of age model uncertainties. In our opinion, the deglacial increase at site 1242 occurs also at 18 kyr, and is then synchronous with the other two records. Off Costa Rica, the $d_{15}N$ record show an increase of $\sim 0.5\text{‰}$ during the interval 20-18 kyr ; this 0.5‰ change is on the same range than the precision of the $d_{15}N$ analyses which are $\sim \pm 0.2\text{‰}$. Therefore, we can admit that this change between 20 and 18 kyr is rather small. On the other hand, a

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large d15N increase of ~2‰ is observed between 18 kyr and the deglacial maximum at 15 kyr. Therefore, we think that our observation that the 3 cores show a synchronous d15N increase between 18 kyr and a deglacial maximum is supported by the data. But because this is an important comment, we will give these precisions in the revise manuscript.

General comment 2 of Reviewer 2 In the same line, when one compares the different records of organic C or N export from the surface to the ocean floor (MAR, %wt, 230Th fluxes), there seems to be more heterogeneity between them to accept the blank statement that "a good agreement between all the cores is observed" (p.5145, line 10). For example, the ODP 1242 Site (off Costa Rica) shows initial TOC and TN increase at 25ka BP, the same can be argued in the lower resolution 230Th-normalized C fluxes in cores ME0005-24JC and TN in ODP Site 1240. Paradoxically, the d15N records presented in Figure 3 show decreasing! trends (lower denitrification) during this time. Again, I want the authors to discuss how these differences could arise if oxygen demand in the equatorial region is the main driving mechanism.

Our paper discuss principally the influence of export production and hence oxygen demand recorded at sites upstream in terms of oceanic circulation on d15N variations and hence denitrification along the Eastern tropical Pacific during the deglaciation. We produced new data that are also further compared to published records. We decided to show the entire records and not to cut them for the period of interest, i.e. the deglaciation. Therefore, our interpretation that we expect valid for the deglaciation period may be not for older or younger intervals, which are not really discussed in our manuscript indeed. We understand that lack of course lead to some questions. It is true that the "equatorial organic export – oxygen demand" leads changes in denitrification. Denitrification is known to occur in oxygen minimum zones when dissolved oxygen concentrations fall down to 0.1-0.2 ml/l (Lipschultz et al., 1990; Codispoti et al., 2001). There is thus clearly a threshold level of oxygen for bacterial denitrification to occur if metabolizable organic matter is locally available. Our suggestion is that the oxygen demand

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in the Equatorial Pacific must have reached a certain level in order to trigger denitrification in the water column of the Eastern north and south pacific. Clearly, the work of Kienast et al. (2006) demonstrate that

General comment 3 of Reviewer 2 To wrap up this comment and touching what the authors discuss in the last paragraph of the paper (p.5153, lines 7-19), I would want the authors to explain in more detail why denitrification levels remained high during the Holocene in the site off Chile and Costa Rica. In my view, there are different mechanisms operating in the region not only during the Holocene, but also different mechanisms behind the deglacial onset of denitrification in the different areas. I therefore, highly encourage the authors to provide a revised version of the paper where this differences are brought to the surface instead of trying to overlook them. The all too brief discussion about these differences in the last paragraph of the manuscript is no enough. I would like to remind them that they are presenting only one additional record that seems to open more questions than actually it resolves.

It is the balance between denitrification (both in the water column and within the sediments) and nitrogen fixation that determines the abundance and isotopic composition of nitrate in the ocean on glacial-interglacial timescales (Codispoti and Christensen, 1985; Deutsch et al., 2004). These data suggest no clear change between the last glacial period and the present day and a similar global d15N of nitrate during the glacial period and the Holocene. N2 fixation by diazotrophic organisms and its effect on the global modern and past cycle of nitrogen is certainly not as well constrained and understood as the role of denitrification. N2 fixers (diazotrophic organisms like *Trichodesmium*) have a clear ecological advantage in oceanic regions when the availability of nitrates (or even fixed nitrogen) is very low but the availability of phosphate (and iron) are particularly high (low N/P, or positive N* values; Gruber and Sarmiento, 1997). Hence, *Trichodesmium* blooms are expected to occur typically in oligotrophic oceanic regions, where high insolation, water column stability (stratified conditions), and warm temperatures favor this group of organisms together with their specific requirements

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for nutrients (Karl et al., 2002). Then, N₂ fixation has been estimated to account for ~50% of the organic carbon exported from the photic zone in oligotrophic regions of the warm subtropical ocean (Karl et al., *Nature* 388, 1997). However, there are now several lines of evidence for the co-occurrence of water column denitrification and N₂ fixation within the same suboxic areas (Deutsch et al., *Nature* 445, 2007). However, on a regional scale, global and basin scale rates of nitrogen fixation remain poorly constrained due mostly to undersampling. There is ongoing debate as to how closely coupled nitrogen fixation and denitrification are, but geochemical evidence is also accumulating that nitrogen fixation may be associated with oxygen minimum zones of the tropical ocean as well. In addition, N₂ fixing organisms present a large variety, each with their own ecological and physiological requirements; some live in the water column as free organisms whereas others live as symbionts with algae such as Diatoms (Karl et al., 2002). Capone, Subramanian et al. (1998) have found large populations of N₂ fixing cyanobacteria in the Arabian Sea, a region also characterized by its intense oxygen minimum zone and denitrification. N₂ fixation introduces 15N-depleted nitrogen to the ecosystem, resulting in a clear isotopic contrast between the surface mixed layer and the OMZ (Montoya and Voss 2006). The isotopic signature of N₂ fixation propagates into the OMZ via sinking particles, but on average data seem to suggest that denitrification is the dominant process determining the isotopic composition of suspended particles in the Arabian Sea OMZ. Blooms of cyanobacteria like *Trichodesmium* have been also reported in non-suboxic coastal upwelling like off NW Africa (Ramos et al., MEPS 301, 2005). We can therefore not exclude that the balance between N₂ fixation and denitrification, whose effect on d15N are opposite, may lead to some regional differences as seen in the nitrogen isotopes records during the Holocene. Of course, a change in ventilation associated with the bimodal climate variability and the physical controls on oxygen supply (Meissner et al., 2005) or local fluctuations in export and oxygen demand are also possible explanations for different Holocene d15N trends. Off Costa Rica and off Chile (this study; De Pol-Holz et al., 2006; Robinson et al., 2007), local oxygen demand cannot explain the d15N changes during the Holocene,

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and ventilation changes could be one of the explanation. In their study, Meissner et al. (2005) show that water masses can significantly change the supply of oxygen to suboxic zones and therefore; however, their model experiments focused on differences between glacial and interglacial periods and not on the variability during an interglacial period like the Holocene. SAMW and AAIW are the dominant water masses that feed the EUC and then control subsurface dissolved oxygen concentration in the Equatorial Pacific with oxygen demand. The conversion of AAIW and Subantarctic Mode Water in the Southern Ocean increased substantially during the Holocene (Pahnke and Zahn, 2005) and could be responsible for a gradual decline in denitrification as observed off Chile for instance. It seems that this enhanced flux of oxygen did not influence site 1242; this could be the result its location in a more confined area largely influenced during the Holocene by elevated freshwater input (Benway et al., 2006).

We hope that our reply will satisfy all the comments and the demands of Reviewer 1. Sincerely.

Philippe Martinez, on behalf of co-authors

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