Clim. Past Discuss., 10, C1893–C1903, 2014
www.clim-past-discuss.net/10/C1893/2014/


Climate of the Past
Discussions
Open Access

# *Interactive comment on* "Nutrient utilisation and weathering inputs in the Peruvian upwelling region since the Little Ice Age" *by* C. Ehlert et al.

**C. Ehlert et al.**

cehlert@mpi-bremen.de

Received and published: 12 November 2014

We would like to thank the reviewers for their constructive reviews and positive recommendations, which we took into account in preparing the revised manuscript and which we reply to in detail below.

Reply to Referee #1 "In this manuscript, the authors present sediment Nd and Sr isotopes, biogenic silica%, organic nitrogen% and the isotopic composition of biogenic Si and N between 1300 and 2000 AD along the Peruvian coast. They found marked environmental changes between the little ice age (LIA) and recent times with higher riverine input and low productivity during the LIA due to "El Nino" like conditions. Furthermore, the author interpret the parallel increase between d30Si and d15N during the transition period as indicating that nutrient relative utilisation is the main process con-



trolling n isotopic composition while denitrification has a relatively marginal influence on the isotopic signal. The author s are using a neat set of proxies to reconstruct past changes in climate and productivity in the study area. The Nd and Sr isotope data are quite compelling. Therefore I would support publication of this paper in Climate of the Past. However, I have issues with the interpretation of the d15N and d30Si data and especially the conclusion that d15N responds mostly to changes in utilisation rather than denitrification. Therefore, the authors need to address this before I can fully support publication. First, the authors describe in both cores M771-470 and B0405-6 an increase in d30Si just after the LIA. If you take into account the error bars, only a couple of points in total fall below or above the others. To me the trend is not as marked as the authors describe it. Therefore I would argue that there is at most a 0.2 permil (from 0.7 to 0.9 permil) increase between the LIA and the rest of the record (which is as much as the error bars) and would suggest only a modest increase in silicic acid utilisation. If you use a Raleigh fractionation model you would get something like 12% increase in utilisation."

Both cores show, as described and discussed in the manuscript, similar average $\delta$30SibSiO2 values of +0.73‰ (B0405-6) and +0.85‰ (M771-470) during the LIA (see Fig. 2 of the manuscript). These are followed by a drop to +0.6‰ at the very end of the LIA and a subsequent rapid increase to +1.2‰ during the transitional period. Thereafter a decrease back to lower values near +0.9‰ similar to the LIA, in the most recent samples occurred, which is in full agreement with surface sediment samples from the area (see Fig. 4 in the manuscript and Ehlert et al., 2012). This corresponds to an overall change in $\delta$30SibSiO2 of 0.6‰ and is therefore significantly higher than the uncertainties of the measurements. In addition, this range in $\delta$30SibSiO2 is essentially the same as the entire range measured in surface sediments along the Peruvian shelf region, which reflects silicic acid utilisation rates between 50 and 90% from the available pool (Ehlert et al., 2012). The maximum 0.6‰ difference in both records therefore corresponds to a change in utilisation between $\sim$35% before the end of the LIA and 85% during the transition period, corresponding to an increase by 50% i (see

Fig. 5a in the manuscript). Given that these calculations are based on few data points we decided to use average values for the different time periods which decreases the maximum $\delta$30SibSiO2 range, but the pronounced change in utilisation between the LIA and transition period remains significant.

"At the same time, the opal % records and valve accumulation rates show a 2 to 3 fold increase depending on the core site. Figure 5 shows a much greater gradient in utilisation between the time slices considered but I believe this is because for the transition period for instance only one d30Si data point is taken into account."

Actually, the values are exactly the ones described above, which in the case of the transition period varies between +1‰ and +1.2‰ as plotted in Fig. 5. The values are defined by a total of 4 data points, 2 for each core.

"I am also wondering whether the authors took into account the fairly low modern d30Si values from core b0405-6 (to me indistinguishable from the LIA values) when they plotted the period-specific relative utilisations on the fractionation curves (Fig 5)."

This is correct and it is in fact one of the most important points of our entire manuscript (!) that the $\delta$30SibSiO2 during the LIA and in modern sediments show essentially the same values (and therefore the same silicic acid utilisation), but at the same time show significantly different bSiO2 concentrations, which leads us to the conclusion that the total amount of dissolved nutrients (in partuicular silicic acid) must have been markedly different between the LIA and the present (see section 4.1.4 in the manuscript). Yes, all measured $\delta$30SibSiO2 values have been taken into account when calculating the mean $\delta$30SibSiO2 as well as $\delta$15Nsed values for the period-specific utilisation calculations (except for the oldest $\delta$30SibSiO2 data point of core B0405-6, because it is slightly older than the LIA according to the age model but shows essentially same value as the LIA-samples,).

"Now the d15N records show a much more defined trend with about 2 permil lower values during the LIA compared to modern. That's an increase of about 40% in N



utilisation between the LIA and the modern (according to figure 5) if you believe denitrification had only a marginal impact on the d15N signal."

This translates into an increase in utilisation very similar to the one indicated by silicon isotopes (see comment above). The only difference is that the signal obtained from the $\delta$15N shows a one step increase from the LIA to modern, whereas the $\delta$30Si shows a (slight) decrease at the end of the LIA and after the transition period. This is discussed in detail in the text of the manuscript.

"The timing of change is very consistent between all core sites while it is not for the d30Si. Therefore, this casts doubt on the assertion that nitrate and silicic acid utilisation increased in parallel during the transition period in response to increased upwelling."

A difference in timing between the $\delta$15N and $\delta$30Si changes is not clearly resolvable based on the coarser resolution of our $\delta$30Si record (these $\delta$30Si values are much harder and more time consuming to produce) given that there is no data point for the earliest part of the transition period in core B0405-6, which in core M771-470 is clearly already marked by high $\delta$30Si values. So, the timing of the changes may well be exactly the same which led us to the interpretation that the changes were in both cases mainly caused by an increase in utilisation given the pronounced increase in diatom abundance, $\delta$30Si and N concentrations.

"Now there is a theoretical problem as well: With increased upwelling, studies have overwhelmingly shown that nitrate utilisation should decrease due to the influx of a great quantity of nitrate to the surface (more nitrate is utilised by the blooming algae but even more is left behind unutilised, hence reducing the recorded relative utilisation (see early papers from Francois and Altabet)). The author of the present paper argue that increasing upwelling and biological production at the end of the LIA resulted in an increase in d15N and d30Si and that it shows that relative utilisation of both nutrients increased together. I have to disagree with this interpretation. To me d15N increased because of increased denitrification promoted by higher organic matter rain rate (higher oxidant demand at depth or in the sediment). D15N indeed increased more than d30Si because it is mostly responding to denitrification and not relative utilisation. The modest and spatially variable increase in d30Si after the LIA does not match the very clear, consistent 2 permil increase in d15n. To me that tells us that both proxies are governed by different processes. It is possible to imagine that Silicic acid was abundant at the sea surface due to increased run off and was also less utilised during the LIA because the conditions where unfavourable to the diatom community (stratification) but that during the transition period they became favourable and hence the diatoms where able to utilised a greater proportion of the available Si (diatom production more than doubled while Si utilisation increased only slightly). I expect in the other hand that nitrate relative utilisation (which depends on diatoms and other planktonic producers) overall decreased or only slightly increased between the LIA and the modern period but the large d15N increase is mostly due to the kick off of denitrification."

We are thankful that the reviewer's comment gives us the possibility to highlight again our interpretation of the Si/N isotope records. We would like to point out here that we do not neglect the influence of NO3–loss processes on the preserved $\delta$15Nsed record, and we did not do so in the manuscript. In contrast, we mentioned at several points that both utilisation and NO3–loss processes played a role. However, we would like to emphazise in this manuscript that utilisation is an important factor that is often underestimated in the interpretations of the records, especially in a region like the EEP where studies have shown that the heavier N isotope signatures during NO3–loss processes are only preserved in the sediments under conditions of near-complete surface water utilisation of the nutrients (Mollier-Vogel et al., 2012). This, however, did not occur most of the time during the past ~600 years, as our $\delta$30Siopal records document. The patterns and changes in Si isotope composition of both cores presented in this manuscript are fully consistent with the record presented in Ehlert et al. (2013), where we demonstrated for the past ~20,000 years that periods of high biogenic opal deposition, i.e. high PP, consistently corresponded to periods with high utilisation of silicic acid/nutrients. In the records presented here biogenic opal concentrations, to-



tal amount of diatom valves, and total nitrogen concentrations all start to increase at the same time documenting that diatoms where the drivers of the increased PP at the end of the LIA and during the transition period. Additionally, higher biogenic opal deposition also corresponds to higher $\delta$15N values, i.e. higher nitrate utilisation. The relative increase in $\delta$15N is NOT higher than the increase in $\delta$30Si. When applying the utilisation models both show an approximately doubling in utilisation from the LIA to the transition period (see Fig. 5 in the manuscript). However, it is true that after the transition period, the calculated utilisation from the $\delta$15N is ~20% higher than from the $\delta$30Si, which we interpret to be indicative of the influence of enhanced denitrification. To clarify that point in the manuscript we propose the following additional paragraph in section 4.2.1: "In the modern (~1860AD - present) samples the $\delta$30Siopal signatures are characterised by a slight decrease after the transition period from a mean value of +1.12‰ to +0.82‰ whereas the $\delta$15Nsed values remain at the same level near +7‰ (Fig. 2). This corresponds to a ~20% higher NO3- than Si(OH)4 utilisation (Fig. 5). However, when assuming that diatoms are the dominating primary producers with a NO3-:Si(OH)4 uptake ration of ~1, these 20% most likely reflect the increase in subsurface NO3âĂŤloss, which is not observable during the LIA or the transition period. This means that during the LIA and the transition period nutrient utilisation was the dominating process influencing the $\delta$15Nsed signal, whereas in modern times NO3–loss enhanced the $\delta$15Nsed signal. Combining the $\delta$30Siopal and the $\delta$15Nsed records allows estimation of this "additional" signal: If only utilisation controlled the system, the expected $\delta$15Nsed signal would be ~+6‰ (corresponding to the measured ~+0.8‰ for $\delta$30Siopal, Fig. 5). The additional 1‰ in $\delta$15Nsed observed would correspondingly be caused by NO3–loss."

"I also note that the authors use a d15N-nitrate source signal of 4 permil (fig. 5) while today this signal is known to be much higher in this region due to intense denitrification. At least for the reconstruction of the modern nitrate relative utilisation a greater d15N source value should be used."

No, we used a source signature of +9‰ as described in the text (e.g., p.3373 L.15) and also shown in the Figures (left scales in Fig. 5). This is the signature that has been measured in the present day Peruvian Undercurrent (Mollier-Vogel et al., 2012), which is the source water for the upwelling and therefore delivers the nutrients to the surface waters.

"Minor comments: Line 12 p3360: “this fractionation process is mainly controlled by the availability of Si(OH)4: : :” I believe this is incorrect. I would rephrase this as follow: “Si isotopic fractionation is mainly controlled by the utilisation of silicic acid in the sea surface by the biota”."

Yes, we have changed the sentence as suggested.

Reply to Referee #2 "I have reviewed Ehlert an co-authors' results on radiogenic sedimentary Nd and Sr isotopes, biogenic silica, total nitrogen and the isotopic composition of biogenic Si and bulk N between 1300 and 2000 AD from 2 new sedimentary archives off the Peruvian coast. The paper is well written and it could provide the community with a better understanding of the relationship between global climate and local oceanographic changes happening during the past 700 years and the LIA potential impacts on the eastern South Pacific. I think that this would be very relevant for future predictions on how this critical part of the ocean for food supply will evolve as climate changes. The new data (radiogenic isotopes and silicon isotopes) definitely merits publication in Climate of the Past but I would suggest some major revisions to the way the authors have presented their dataset. My main concern is the following: since a great deal of the data presented here has been already published elsewhere, (Gutiérrez et al 2006, 2009; Siffedine et al., 2008), and the true novelty comes from the Nd, Sr and Si isotopes, it would be more natural to focus the bulk of the publication on these variables and how they fit in a more global picture of changes associated with ocean circulation and climate change, specially at the critical period that they have highlighted following 1820-1870AD. Instead, it was very disappointing to see that in its present form, the paper presents a very long discussion on nutrient utilization, which is



highly debatable."

In fact, only bSi, TN, diatom accumulation rates and the $\delta$15Nsed data of core B0405-6 have been published before and are compared to our new Si, Nd and Sr isotope data, as well as to the new bSi and TN concentration data of core M771-470. So the amount of new data in this manuscript is high and the novelty comes from the direct comparison of the different proxies, in particular of the Si and N isotope data. The (long) discussion of nutrient utilisation, in particular the comparison between Si and N isotope data arises from the fact that we have to interpret especially the $\delta$15Nsed data in a way that differs from other open ocean and near costal sites (see review #1). This is one of the key and novel parts of the implications of our data, which correspondingly needs a thorough discussion. We decided not to speculate about any global implications of the data but rather focused on comparison to other regional data sets in the eastern Pacific.

"What can the authors say about the Nd signature of the 2 cores and changes associated with ENSO or SAM during this period? In my opinion, the paper's major strength and novelty should be set in linking the radiogenic isotope results (and silica isotopes) to climate and leave the nutrient utilization discussion as it is or shorten it up."

As described above, we wanted to focus in our manuscript on the comparison between our novel Si (and Nd, Sr) isotope data to existing records from the region, which we then put into a wider regional or global context of oceanic and atmospheric circulation changes. Our new data are consistent with these records and support and strengthen the interpretation of a change from predominant El Nino-like conditions during the LIA to La Nina-like conditions in the modern EEP. In addition, we show that centennial scale changes in the records presented in our study are caused by similar processes as changes on millenial and glacial-interglacial time scales. We also see that both reviewers highlight the radiogenic isotope data as being interesting and useful but that the potential of discussion has not been fully exploited, which we try to improve in the revised version of the manuscript. We strengthened our argumentation by better linking the radiogenic and stable isotope data and by highlighting the comparison and agreement with existing interpretations in section 4.2.

"My second concern with the paper in its present form deals with the M771-470's age control during the critical transition period highlighted and discussed thoroughly in the paper. The core's age model beyond 1850AD was constructed by adopting the sedimentation rates of (not so) nearby core B0405-13. In this respect, it is worth noting that sedimentation rates at both sites appear to be very different. Just take the case of the sed. rate of M771-470 from 10 to 25cm being as low as half of B0405-13's sed. Rate (0.9 vs 1.78 mm yr-1). Why should these 2 cores have a similar sed. rate in the past if recent sedimentation regimes are so different? I am not disregarding the age model proposed here, but I would like to see a much thorough justification of it."

It is notoriously difficult to obtain reliable age models for sediment cores from the shelf off Peru but in our case it was possible to make use of a lot of independent information to establish the chronology, which thus can be considered well-constrained. The major change in biogeochemical proxies at ~28 cm core depth in core M771-470 is considered a reliable and independent time marker, which has been found in many cores from the region and has been dated to 1820 ± 15 years AD (Salvatteci et al., 2014, and references therein), which agrees well with our estimated age based on 210Pb dating. Before that, during the LIA, the Peruvian upwelling system was less productive all along the coast leading to much lower sedimentation rates. Both cores B0405-13 at ~12°S and B0405-6 at ~14°S show a sedimentation rate of 0.6mm/yr during the LIA, which we used for the age model of core M771-470. After the LIA, productivity increased markedly. The 210Pb dating gives an age of 214 years for the uppermost 25cm (with no indication of any hiatus), which results in an average sedimentation rate of ~1.2mm/yr, which compares well to the sedimentation rates of cores B0405-6 and -13, as well as other cores from the region. However, there is bioturbation in the uppermost 10cm of core M771-470 (=same 210Pb age for 0-10cm depth), which is why we were only able to calculate sedimentation rates only for the depths 10-25cm, which resulted in 0.92mm/yr. We decided to use a higher sedimentation rate of 1.5 mm/yr



of core B0405-13 for our age model of the transition period because this core reveals comparable sediment properties, was recovered from a similar water depth, etc. The increase in PP parameters (diatom valve amount, bSiO2 and TN concentration) is a typical pattern of the transition period that was also found in other records (e.g., Salvatteci et al., 2014). In addition, the increase in porosity in core M771-470, similar to the change in density in cores B0405-6 and -13 and multiple others (9 in total, Salvatteci et al., 2014), is a suitable marker for the transition period. These considerations lead us to the conclusion, that the adaptation of the sedimentation rate of core B0405-13 is appropriate.

"Another minor comment would be to ask the authors to refrain from asserting certain climate connection as certain since this is all very speculative yet. For example, in the abstract the authors write "...These patterns were caused by permanent El Niño like conditions characterized..." (emphasis added). This is too strong phrasing that implies complete certainty. I would advice the authors to try to keep a more speculative language when asserting hypothetical causalities that are going to be surely subject of confirmation (or rejection) by future work."

The text of the Abstract was changed as suggested. However, we would also like to state here that e.g. the characterization of El Nino-like conditions during the LIA in the Tropical Pacific has been shown by several studies using different proxies, to which our work agrees well. Thus the causal relationships presented in the Abstract and throughout the text are not as hypothetical as the reviewer suggests.

"In summary, I would recommend the editor to accept this manuscript for publication considering the comments that I just mentioned."

References: Ehlert, C., P. Grasse, E. Mollier-Vogel, T. Böschen, J. Franz, G. F. De Souza, B. Reynolds, L. Stramma, and M. Frank (2012), Factors Controlling the Silicon Isotope Distribution in Waters and Surface Sediments of the Peruvian Coastal Upwelling, Geochimica et Cosmochimica Acta, 99, 128–145.

doi:10.1016/j.gca.2012.09.038 Mollier-Vogel, E., E. Ryabenko, P. Martinez, D. W. R. Wallace, M. A. Altabet, and R. R. Schneider (2012), Nitrogen Isotope Gradients off Peru and Ecuador Related to Upwelling, Productivity, Nutrient Uptake and Oxygen Deficiency, Deep-Sea Research I, 70, 14–25, doi:10.1016/j.dsr.2012.06.003 Salvatteci, R., D. Field, A. Sifeddine, L. Ortlieb, V. Ferreira, T. Baumgartner, et al. (2014), Cross-Stratigraphies from a Seismically Active Mud Lens off Peru Indicate Horizontal Extensions of Laminae, Missing Sequences, and a Need for Multiple Cores for High Resolution Records, Marine Geology, 357, 72–89, doi:10.1016/j.margeo.2014.07.008

---

Interactive comment on Clim. Past Discuss., 10, 3357, 2014.