

Interactive comment on “Rapid reorganization in ocean biogeochemistry off Peru towards the end of the Little Ice Age” by D. Gutiérrez et al.

D. Gutiérrez et al.

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We thank the three anonymous referees whose comments have significantly improved our paper. We have modified the manuscript following mostly their suggestions, however, in some instances we have clarified rather than changed the text since we felt the reviewers did not, understandably, follow our explanations. We have corrected typographical mistakes and minor details in the main text and in the supplementary material. Below we respond to the main comments from the reviewers.

Referee 1 The reviewer indicates that the manuscript has some problems in structure and organization that should be resolved before publishing, and presents three main points to be considered. The first concern is that the paper needs to be more explicit in the discussion about the LIA and the ITCZ position during the LIA in the introduction, also stating the effects on biogeochemistry and oceanographic conditions in the ETSP.

We have added one paragraph in the introduction to resolve this observation. We briefly mention the time-frame and manifestations of the LIA and the possible drivers involved (solar forcing, volcanism). We also discuss the possible mechanisms that triggered the southward displacement of the ITCZ during this climatic period. Regarding how the ITCZ displacement affected biogeochemical and oceanographic conditions that is largely dealt with in the second section of the Results and Discussion (R and D), and also briefly touched on in the third section of the R and D. The second concern was about the organization of the paper, which the referee suggested should be re-arranged to start with the past and move to the present. We have re-organized the paper, particularly the second section of the R and D, which has been re-titled as "Multidecadal to centennial variability in multiple proxies". The second introductory paragraph of this section describes the major centennial patterns of change of the multiple proxies before going to different aspects of the biogeochemical change (water column, sediment redox conditions, etc.). Then in each case we maintain a linear description from the past to the present, but still giving more emphasis to the biogeochemical shift at the end of the LIA. Finally we compare the behaviour of the multiple proxies from the late nineteenth century to the present and make some inferences regarding the oceanographic conditions. The third concern was with the "Concluding remarks" chapter of the paper, which the reviewer regarded as being difficult to relate to the paper's abstract. We recognize that the title was misleading and we changed it to "Implications for climate and ecosystem changes". Finally we include a short paragraph with the main conclusions of the paper.

Specific comments: a) We have expanded the discussion of our proxy records and included several more references of paleostudies, particularly for $\delta^{15}\text{N}$ and Cd. b) Similar or higher fish scales abundances in the Pisco core than in the Callao core is biased due to the better preservation conditions at nearly 300 m off Pisco (within the OMZ absolute minimum layer) than at 184 m off Callao, so that direct comparison of abundances or fluxes is not possible. c) The goal of Figure 5 is to illustrate the difference between El Niño-like conditions of winds and precipitation relative to conditions

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more similar to an austral summer-like southward shift of the ITCZ, which is more consistent with the proxy records of this study and others, (e.g. those of SST and salinity changes in Makassar Strait). While it is true that atmospheric pressure changes are the main driver of winds and precipitations, we feel the winds give a more intuitive view of how ocean circulation would change in association with the climate change. For our purpose we prefer to present winds rather than pressure fields in the figure.

Referee 2 The two major concerns of this reviewer relate to the age models and to the reliability of the flux estimations. In relation to the age models, here we give additional details and support to the three lines of evidence of the age modelling (241Am as time-marker, stratigraphic anomalies and radiocarbon ages of the sedimentary organic matter). We have included a supplementary table providing all the tie-points that we used in the age models for both cores. These tie-points consist of features of the 241Am activity records that can be associated with the rainfall of nuclear debris since the beginning of atomic testing (the onset of 241Am in the records at detectable values is used for the average flux calculations since 1952 AD), the 210Pb-derived oldest estimated dates, according to the CRS and CFCS sedimentation models (1860 and 1870 AD for Pisco and Callao, respectively), and for the Callao core, the slump positions as time-markers of large marine historic earthquakes off Callao. The reviewer asks whether the 1687 AD (8.6 Mw) and 1746 AD (8.4 Mw) earthquakes were much larger than other historical earthquakes, and how can we be confident that the two nearby slumps in the mid-section of the cores correspond to these events. We believe that minor chronological adjustments can be made based on comparison of seismic events with slumps. There was only one large historical marine earthquake (8.1 Mw) that had a rupture zone over Callao and it occurred in 1586 AD, which is nearly 160 years before the one at 1746 AD. As mentioned in the supplementary material, the inferred sedimentation rate on the calibrated 14C ages after the removal of the slumps yields a time period of about 50 years between the two slumps, that is in the order of the time elapsed between the two seismic events. If no assumption would be made on the slump ages, the sediment mass accumulation rate (MAR) inferred from the calibrated

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14C values date the upper slump at 1736 ± 13 years. Thus based on the 14C-derived MAR and on the short period between the two slumps, we infer that these correspond to the two seismic events mentioned above. Certainly there is a chance that the slumps were not triggered by these two large earthquakes, but if the MAR were used only, the whole age of the record would be increased in ca. 10 years, within the error of our current estimation of the age of the whole record. Finally the reviewer questions the validity of the 14C-dated organic matter for geochronology purposes, since, he (she) argues, bulk organic matter is a mixture of young and older, reworked material, which bias the dates towards maximum values. Hence, he concludes, 14C ages would be maximum ages and then MAR would be minimum values. First of all, our dating is not based on the calibrated radiocarbon ages directly, but on the MAR because we wanted to fit the best age curve from the calibrated radiocarbon data. Even if radiocarbon ages were biased to older values, that should not affect the calculation of MAR, which is based on the last 210Pb-dated age to tie the MAR and the chronology down-core. For example, Vargas et al. (2007) employed 14C-ages on organic matter and 210Pb to estimate MARs for a sediment core in Mejillones Bay, northern Chile, and both MAR estimations were the same; in that case a single MAR characterized the past 250 years. Second, Higginson Altabet (2004), supported the reliability of dating based on the bulk organic fraction 14C, by comparison with dating on sedimentary alkenones 14C in Peruvian shelf sediments. Nevertheless, in order to minimize source effects on the dated organic material, we avoided including in the age model 14C-ages of samples dominated by dispersed marine organic matter, or with higher content of terrestrial organic matter (showing older 14C leading to age inversions). Rather we used samples dominated by homogenous or granular amorphous organic matter (H-AOM and G-AOM), which characterize high productivity/strong upwelling conditions (Boussafir et al., 1995; Valdés et al., 2004; Pichevin et al., 2004). This approach was mainly applied to the Pisco core, where dispersed and terrestrial organic matter had more contribution, before the shift. For the Callao core, more dominated by H-AOM and G-AOM, 14C-age inversions were excluded as they were more probably related to

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transient enhancement of reservoir effects. Therefore, since source effects are minimized by this approach, it follows that our MAR estimations before the regime shift are realistic and flux calculations are reliable. Furthermore, as it will be explained below, downcore concentrations of several of the proxies have already been compared with fluxes by Sifeddine et al. (2008) showing the same patterns with time.

Specific comments: a) We have expanded the discussion on $\delta^{15}\text{N}$, particularly in relation with the Agnihotri (2008) paper. b) We have included more references and hopefully provided a clearer explanation of our interpretation of Cd records. In particular we bring attention to the Cd signature in the upwelled waters of the Eastern South Pacific, and the use of Cd as a proxy of paleoproductivity and paleoupwelling off Baja California (Dean et al., 2006). While we recognize that redox conditions enhance the preservation of Cd in the sediments, the different behaviour after the shift of Cd and Mo (the latter showing a positive trend, while the former is not), and the similarity with $\delta^{15}\text{N}$ variability leads us to postulate that the main control of Cd variability is the fertility of the upwelled waters (e.g. nutricline changes). c) Organization of the paper was improved relative to the description of proxy changes with time (see response to referee 1). d) LIA and El Niño. The controversy arises from the fact that coral records show that during part of the LIA there were higher frequency and amplitude of $\delta^{18}\text{O}$ changes in the central tropical Pacific (Cobb et al., 2003), but more comprehensive SST and climate reconstructions rather indicate lower ENSO activity during the LIA (d'Arrigo et al., 2005, Gergis Fowler, 2006), and paleoclimatic studies based on historical archives suggest scarce EN occurrences for the Peruvian coast (Ortlieb, 2000, 2004). These historical records from Peru are the most relevant to our study site. Other authors have found a weakening of the Eastern Pacific cold tongue during the LIA, a feature that resembles the present-day EN conditions (Koutavas Lynch-Stieglitz, 2004.). Our suggestion is that the warmer centennial conditions in the Equatorial and Tropical Eastern Pacific during the LIA were ultimately driven by a persistent southward displacement of the ITCZ and wind fields in the ETSP, rather than EN-like changes in winds and precipitation patterns. e) We have improved the interpretation of $\delta^{15}\text{N}$ records in Mejil-

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lones. The pattern of change during the nineteenth century differs between Peruvian and Mejillones records. The rise of $d_{15}N$ in Mejillones takes place in about 50 years, starting around 1820 AD (Vargas et al., 2007) while for Callao and Pisco it shows a rapid change within two decades, considering chronological errors. We propose that the gradual rise of $d_{15}N$ was due to the persistence of ventilation process originated at higher latitude, delaying for some time the expansion of the oxygen-depleted waters towards the south. f) We deleted the phrase "stratigraphic boundary" and just explain that the lithological shift represents a boundary between different sedimentation regimes.

Referee 3 The reviewer indicates four major concerns to the paper. The first concern of the reviewer is on the parallel publications. The reviewer comments that the new and the previously published data and conclusions should be clearly distinguished. We have now re-organized the main text in order to separate the new findings from the present paper, which relates to water column chemistry and biogenic proxies, to distinguish these from the results of the Siffedine et al. (2008) paper. Thus, we have emphasized the discussion of $d_{15}N$ and Cd relative to water column biogeochemistry. Likewise, the revised conclusion refers more explicitly to water column and marine production. In the R and D we have highlighted the records of foraminiferal preservation and of the percent contribution of *Bolivina seminuda* to the benthic foraminiferal assemblage, which support the previously inferred changes of sediment redox conditions. We also maintain focus on the diatom and fish debris records as indicators of biological productivity that supplement the TOC record. Nevertheless in order to facilitate the comprehensive interpretation of the records, we keep the published records of TOC, Mo and lithic fluxes in Figure 3, with proper citation (Sifeddine et al., 2008).

The second concern of the reviewer is on the age models as well. We resolve this concern point by point: MAR and flux calculations. We have expanded the text of the supplementary material, explaining the compaction artifacts and the downcore density changes of the cores, which obliged us to use mass accumulation rather than sediment depth for the sedimentation models. In the response to referee 2 we explain why we

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rely on the MAR and flux calculations, but we also mention in the text the similarity of the temporal patterns of concentrations and fluxes, already clearly shown by Sifeddine et al. (2008). As mentioned above, we included a table of the chronological tie-points and how they were derived. Figure SF3 has been modified to include the last 210Pb-derived data point and help to visualize the offset with conventional 14C-ages that is explained by reservoir effects. Local reservoir (DR) estimations and dating reliability. We include additional text discussing our DR estimations versus the marine radiocarbon reservoir database (<http://intcal.qub.ac.uk/marine/>). Our estimations, which are average values for the period between ca. 1300 AD and 1860 AD, are within the DR database range of 217 +/- 133 years. We employed the mean values of DR to calibrate the conventional 14C-ages, and after that, we estimated the MAR and the chronology, based on the calibrated 14C-ages (mean values), so that the error estimation of the age models depended on the dispersion of the calibrated 14C-ages. Dating error for the shift was minimized in the case of the Callao core by the inclusion of the 1746 AD earthquake as a time-marker. In the case of the Pisco core, date of the shift was the mean value of the 14C-derived date and the extrapolation downcore of the 210Pb-MAR. Finally we include a Table with the main text, showing previous MAR estimations of other authors for the study region. Our estimated MARs are well within past reports (Rein et al., 2004, Goide Koldberg, 1982; Agnihotri et al., 2008), supporting the reliability of our age models and shift dating. The third major concern is on the interpretation of the d15N record. We rule out an important role of organic matter source driving the d15N changes. First, palynofacies work indicate that only in Pisco before the shift is there a higher input of terrestrial organic matter, but this terrestrial OM only exceptionally reaches 25The last concern is about the organization of the temporal sequencing. As previously, mentioned, the temporal sequencing has been addressed in accordance with comments of the reviewers.

Specific comments: All the minor observations were explained or corrected in the text (subsampling, counting of foraminifera, typos). The relationship between the LIA and ENSO was explained before and also expanded in the text. The oldest 14C-datapoint

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of Pisco was in fact included in the age model; disperse OM was lower and the $\delta^{13}\text{C}$ value was less negative than the excluded datapoints.

Note: All the references listed will be included in the revised manuscript.

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