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Biogeosciences Discussions

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

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Reply to REVIEWER 1

We acknowledge Reviewer 1 for his/her comments on our manuscript. First, Reviewer 1 makes one central statement, writing that our manuscript provides an original approach for the understanding of deglacial increase in water column denitrification in the eastern Pacific. Our manuscript describes first the good agreement in terms of export organic production over the last 30 kyr between cores located in the eastern equatorial and tropical Pacific. Then we explore the linkages between oxygen demand due to variable organic export production in the equatorial Pacific upstream in terms of oceanic circulation and water column denitrification.

General Comment 1 of Reviewer 1: - Corg (and related TN) is the only proxy considered to reconstruct changes in export production through time. As the authors certainly reckon, the sedimentary Corg mass accumulation rate (MAR) is highly dependent on oxygen exposure time and the oxygen concentration at the water-sediment interface as well as within the sediment (e.g. Hedges et al., 99). I agree that there seems to be a "good agreement between all cores" shown in Fig. 2 but this does not necessarily mean that the main and only parameter controlling Corg accumulation is export from the surface as inferred by the authors in a very vague unreferenced statement (p. 5151, l. 1-2). In particular it is striking that the Corg MAR at site ODP 1242 (where "biological productivity is relatively low compared to other continental margin settings" - p. 5149, l. 22-23) is at least five times higher (if I'm correct – there is a typo in the label) than at site Me05-24JC (Kienast et al., 06) and almost 10 times higher than at ODP 1240 (Pichevin et al., 09). Can this exclusively be explained by changes if export flux of organic carbon? The study would benefit a lot by considering additional proxies for export production such as opal, biogenic barium (where applicable) and/or biomarkers as well as records of redox-sensitive trace metals. I do not necessarily mean that the authors should provide more measurements from their own archive but they should significantly expand the argumentation to other available records from the literature as well as to discuss the potential for lower oxygenation to modulate to sedimentary Corg distribution and its related impact on the discussion.

We agree with Reviewer 1 that Corg concentrations and mass accumulation rates variations recorded within sediments could be related to oxygen exposure time and oxygen concentration at the water-sediment interface and in the sediments, therefore to mineralization and diagenetic processes, and not only to the intensity of the biological production and its exportation. And we recognize that this is an aspect that we did not discuss in our manuscript, assuming that exportation from the euphotic zone was the dominant process.

Since more than 3 decades and the work of Demaison and Moore in 1980, the question of what control organic matter preservation in oceanic sediments is recognized as a very complex matter of debate, still controversial. Some authors argued that the absence or the near-absence of oxygen favored the preservation of sedimentary organic matter (Demaison and Moore, 1980; Henrichs and Reeburg, 1987; Canfield, 1989; Ingall et al., 1993). For instance, it was shown that anaerobic processes like sulfate-reduction were less efficient for organic matter degradation and would favor sulphurization process (REF). Based on these results, anoxic basins (e.g., the Black Sea) have been considered as the best modern analogs to understand source rocks and fuel resources formation. However, many studies have also reported evidences for the opposite, i.e. that there is no clear evidence, or even no evidence at all, for higher organic matter preservation in the absence of dissolved oxygen (Pedersen and Calvert, 1990; Calvert and Pedersen, 1992; Bertrand and Lallier-Vergès., 1993; Ganeshram et al., 1999; Calvert et al., 1995). It was shown for instance that maxima in Corg concentrations on continental slopes do not systematically coincide with oxygen minimum (Pedersen and Calvert, 1990; Calvert et al., 1995; Ganeshram et al., 1999). Besides, other studies demonstrate that organic matter degradation kinetics by anoxic processes like sulfate-reduction was comparable to suboxic (e.g., denitrification) or oxic processes (cf. Lee, 1992; Henrichs, 1992). Based on these observations, organic matter accumulation rates in oceanic sediments will be first controlled by the export flux from the euphotic zone (Pedersen and Calvert, 1990; Calvert and Pedersen, 1992). We agree with Reviewer 1 that the exposure time to oxidants like dissolved O2 is one important parameter that might control Corg concentrations and then Corg-MAR in marine sediments (Hartnett et al., 1998)). The exposure time of organic matter is calculated by dividing the thickness of the layer within which oxygen is found by the sedimentation rate. In the study of Hartnett et al. (1998), the oxygen penetration within the sediments is only a few millimeters, and this is also certainly the case in the sediments off Costa Rica at site 1242 as well as within the sediments of the different regions we compare to site 1242 in our manuscript because of the elevated organic carbon rain rate in all these areas. The data 2 of Hartnett et al. (1998) reveals that the burial efficiency of Corg is always lower than 30% certainly because of high remineralization efficiency by aerobic and anaerobic processes. It is of course higher than at deeper sites in the open ocean where dissolved oxygen penetrate at depths greater than several decimeters and sedimentation rates are low (Rabouille and Gaillard, 1991). Of course, the results of Hartnett et al. (1998) show that Corg burial efficiency is higher for shorter oxygen exposure times. However, the relationship between the two is noisy, indicating certainly that other factors might play a role as well (Reimers, 1998), like the influence of organic matter composition and lability, redox oscillations (oxic/anoxic), and also the role of inorganic minerals in protecting organic matter from degradation (Mayer, 1999; Ransom et al., 1998; Kennedy et al., 2002). Therefore, our conceptual model is that higher primary production in the euphotic zone will generally be associated with higher export of organic matter to the sediments, thus to reduced organic carbon degradation in the water column, then reducing the oxygen concentration in the sediment, and thereby reducing the oxygen exposure time. Finally, sedimentation rates will have a direct impact on oxygen exposure time. In our revised manuscript, we will however expand our argumentation as requested by Reviewer 1 and deal in more details with the impact of oxygen on Corg concentrations. Sedimentation rate is then one of the key parameter, especially in our study where we compare Corg records both temporally and spatially. Sedimentation rates (SR in cm. ka-1) and mass accumulation rates (MAR in g.cm-2.ka-1) can be estimated (calculated) using the traditional approach or the 230Th normalization (e.g. François et al., 2004). In the traditional approach, MAR are often biased or overestimated because of sediment redistribution processes (sediment focusing and winnowing) (François et al., 2004; Dezileau et al., 2004). The 230Th method constrains both the vertical and the lateral fluxes of particles to the sediments and thus produces unbiased estimates of a component mass flux deposition (Bacon, 1984; François et al., 2004). There are however some limits inherent to this method as well. For instance, 230Th normalized flux calculations are based on the assumption that the flux of 230Th to the seafloor is constant and equal to its rate of production in the overlying waters, a balance that can be disturb by the deep water circulation or boundary scavenging process. We thus make a comparison of Corg Fluxes or MAR between different core sites retrieved in continental margin regions and/or under eutrophic regimes (see table below) using either the traditional or the 230Th approach to calculate Corg MAR. Clearly, the lowest Corg Fluxes are found when the 230Th method is used (in blue in the table); as indicated also in the table, this low fluxes do not result from lower Corg content or lower sedimentation rates when compared to some of the other sites. In addition, when both techniques are used for one single core like in the NW Pacific (Crusius et al., 2004), large differences in absolute Corg fluxes are observed too, but not so much in timing (see Crusius et al., 2004). The same conclusion can be deduced from the work of Kienast et al. (2007): the traditional method to calculate MAR give always higher values than the 230Th normalization. Clearly, based on this comparison, if the traditional approach may overestimate the Corg fluxes, they are certainly underestimated by the 230Th approach as indicated by François et al. (2004). In our work, we do not compare the absolute values of Corg contents and fluxes over the last 30 ka (see also our reply to the last technical comment) but rather their climatic variability, and thus we assume that the good agreement between all cores is indeed a good indicator for large regional increase in export production during the deglaciation. See the Table attached to our reply : comparison of Corg Fluxes and MAR.

General Comment 2 of Reviewer 1: - the entire argumentation is based on the assumption that “nitrates are (AND WERE) completely consumed annually” (p. 5149, l. 24) at the site location. While this does not seem unreasonable I would urge the authors to

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provide at least a reference to support their assertion or even better a map of annual mean nitrate concentration in Fig. 1.

In the revised manuscript, we will add a map of annual mean nitrate concentration in Fig. 1 to support our assertion that nitrates are now completely consumed annually.

Specific comments of Reviewer 1 : - p. 5150, l. 23-24 One should keep in mind that "conventional mass accumulation rates calculations" are highly dependent on age model constraints and are nothing more "than a little better than a guess (Catubig et al., 98). Please clearly state that this approach can only be used as a first approximation especially in a sediment record where the sedimentation rate varies significantly over time.

We agree with Reviewer 1 and that's also why we decided to use the 230Th normalized Corg Flux record of Kienast et al. 2006) as the best guess for regional (equatorial) export production and oxygen deland changes over the last 30 ka. Indeed, for site 1242, since we used the traditional method, we know that Corg fluxes or MAR should be calculated only for intervals between dated boundaries and not for each Corg concentration values since it cannot be proved that the sediment accumulation rate remained constant over the depth interval considered. See also our reply to the specific comment below.

- Moreover, the "double peaked maxium during the deglaciation" while undoubtedly present in the ODP 1242 record does not show significantly higher values when compared to the LGM. - p.5152, l. 22 " The deglacial peaks in export production in the EEP are COINCIDENT with the peaks in denitrification: : :" The "equatorial organic export – oxygen demand" on Fig. 3 clearly LEADS (and is certainly not coincident with) changes in denitrification inferred from bulk d15N records.

We agree that at ODP site 1242 the double peak maximum in Corg contents during the deglaciation does not show higher values than during the last glacial maximum. This is certainly the result of a variable dilution effect by the dominant component of

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the sediment, the silicoclastic fraction. Site 1242 is indeed located close to the coast, in a region where rainfall over the continent and then erosion and terrestrial runoff are important (ODP 202 Scientific Results, Mix et al., 2003). In order to estimate the effect of this dilution effect on the Corg profile, we have normalized Corg to Titanium. Ti, like Al, is often used to estimate the lithogenous fraction of a sediment; in addition, the conservative behavior of these two elements led to their use as normalizing parameter (Calvert and Pedersen, 2008). When Corg is normalized to Ti, a clear deglacial maxima is observed, and lower values are observed during both the last glacial maximum and the Holocene. (see also our reply to the specific comment below).

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 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.

General Comment 2 of Reviewer 1: - the entire argumentation is based on the assumption that "nitrates are (AND WERE) completely consumed annually" (p. 5149, l. 24) at the site location. While this does not seem unreasonable I would urge the authors to provide at least a reference to support their assertion or even better a map of annual mean nitrate concentration in Fig. 1.

In the revised manuscript we will provide a map to support our interpretation that nitrates are actually totally consumed annually. We assume that this interpretation is also valid for the last 30 kyr since the biological pump of nutrients (and carbon) was even higher during the glacial period.

- Specific comments of Reviewer 1 : - p. 5150, l. 23-24 One should keep in mind that "conventional mass accumulation rates calculations" are highly dependent on age model constraints and are nothing more "than a little better than a guess (Catubig et al., 98). Please clearly state that this approach can only be used as a first approximation especially in a sediment record where the sedimentation rate varies significantly over time. Moreover, the "double peaked maxium during the deglactiation" while undoubtedly present in the ODP 1242 record does not show significantly higher values when compared to the LGM. - p.5152, l. 22 " The deglacial peaks in export production in the EEP are COINCIDENT with the peaks in denitrification: : :" The "equatorial organic export – oxygen demand" on Fig. 3 clearly LEADS (and is certainly not coincident with) changes in denitrification inferred from bulk d15N records.

We recognize that the traditional method for mass accumulation rates determinations of a sedimentary component like Corg must be used with caution. First, indeed, the temporal resolution is limited to the age control points, and then only mean Corg MAR should be determined for each interval between dated limits. At Site 1242, the age model which was published elsewhere is quite well constrained with six AMS 14C dates (Benway et al., 2006). Of course, the variations in MAR between dated boundaries should not be determined and only a mean of the Corg MAR should be calculated and plotted since sedimentation rates may have varied between the time period considered. Therefore, the variability in the Corg MAR cannot be considered, and that's also why we preferred to consider the 230Th normalized profile of Kienast et al. (Kienast M. et al., 2006, Eastern Pacific cooling and Atlantic overturning circulation during the last deglaciation, Nature Vol 443| 19 October 2006| doi:10.1038/nature05222) to give a picture of export production and oxygen demand in the equatorial Pacific. However, as indicated by Kienast et al. in 2007 (Kienast S., Kienast M. et al., 2007, Thorium-230 normalized particle flux and sediment focusing in the Panama Basin region during the last 30,000 years, Paleoceanography. 22, PA2213, doi:10.1029/2006PA001357), sediment focusing leading to higher MAR especially during the last glacial interval in the Equatorial pacific is mostly the result of higher material associated with the terrigenous and hydrothermal fraction. Similarly, our Corg content profile at site 1242 is largely affected and diluted by the silicoclastic fraction derived from the erosion of the nearby continent. In order to produce a Corg based productivity profile free of any dilution effect, we calculated and plotted the ratio of Corg to Ti (Corg/Ti; Fig. Corg-Ti ratio, pdf attached file), Ti being typically associated with the silicoclastic fraction in margin sediments (like Al, Fe) (see Haug et al., Science 299, 1731-1735, 2003 for instance). These Titanium measurements were measured using an Avaatech core-scanner, and generously provided by F. Lamy (AWI, Bremerhaven). Not surprisingly, Corg/Al and Corg records look similar but present some subtle differences; in particular, the Corg/Ti curve shows a large peak between 15 and 17 ka, and perfectly covary with the 230Th –Corg profile of Kienast et al. (2006) offshore in the Equatorial Pacific. We are thus confident that our Corg/Ti profile provides a good estimation of past export production off Costa Rica. In our revised manuscript, we will show this new profile which greatly reduces uncertainties on the reconstruction of export production at Site 1242.

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

Philippe Martinez, on behalf of co-authors

Interactive comment on Biogeosciences Discuss., 6, 5145, 2009.

Core / Geographic area	References	Sedimentation Rates cm/ka	Corg wt%	Corg accumulation rate	Method for acc. Rates determination
ODP 1242	this study	4 to 15	2.2 to 3.8	0.2 to 0.74 g/cm2 ka	Traditional approach
ODP 1240 Eastern equatorial Pacific	Pichevin et al., 2009	6.4 to 25.2	1 to 3	0.1 to 0.35 g/m2 a = 0.01 to 0.035 g/cm2 ka	230-Th normalization
ME005A-24JC Eastern equatorial Pacific	Kienast et al., 2006	23 to 29	1 to 4	0.1 to 0.65 g/m2 a = 0.01 to 0 .065 g/cm2 ka	230-Th normalization
P7 Panama Basin, Eastern equatorial Pacific	Pedersen et al., 1991	No indication	1 to 2.4	15 to 85 mg/cm2 ka = 0.015 to 0.085 g/cm2 ka	Traditional approach
ME 0005A 03 Mexican margin	Thunell et al., 2004	40-70		0.5 to 3.5 g/cm2 ka	Traditional approach
W8709 13PC Oregon margin	Kienast et al., 2002		0.75-1.7	50-250 mg/cm2 ka = 0.05-0.25 g/cm2 ka	Traditional approach
MD962098/MD962086 Namibian margin, Benguela current	Bertrand et al., 2003; Pichevin et al., 2005	6.5 to 9	0.5 to 12	0.01 to 0.75 g/cm2 ka	Traditional approach
GeoB 1710 Namibian margin	Abrantes et al., 2000		0.5-6	0.01-0.15 g/cm2 ka	Traditional approach
GeoB 1016-3 Angola margin	Schneider et al., 1997	No indication	0.5-4.5	0.02-0.12 g/cm2 ka	Traditional approach
SU94-20bK SU94-11K Mauritanian margin	Martinez et al., 1996, 1999, 2000	7-12.5	0.5-3	0.03-0.3 g/cm2 ka	Traditional approach
GeoB 1016-3 Mauritanian margin	Romero et al., 2008	96 (on average)	0.5-2.5	0.1-2.4 g/cm2 ka	Traditional approach
M12392-1 Mauritanian margin	Abrantes et al., 2000		0.2-3.5	0.01-0.24 g/cm2 ka	Traditional approach
GeoB 3302 and 17748 Chile margin	Hebbeln et al., 2002	5-40	0.5-1.5	0.1-0.3 g/cm2 ka	Traditional approach
ODP 1233 Chile margin	Martinez et al., 2006	2000 (on average)	0.5 to 2.5	0.7 to 3 g/cm2 ka	Traditional approach
GeoB 3375 and 7101 Peru margin	Dezileau et al., 2004	5 (on average)	0.4-0.8	0.007-.0.021 g/cm2 ka	230-Th normalization
MD0112404 and MD0112403 Japan margin	Kao et al., 2008		0.6-1.1	0.0003-0.00085 g/cm2 ka	Traditional approach
RAMA 44 NW Pacific Meiji Seamount	Crusius et al., 2004	7-29		0.003-0.043 g/cm2 ka 0.01-0.19 g/cm2 ka	230-Th normalization Traditional approach
RAMA 44 NW Pacific Meiji Seamount	Crusius et al., 2004	7-29		0.003-0.043 g/cm2 ka 0.01-0.19 g/cm2 ka	230-Th normalization Traditional approach

Fig. 1.

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Interactive Comment

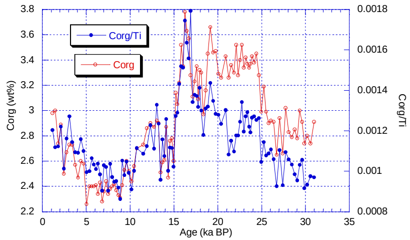

Fig : Comparison between Corg (wt%) and Corg/Ti in ODP Core 1242 over the last 31 kyr

Fig. 2.