Response to the reviews

Please find in the following a point-to-point response to the reviews, a list of the relevant changes in the manuscript and the revised manuscript version with mark ups.

Please note that all line references given in the following refer to the manuscript with mark ups.

Review #1

In section 3.1. I'm not very convinced by the descriptions – they don't seem to match up well with the plots in figure 3 to me. For example, the on line 193 say that between 12 and 15°S the d30Si have a mean lower value during the LIA than the CWP – however, this really isn't the case for B0405-6, and isn't thoroughly convincing for the other cores either.

The reviewer is right in that the actual mean LIA $\delta^{30}Si_{BSi}$ value for BO405-6 is not significantly different from the CWP. To highlight the individual changes in all cores we now present mean values and 2SD variability for 12, 14 and 15°S in Line 315-317: 'The $\delta^{30}Si$ records follow a similar trend of lower mean $\delta^{30}Si_{BSi}$ values of 0.8 ± 0.2‰ (2SD, 12°S), 0.8 ± 0.1‰ (14°S) and 1 ± 0.2‰ (15°S) during the LIA to more variable and higher mean values of 1.3 ± 0.4‰ (12°S), 0.8 ± 0.4‰ (14°S) and 1.5 ± 0.2‰ (15°S) during the CWP.'

This statement also hides variability observed within the LIA. There are other examples of this throughout the section when referring to both d30Si and d15N. There are also examples of this in section 3.2.2 e.g. lines 379 onwards – at both 12 and 15°S there are d30Si values from the humid LIA that are the same as the modern values (if I've interpreted the grey horizontal bars on figure 3 correctly). Please make sure that your words fit the data

Thanks to the remarks of the reviewer we found that there was an error in Figure 3, in that the grey horizontal bars which mark the humid conditions throughout the last 600 years were accidentally displaced by 50 years. The figure was corrected accordingly and thus the text now matches the figure.

The authors use -1.1 per mil as a fractionation factor, but there is, in fact, a large range in this fractionation factor. The authors use this value in their calculations (line 261) but how does the uncertainty on this value influence the findings? Perhaps the authors could think about some sensitivity studies?

The changes in the diatom abundances are not large enough (10-20% changes maximum) to substantially affect the isotopic values and there is only the fractionation factor for Chaetoceros brevis (-2.1; a polar species, not resting spores) available which is on average significantly different from the -1.1‰ value generally assumed. When calculating the changes in ε following Doering et al., (2016), the potential effect of the Chaetoceros fractionation factor on our data is less than 5%. This information was added in Lines 220-225:

'To evaluate the impact of changes in $^{30}\varepsilon$ on the $\delta^{30}Si$ signatures the potential influence of species-specific fractionation was tested based on the impact of a -2.1‰ enrichment factors of *Chaetoceros brevis* (Sutton et al., 2013). However, the estimated impact on past $\delta^{30}Si_{BSi}$ records due to a change in the amount of *Chaetoceros* sp. Present in the sediment was less than 5% for all cores (M77/2-024-5TC, 005-3TC and 003-2TC) and thus did not alter the assumed $^{30}\varepsilon$ of -1.1‰ substantially (based on calculations presented in Doering et al., 2016; calculations not shown).'

2. Methods:

There is no mention in the manuscript about the uncertainties that we have about the fractionation factor of silicon isotopes during uptake by diatoms (see comment below). It is possible that the downcore variations are driven by diatom species differences (I'm not saying that they are – it's just a possibility). This possibility can be readily dismissed by including information about downcore species differences. Ideally, diatom counts would be done on the separated and cleaned material (mentioned in lines 143 onwards). However, if this isn't possible at this stage (i.e. there is not cleaned material remaining), then perhaps the authors could at least plot their downcore isotope variations relative to the diatom abundance data mentioned on line 181 (Fleury et al., 2015)? This would at least give some indication of whether or not species changes are driving the isotope variations.

As the reviewer suggested we now plotted the diatom abundances as provided by Fleury et al., (2015) versus our δ^{30}Si data (added to fig.3). In the Methods section a paragraph was added to explain the diatom abundances, Line 193-206:

2.3 Diatom assemblage data

Diatom analysis of cores M77/2-024-5TC, 005-3TC and 003-2TC were published previously based on three slides per sample and counting of a minimum of 300 valves for each sample (for details see Fleury et al., 2015). The diatom abundances are presented here for three groups representing different environmental conditions (Fig. 3): Upwelling species – Chaetoceros sp., Skeletonema costatum, Thalassionema nitzschioides var. nitzschioides; Coastal planktonic – Actinocyclus spp., Atinoptychus spp, Asteromphalus spp., and Coscinodiscus sp.; Other diatom species – Nitzschia spp., Rhizosolenia spp. and Thalassiosira spp., Cyclotella spp., Cocconeis sp.;

The diatom assemblage abundance is compared to $\delta^{30}Si_{BSi}$ compositions for cores M77/2-024-5TC, 005-4TC and 003-2TC to investigate if changes in the assemblage have influenced the isotopic record. While diatom counts have been performed on bulk sediment samples $\delta^{30}Si_{BSi}$ was measured on the 11-32µm size fraction. However, it was shown previously that this size range closely resamples the main assemblage, which allows studying the influence of changes in the diatom assemblage on the $\delta^{30}Si_{BSi}$ record (Ehlert et al., 2012; 2013).

Additional text concerning the diatom assemblages has been added:

Line 402-406: ‘However, comparison with the cumulative diatom assemblage indicates overall little difference in the amount of upwelling and coastal planktonic diatom species between the LIA and the CWP at 11°S (Fig. 4), with intervals of reduced abundances of upwelling species of generally less than 50 years, much shorter than the 100 to 150 year intervals observed at 12 and 15°S.’

Line 409-411: ‘…, as $\delta^{30}Si_{BSi}$ analysis do not cover all short events (~50 years) of reductions in the abundance of upwelling diatom species (Fig. 3f).’

Line 320-327-: The diatom assemblages (Fig. 3e-g; based on Fleury et al., 2015) show a strong association of the amount of upwelling species and $\delta^{30}Si_{BSi}$ signatures, with decreases of up to 20% in upwelling species often accompanied by a reduction of $\delta^{30}Si_{BSi}$ by about 0.5-1‰. However, not every decrease in $\delta^{30}Si_{BSi}$ is mirrored by a change in the diatom assemblage and vice versa (e.g. Fig. 3f at 1650 AD). Overall the diatom assemblage data indicates little changes in the mean conditions at 11°S (024-5TC) and a slight reduction of upwelling strength at 12°S and 15°S during the LIA in comparison to the CWP. The most distinct shift of lower abundances of upwelling species (~50%) to higher values during the CWP (~70%) is found at 15°S (003-2TC) corresponding to the strongest changes in BSi and $\delta^{30}Si_{BSi}$ at this location.’

We further refer to the interpretation of the Doering et al., (2016), that the δ^{30}Si values are mostly affected by changes in the system off Peru, namely upwelling strength, and the associated diatom assemblage. This is emphasized now in the revised manuscript in response to the reviewers wishes, in Line 77-82: ‘Accordingly, downcore records of $\delta^{30}Si_{BSi}$ off Peru are closely coupled to changes in the diatom assemblage with high signatures (>1‰) reflecting strong upwelling conditions and lower signatures (0-5-1‰) reflecting weak upwelling conditions (Doering et al., 2016). This coupling was previously shown to be mainly the consequence of changes in the abundance of different diatom groups during diatom succession linked to different upwelling strength (Doering et al., 2016) rather than potential species-specific fractionation (i.e. -0.5 to -2.1‰; Sutton et al., 2013).’

Lastly, there is no real mention in the methods section about how the sampling was carried out with respect to the fine-laminations (line 132). Were the samples taken from individual laminations? Was there any possibility of signal aliasing? Given the discussion about resolution in the manuscript later on (e.g. line 209), I think it would be valuable to clarify the sampling resolution upfront in the methods section.

δ^{30}Si and BSi measurements were generally performed on samples from 1 cm slices integrating several laminations. Only for core 003-2TC additional BSi measurements on material form single laminations was possible. For comparison data from laminations was interpolated to 1cm resolution. This information was added in Line 158 to 163 in the method section.:

'One cm slices of the sediment cores were sampled for BSi and silicon isotope measurements to ensure the availability of sufficient amount of diatoms for silicon isotope analysis (Tab. 1). For core 003-2TC additional BSi measurements on the extraction of sample material from individual laminations was possible (Fleury et al., 2015). As previously published $\delta^{15}N_{bulk}$ values are based on samples from single laminations these were averaged to 1 cm resolution when directly compared to the δ^{30}Si data in the following.'

3. Minor comments:

The title is appropriate for the contents of the paper. The abstract is a generally good, concise summary, although the authors should make it clear in the abstract that it's only some of the d30Si data that are new to this study. I didn't glean initially that the d15N data were published, and was confused to start with as to why there was no d15N methods section!

It is clearly stated in line 22 to 23 in the abstract that we present three new δ^{30}Si records and compare them to previously published δ^{30}Si and δ^{15}N records. Although we acknowledge the comment of the referee, we do not see the need to further emphasize this.

The references are generally good. However, in the introduction, the authors should at least mention some of the caveats associated with diatom d30Si interpretation, namely the possibility of species specific fractionation (e.g. Sutton et al., 2013) and dissolution (Demarest et al., 2009). See comments above regarding species specific fractionation; dissolution impacts on d30Si is more challenging to investigate as there isn't agreement in the literature about how big the dissolution signal might be (Egan et al., 2012; Wetzel et al., 2014) – however, I think at least a sentence should be included to note it as a possible complicating factor.

A sentence about potential biogenic opal dissolution has been added accordingly in in Line 47-53:

While a potential fractionation of δ^{30}Si signatures of biogenic opal during dissolution of -0.55‰ has been reported previously (Demarest 2009), subsequent investigations from the water column of the Southern Ocean did not see significant difference in the δ^{30}Si values of material from the and δ^{30}Si values in surface sediments is found (Varela et a., 2004; Fripiat et al., 2012; Closset et al., 2015). Furthermore, field studies and laboratory experiments based on sediments have so far indicated that δ^{30}Si signatures of diatoms within the sediments are generally unaffected by diagenetic alteration (e.g. Egan et al., 2012; Wetzel et al., 2014; Ehlert et al., 2016).

On line 91, the authors should be more specific than "high amounts" – are you referring to high concentrations, fluxes, or both?

We are referring to concentrations here, accordingly concentration values for $Si(OH)_4$ and NO_3- are now given in brackets. Line 108-109: 'Along the Peruvian margin the main source for the high amounts of upwelled nutrients (30 µmol L^{-1} for both $Si(OH)_4$ and NO_3^-; Bruland et al., 2005)'

What do the +/- signs on lines 97 onwards represent?

For the δ^{30}Si the +/- always indicates the 2SD external reproducibility, only for the δ^{15}NO3- values taken from Rafter 2012 the +/- indicates the 1SD variability of several water masses. This has now been added to the text in brackets in lines 114 and 115.

One line 114, the authors could add a few words to explain why the steady-state system is appropriate here. This arises again mater in the manuscript, but I think it would help to clarify the choice here as well.

Based on observations of Ehlert et al. 2012, the corresponding reference was added to Lines 132-33.

On line 138, the authors should remove “in study of”.

Line 164: ‘study of’ has been removed accordingly.

The sentence on line 178 is not complete – please rewrite. Also the short paragraph on line 186 onwards seems a little misplaced – I’d suggest the end of that section is rephrased.

The paragraph (Line 379-386) was rephrased as follows:

‘This scenario is supported by a marked reduction in the concentrations of sedimentary redox sensitive trace metals such as molybdenum and rhenium (Salvatteci et al., 2014b; Sifeddine et al., 2008). However, these conditions were not constant, instead short-term variations during both the LIA and the CWP are reflected for example mirrored by changes in diatom abundances, productivity sensitive element ratios (Br/Fe) and $\delta^{15}N_{bulk}$ values (Fleury et al., 2015). These proxy records indicate multidecadal shifts between arid/humid conditions during the CWP and particularly the LIA during which marked short-term periods of arid conditions occurred (Fleury et al., 2015) (Fig. 3).’

Line 290: please avoid using “a bit lower” – rephrase.

The sentence was rephrased accordingly:

Line 446: ‘The shift towards a higher 1:2 NO_3^-:$Si(OH)_4$ utilization during both the CWP and LIA (arid) indicates enhanced utilization of $Si(OH)_4$ over NO_3^- leading to $Si(OH)_4$ limitation as indicated by high $Si(OH)_4$ utilization rates between 40% and 90%, and lower NO_3^- utilization rates between 25% and to 80% (Fig. 6b).’

Line 327: I’m not sure what you mean by “horizontal alignment” – could you please clarify?

The text (Line 489-490) was changed accordingly: ‘horizontal alignment of the $\delta^{15}N_{bulk}$ versus $\delta^{30}Si_{BSi}$ values’

Line 311: Is there no means of assessing changes in downcore phytoplankton assemblages, as a comparison to the modern data from Sanchez et al? Biomarkers?

It is possible to compare the diatom assemblages as done by Fleury et al., 2015. What we wanted to highlight here is that there are no modern $\delta^{15}N$ and $\delta^{30}Si$ isotope values available to compare modern El-Nino conditions with El-Nino-like conditions in the past as claimed for the LIA.

Figure caption 4: The caption points towards figures c-e, when they should be figures b-d.

The figure caption has been corrected accordingly.

Figure 6: The fonts are too small in places.

The fonts of the figure have been enlarged accordingly (see figure attached).

Additional references:

Demarest, M.S., Brzezinski, M.A. and Beucher, C., 2009. Fractionation of silicon isotopes during biogenic silica dissolution. Geochimica et Cosmochimica Acta, 73: 5572-5583.
Egan, K. et al., 2012. Diatom silicon isotopes as a proxy for silicic acid utilisation: A Southern Ocean core top calibration. Geochimica et Cosmochimica Acta, 96: 174-192.
Sutton, J., Varela, D., Brzezinski, M.A. and Beucher, C., 2013. Species dependent silicon isotope fractionation by marine diatoms. Geochimica et Cosmochimica Acta, 104: 300-309.
Wetzel, F., de Souza, G. and Reynolds, B., 2014. What controls silicon isotope fractionation during dissolution of diatom opal? Geochimica et Cosmochimica Acta, 131: 128-137.

The references have been included in the text and accordingly been added to the reference list.

Review #2 (by Patrick Rafter)

First, I think the $d^{30}Si$ and $d^{15}N$ relationship in Figure 4A must be examined in a more robust manner. For example, I don't think it is appropriate to simply state that the surface sediment core measurements "remain close to the respective 1:1 utilization line" for nitrate to silicate in Figure 4A. This needs to be shown, regardless of this approach being previously published by Ehlert et al. (2015). Specifically, the study would be improved with a more precise quantification of this relationship in Figure 4A. Similarly, the frequent use of "correlation" in the text (n=9) is not supported with any statistics. This must be fixed.
We added a more comprehensive explanation of what is shown in Fig. 4a and how it relates to our results in S1 and Fig 4 b-d. To address this issue we improved the text explaining Fig. 4 a and the conclusions we draw from it. This point will also be further addressed below, under the last point concerning the restructuring of the Results and Discussion sections.

This point will be also further addressed below, under the last point concerning the restructuring of the Results and discussion.

The improper use of the word "correlation" was checked throughout the whole manuscript. See lines: Lines 25, 99, 572, 574 and 575, as well as in the figure captions.

Second, I think it would improve this study if the "nutrient utilization" plots in Figures 2 and 3 were separated instead of overtop each other. The estimated nitrate and silicate utilization by phytoplankton should be on separate plots.
Following the reviewer's suggestion we changed figure 2 to improve the visibility of the nutrient utilization. However we did not separate NO_3^- and $Si(OH)_4$ utilization given that the purpose of this figure is exactly to illustrate the relationship of the changes in both systems. See revised Figures 2 below.

Another strong recommendation is to compile the sediment core measurements per latitude in Figure 3 in a more comprehensible way. The reader will have a much easier time understanding the relationships in Figure 3 if they: (1) Show one measurement at a time and (2) Are "stacked" from low to high southern latitudes. In this new figure, the bulk sediment d15N for all sites will be shown 'stacked' in one column that moves from 11ºS at the top to 15ºS at the bottom. This new arrangement of the Figure 3 data will include the same data, but in a more easily understood arrangement and will allow the reader to identify the spatial and temporal variability of each proxy.
Figure 3 was modified and we now separated the different proxies (see below). Furthermore, the records are now sorted from 11 to 15ºS from top to bottom.

Fourth, the use of sedimentary percentages is not appropriate; we must see the percentage data expressed as a mass accumulation rate or MAR. This needs to be changed before I would have confidence in the interpretation (any interpretation) of the percentage measurements. The addition of MARs may actually improve the interpretation of the data, since there seems to be some confusion in the interpretation of these measurements (see Lines 204 and on).
For presentation of the BSi and TN data in Figures 2 and 5, we now calculated the respective accumulation rates based on data presented by Gutierrez et al., 2009 given for 12ºS and 14ºS, respectively, as there are no accumulation rates available for cores M77/2-24, 005 and 003. As the BSi (wt%) data is new we still show these values in Figure 3.
However, we want to point out that there is no confusion about the interpretation of BSi data. As visible in the comparison of the records of core M77/2-24 with the previously published core M77/1-470 from the same latitude the BSi (wt%) is overlapping during the CWP, but BSi values of core 24 remain high throughout the LIA and $\delta^{30}Si$ signatures of core 24 are higher by about 0.5‰ at all times. From line 204 onwards it is discussed how this difference in $\delta^{30}Si$ can occur in the 2 records located so close to each other.

Text added:

Lines 169-174: Unfortunately, no material was left of the cores studied to estimate dry bulk densities to calculate mass accumulation rates (MAR), therefore values were used from cores BO413 (12 ºS) and BO406 (14 ºS; Gutierréz et al. 2009) which were generally close to 0.02 (g cm^{-2} yr^{-1}) during the LIA and 0.03 (g cm^{-2} yr^{-1}) during the CWP. The exact bulk MAR values (g cm^{-2} yr^{-1}) for each time period were multiplied by the fractional concentration of BSi and TN (Fleury et al., 2015) to calculate the MAR BSi and MAR TN (Figs. 2 and 5).

Finally, I don't think the Discussion section is the location for describing every individual wiggle of the observations and /or the estimated source nitrate d15N. I think that an improved manuscript would have a robust statistical examination of the surface sediment d15N and d30Si (from Figure 4) in the Results section followed by text that describes the temporal variability of Figures 4 and 5. In this way, the Discussion section can be used to discuss the observed / estimated spatial and temporal changes, which will be more easily understood and (I think) enjoyable for the reader. No one wants to read a listing of which way the wiggles are wiggling and when.

Following the suggestion of the reviewer the Results and Discussion section was restructured i.e. split. The Equation for Nutrient utilization was moved to the Methods section (new section 2.4; Lines 208-227).

To address the statistical examination we added a supplementary figure (see below) that gives all linear regressions and r^2 used for the calculations of the $\delta^{15}NO_3^-$ source signatures. For the surface sediment samples a statistical examination is of little gain due to the small sample amount concerned, however we added a more detailed explanation about the information gained by Fig. 4a that should resolve this issue.

Lines 238-264:' Based on modern observations from the water column it is known that NO_3^- and $Si(OH)_4$ are incorporated in a 1:1 ratio when diatoms dominate the phytoplankton assemblage (Brzezinski, 1985; Ragueneau et al., 2000) this ratio, however, can vary between 2:1 and 1:2 on the shallow Peruvian shelf (Grasse et al., 2016). Assuming this is true for the past as well, a change in relative uptake will be visible in the $d^{15}N_{Bulk}$ versus $d^{30}Si_{BSi}$ relationship in surface sediments. We therefore applied a direct comparison of both isotope signatures in the surface sediments, following an approach of Ehlert et al. (2015). To evaluate how modern sediments record the relative nutrient utilization of both NO_3^- and $Si(OH)_4$, surface sediment values were sorted by latitude (9, 11, 12 and 15ºS) and compared to their respective $d^{15}NO_3^-$ and $d^{30}Si(OH)_4$ source and utilization relationship at each location.

First, based on the known $d^{30}Si(OH)_4$ and NO_3^- source signatures of subsurface waters we can calculate a theoretical utilization assuming 1:1 incorporation ratios of both $Si(OH)_4$ and NO_3^-. There are several factors that may cause $d^{15}N$:$d^{30}Si$ ratios to deviate from this 1:1 utilization uptake ratio of both nutrients: 1) under iron-limitation more $Si(OH)_4$ relative to NO_3^- will be taken up resulting in heavier silicified diatoms and shifting to a 1:4 N:Si uptake ratio (Hutchins and Bruland, 1998; Franck et al., 2000); 2) under prevalence of non-siliceous phytoplankton groups more NO_3^- than $Si(OH)_4$ is incorporated (Conley and Malone, 1992; Wilkerson and Dugdale, 1996), the ratio might shift up to 15:1 (Grasse et al., 2016). Therefore, the deviation from the 1:1 NO_3^- to Si(OH)4 ratio can serve as an indicator for the degree of relative utilization of NO_3^- over Si(OH)4 (Grasse et al., 2016; see utilization schematic indicated in Figure 4a).

The surface samples from 9ºS (Fig. 4) indicate low to moderate utilization of both nutrients. The sample values, however, plot beneath the 1:1 utilization line, reflecting higher NO_3^- than $Si(OH)_4$ utilization, which is supported by the calculated NO_3^- and $Si(OH)_4$ utilization as based on a steady state calculation (Fig. 2b). The data from 11ºS (Fig. 4a) all plot close to the middle of the respective 1:1 utilization line at about the middle indicating about 50% utilization for both NO_3^- and Si(OH)4, agreeing with the calculated utilization values shown in Fig. 2b. For 15º S the sample values plot further to the left of the 1:1 utilization, indicating higher utilization of Si(OH)4 than NO_3^- (Fig. 4a, 2b). This displacement to the left supports a NO_3^-:$Si(OH)_4$ ratio of 1:2 or 1:4, which agrees with direct observations from the surface waters in areas of strong upwelling (Grasse et al., 2016).'

Further, the calculation of the $\delta^{15}NO_3^-$ source based on linear regression was also moved to the Methods (now section 2.4; Lines 266-274). This paragraph was also rephrased accordingly:
Lines 257-265:' For the past time periods of the CWP and LIA conditions are thought to shift between two states (1) high upwelling intensity, high productivity and strong N-loss processes and (2) low productivity and N-loss intensity. For either state we assume that ~~T~~he ~~linear~~ relationship between $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ signatures should thus also be a direct indicator of the $\delta^{15}NO_3^-$ source signatures. ~~in the past during the CWP and the LIA~~. Depending on the exact conditions the uptake of NO_3^- to $Si(OH)_4$ might be in a ratio of for example 1:1, 2:1 or 1:2. If the conditions remain stable over the time periods samples should represent a linear relationship similar to the utilization lines indicated in Fig. 4. Assuming such a linear relationship of $\delta^{15}N_{bulk}$ to $\delta^{30}Si_{BSi}$ samples for past periods, it is possible to first calculate the respective $\delta^{15}NO_3^-$ source values and then further quantify the amount of NO_3^- utilization.'

Lines 291-294:'For all time periods and latitudes, the linear regressions as well as correlation coefficient (r^2) are given in the supplements (Fig. S1). The results are presented in the following as the resulting $\delta^{15}NO_3^-$ source values and the theoretical ratio of nutrient utilization (i.e. 1:1 or 2:1, 15:1, etc.; Fig. 4. b-d) for each latitudinal range to compare the latitudinal trends between the CWP and LIA'

Additionally, paragraphs within the previous Results and Discussion section mainly describing results were taken omitted (see Lines 424-433; 458-466; 522-535) or rephrased (Line 467-471) and a separate Results section was written (subsections 3.1 Biogenic opal and silicon isotope signatures and 3.2 $d^{15}NO_3^-$ source signatures, nutrient utilization and supply) see lines 336- 362.

Line 29: I don't think "humid conditions" is appropriate at this point; it is not common knowledge, it is not supported with evidence, and is out of place in the Abstract.
'humid conditions' has been excluded from this sentence as suggested by the reviewer.

The isotope effects of nitrate assimilation were estimated at sites across the Pacific basin in Rafter and Sigman 2016. This is blatant self-promotion, but it is entirely relevant when citing reasonable isotope effects in the tropical Pacific (we found an average of 6 per mil). We also identify the origin of variability between Rayleigh (closed system) versus Open System isotopic fractionation.
The given fractionation factors actually match values calculated for the Peruvian shelf, the appropriate references were added accordingly.
Line 45: .... , which agree well with estimates for the Peruvian shelf (Ehlert et al., 2012; Mollier-Vogel et al., 2012; Grasse et al., 2016).
However, the reference to Rafter and Sigman 2016 was added in Line 116, as it also gives a detailed overview about the $d^{15}NO_3$- values within the EUC.

Line 81: remove "been"
Line 98 'been' has been removed

89: remove "too"
Line 106 (previously 89) 'to' has been removed accordingly

99: When dealing with nitrate d15N, a difference in source waters of 5.5 to 7.0 per mil is quite large. Especially considering the small spatial difference between these sources.
Line 117: As pointed out by the reviewer a 1.5 per mil difference is not 'slight', therefore we removed 'slightly' from the sentence and replaced it with 'about 1.5‰'.

201: Sedimentary concentration measurements are common, but they are not useful or appropriate proxies in 2018. MASS ACCUMULATION RATES are necessary. Apply and then we can re-examine the records.

As now stated in line 169 and also line 303, there are unfortunately no accumulation rates available for the cores, as no dry bulk density was analyzed to calculate MAR for cores M772-024TC, 005TC and 003TC. Therefore, we used accumulation rates reported of cores BO406-13 and BO406-5 reported for the last 600 years by Guiterréz et al. 2009 to estimate the MAR TN and MAR BSi values in our cores. These data is shown in Figures 2 and 5 now. We left the actual BSi values in Figure 3, also as a comparison of the values with core M77/1-470. As accumulation rates mainly decrease during the LIA in comparison to the CWP, there should be little difference in the comparison of BSI and AR BSi concerning these two cores.

See also Line 169- 174:' Unfortunately, no material was left of the cores studied to estimate dry bulk densities to calculate mass accumulation rates (MAR), therefore values were used from cores BO413 (12 ºS) and BO406 (14 ºS; Gutierréz et al. 2009) which were generally close to 0.02 (g cm^{-2} yr^{-1}) during the LIA and 0.03 (g cm^{-2} yr^{-1}) during the CWP. The exact bulk MAR values (g cm^{-2} yr^{-1}) for each time period were multiplied by the fractional concentration of BSi and TN (Fleury et al., 2015) to calculate the MAR BSi and MAR TN (Figs. 2 and 5).'

List of relevant changes:

- the descriptions of the results have been improved
- figure 3 has been corrected and been improved based on the suggestions of the reviewers
- information has been added about the influences of dissolution and species-specific fractionation for the fractionation factor of Si
- A comparison of the d30Si values with the diatom assemblages has been added
- the sampling resolution has been clarified in the methods section
- the explanation of figure 4 a has been improved and a plot showing all linear regressions was added in S1
- the way how the nutrient utilization is plotted has been changed in figures 2 and 5
- MAR values have been calculated based on DBD values from nearby cores; MAR values are shown now in figures 2 and 5
- The results and discussion sections have been split and text passages including equations have been moved to the methods section.

Latitudinal variations of δ^{30}Si and δ^{15}N signatures along the Peruvian shelf: quantifying the effects of nutrient utilization versus denitrification over the past 600 years

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Abstract

The sedimentary stable nitrogen isotope compositions of bulk organic matter ($\delta^{15}N_{bulk}$) and silicon isotope composition of diatoms ($\delta^{30}Si_{BSi}$) both mainly reflect the degree of past nutrient utilization by primary producers. However, in ocean areas where anoxic and suboxic conditions prevail, the $\delta^{15}N_{bulk}$ signal ultimately recorded within the sediments is also influenced by water column denitrification causing an increase in the subsurface δ^{15}N signature of dissolved nitrate ($\delta^{15}NO_3^-$) upwelled to the surface. Such conditions are found in the oxygen minimum zone off Peru, where at present an increase in subsurface $\delta^{15}NO_3^-$ from North to South along the shelf is observed due to ongoing denitrification within the pole-ward flowing subsurface waters, while the δ^{30}Si signature of silicic acid ($\delta^{30}Si(OH)_4$) at the same time remains unchanged.

Here, we present three new $\delta^{30}Si_{BSi}$ records between 11°S and 15°S and compare these to previously published $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ records from Peru covering the past 600 years. We present a new approach to calculate past subsurface $\delta^{15}NO_3^-$ signatures based on the direct comparison~~correlation~~ of $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ signatures at a latitudinal resolution for different time periods. Our results show that, during the ~~last 200 years,~~ Current Warm Period (CWP, since 1800 AD) and ~~during~~ prior short-term arid events, source water $\delta^{15}NO_3^-$ compositions have been~~are~~ close to modern values increasing southward from 7 to 10‰ (between 11°S and 15°S). In contrast, ~~humid conditions~~ during the Little Ice Age (LIA) ~~reflect consistently~~ we calculate low $\delta^{15}NO_3^-$ values between 6 and 7.5‰. Furthermore, the direct $\delta^{30}Si_{BSi}$ versus $\delta^{15}N_{bulk}$ comparison also enables us ~~we are able~~ to relate the short-term variability in both isotope compositions to changes in the ratio of nutrients (NO_3^-: $Si(OH)_4$) taken up by different dominating phytoplankton groups (diatoms and non-siliceous phytoplankton) under the variable climatic conditions of the past 600 years. Accordingly, we estimate a shift from a 1:1 (or 1:2) ratio during the CWP and a 2:1 (up to 15:1) ratio during the LIA, associated with a shift from overall high nutrient utilization to NO_3^- dominated (and thus non-siliceous phytoplankton) utilization.

1. Introduction

Investigations of the isotopic compositions of the macro-nutrients, such as $Si(OH)_4$ and NO_3^-, have been used to infer changes of biogeochemical cycles in the past (Brunelle et al., 2007; Horn et al., 2011; Robinson et al., 2014). The preferential incorporation of the lighter isotopes ^{14}N and ^{28}Si into organic matter (OM) and biogenic opal (BSi), respectively, during primary production in surface waters leads to an increase in the $\delta^{15}N$ and $\delta^{30}Si$ in the remaining dissolved nutrients (i.e. $\delta^{15}NO_3^-$ and $\delta^{30}Si(OH)_4$) as a results of progressive consumption of the nutrient pools (Altabet et al., 1991; De La Rocha et al., 1997; Wada and Hattori, 1978). This preferential incorporation is associated with an approximate enrichment factor of -5‰ for NO_3^- (Waser et al., 1998) and -1.1‰ for $Si(OH)_4$ (De La Rocha et al., 1997), which agree well with estimates for the Peruvian shelf (Ehlert et al., 2012; Mollier-Vogel et al., 2012; Grasse et al., 2016). While a potential fractionation of $\delta^{30}Si$ signatures of biogenic opal during dissolution of -0.55‰ has been reported previously (Demarest 2009), subsequent investigations from the water column of the Southern Ocean did not see significant difference in the $\delta^{30}Si$ values of material from the and $\delta^{30}Si$ values in surface sediments is found (Varela et a., 2004; Fripiat et al., 2012; Closset et al., 2015). Furthermore, field studies and laboratory experiments based on sediments have so far indicated that $\delta^{30}Si$ signatures of diatoms within the sediments are generally unaffected by diagenetic alteration (e.g. Egan et al., 2012; Wetzel et al., 2014; Ehlert et al., 2016). Accordingly, the degree of utilization of NO_3^- and $Si(OH)_4$ is recorded in the $\delta^{15}N_{bulk}$ and $\delta^{30}Si_{BSi}$ of the OM and BSi produced. In combination with parameters such as organic carbon, BSi or barium accumulation rates, both $\delta^{15}N_{bulk}$ and $\delta^{30}Si_{BSi}$ have been employed as proxies for the evaluation of past productivity and corresponding nutrient utilization (De La Rocha et al., 1998; François et al., 1992; Horn et al., 2011; Pichevin et al., 2005).

However, in coastal upwelling areas, where upwelling of nutrient-rich subsurface waters causes high surface productivity, subsequent degradation of the high amounts of OM leads to extensive oxygen consumption in the water column (Pennington et al., 2006; Zuta and Guillén, 1970). As a result of the low oxygen concentrations, NO_3^- is used as an oxidant during OM degradation and is transferred to N_2 leading to a net loss of bio-available nitrogen (e.g., denitrification and anaerobe ammonium-oxidation; (Codispoti, 2006; Lam et al., 2009). Due to the high isotope fractionation factor (~20‰) associated with denitrification, the $\delta^{15}NO_3^-$ signatures of subsurface waters strongly increase and consequently supply a heavy $\delta^{15}NO_3^-$ signal to surface waters during upwelling (Cline and Kaplan, 1975). This ^{15}N-enriched NO_3^- is incorporated by phytoplankton and ultimately deposited and buried in marine sediments. Accordingly, although $\delta^{15}N_{bulk}$ also varied in phase with productivity proxies, elevated $\delta^{15}N_{bulk}$ values in highly productive and poorly ventilated regions including most of the coastal upwelling areas, have been generally interpreted as the consequence of stronger denitrification associated with intense oxygen depletion (Agnihotri et al., 2006; 2008; De Pol-Holz et al., 2007; Fleury et al., 2015; Gutiérrez et al., 2009; Mollier-Vogel et al., 2012; Salvatteci et al., 2014b). However, given that dissolved $\delta^{15}NO_3^-$ is influenced by both nutrient utilization and denitrification – associated with water column de-oxygenation - both processes should also influence the $\delta^{15}N_{bulk}$ signatures recorded by the sedimentary OM.

In contrast, $\delta^{30}Si_{BSi}$ signatures are primarily controlled by surface water diatom productivity and $Si(OH)_4$ utilization (Brzezinski, 2002; De La Rocha et al., 1998) closely coupled to the amount of upwelling strength in the study area (Doering et al., 2016; Ehlert et al., 2012; 2013; 2015; Grasse et al., 2013). Accordingly, downcore records of $\delta^{30}Si_{BSi}$ off Peru are closely coupled to changes in the diatom assemblage with high signatures (>1‰) reflecting strong upwelling conditions and lower signatures (0.5-1‰) reflecting weak upwelling conditions (Doering et al., 2016). This coupling was previously shown to be mainly the consequence of changes in the relative abundance of different diatom groups during diatom succession linked to different upwelling strength (Doering et al., 2016) rather than potential species-specific fractionation (Sutton et al., 2013).

Thus, the combination of both $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ compositions in the water column and late Quaternary sediments off Peru has been applied as a measure to disentangle modern and past nutrient utilization and denitrification processes (Ehlert et al., 2015; Grasse et al., 2016). Comparison of modern dissolved $Si(OH)_4$ and NO_3^- distributions and their corresponding isotopic ratios has shown that $Si(OH)_4$ and NO_3^- concentrations and their stable isotopic signatures are strongly correlated within the surface mixed layer at near-shore and offshore areas, indicating that the signal preserved in the sediments ~~main~~strongly depends on the degree of utilization of both nutrients (Grasse et al., 2016). Similarly, an initial comparison for the past 600 years based on one sediment core indicated that both isotope compositions were largely~~ma~~inly influenced by nutrient utilization suggesting that denitrification in the water column only had a significant influence since ˜1850 AD ~~was not the main control on past isotopic variations~~ (Ehlert et al., 2015) thus partly contradicting previous interpretations of N-loss having been the main driver of changes in past $\delta^{15}N_{bulk}$ records.

Today, the dissolved $\delta^{15}NO_3^-$ signatures increase southward along the Peruvian margin due to the continuous enrichment in ^{15}N by denitrification in pole-ward flowing subsurface waters (Mollier-Vogel et al., 2012), while $\delta^{30}Si(OH)_4$ values remain stable (Fig. 2). Here, our goal is to verify whether this southward increase of $\delta^{15}NO_3^-$ due to denitrification has ~~been~~ persisted during the marked changes in upwelling intensity of the past ~600 years based on ~~correlation~~ comparison of $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ signatures of four different sediment cores retrieved along the entire gradient of upwelling strength of the southern Peruvian shelf. More specifically, we aim to detect the extent of variability in $\delta^{15}N_{bulk}$ caused as a function of denitrification and nutrient utilization during specific time periods (i.e. Current Warm Period (CWP) and Little Ice Age (LIA)). Therefore, we present three new records for $\delta^{30}Si_{BSi}$ and BSi concentrations from the Peruvian shelf between 11°S and 15°S covering the last 600 ~~to 1000~~ years ~~BP~~. These are compared to previously published $\delta^{15}N_{bulk}$ data obtained from the same cores (Fleury et al., 2015) and ~~to~~$\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ records from a fourth core from 14°S (Ehlert et al., 2015; Fig.1).

Regional Setting

Along the Peruvian margin the main source for the high amounts of upwelled nutrients (30 µmol L^{-1} for both $Si(OH)_4$ and NO_3^-; Bruland et al., 2005) is the subsurface Peru-Chile Undercurrent (PCUC), which flows southward along the continental slope and outer shelf between 4°S and 14°S at a depth between 50 and 150 m, before it detaches from the shelf south of 15°S (Brink et al., 1983; Chaigneau et al., 2013; Toggweiler et al., 1991). Eastward flowing subsurface waters of the Equatorial Undercurrent (EUC) and the Southern Subsurface Counter Current (SSCC) (see Fig. 1a) feed the PCUC. These subsurface currents deliver $Si(OH)_4$ and NO_3^- with mean preformed source signatures for $\delta^{30}Si(OH)_4$ of 1.5 ± 0.2‰ (2SD; Beucher et al., 2011; Ehlert et al., 2012; Grasse et al., 2013) and for $\delta^{15}NO_3^-$ of 7.1 ± 0.3‰ (1SD; Rafter et al., 2012; Rafter and Sigman, 2016) for the EUC. Within the SSCC preformed $\delta^{15}NO_3^-$ values of 5.5 ± 0.3‰ (Rafter et al., 2012) are ~~slightly~~ about 1.6‰ lower than the EUC, resulting in an approximate average PCUC value of ~6‰ (Fig. 2a; Mollier-Vogel et al., 2012).

The modern surface sediment $\delta^{15}N_{bulk}$ and $\delta^{30}Si_{BSi}$ compositions both reflect an increase from North to South (Fig. 2a). However, only the dissolved $\delta^{15}NO_3^-$ of subsurface waters (50-150 m water depth) increases southward from 6‰ to 15.5‰ (EQ to 17°S; Mollier-Vogel et al., 2012) as a consequence of water column denitrification, while the dissolved $\delta^{30}Si(OH)_4$ signature remains close to the source value of 1.5‰ for the PCUC (50-150 m water depth; Fig. 2a; Ehlert et al., 2012). This difference in the evolution of the isotopic signature from North to South is caused by the anoxic conditions off Peru only increasing the $\delta^{15}NO_3^-$ signatures via denitrification in the subsurface, but not the $\delta^{30}Si(OH)_4$ signatures. Accordingly, at the northern shelf between 1°N and 10°S, where subsurface O_2 concentrations $[O_2]$ are >20 µmol L^{-1}, N-loss is not observed and the $\delta^{15}N_{bulk}$ values in the sediments range between 4 and 5‰ close to the source value of 6‰ of $\delta^{15}NO_3^-$, thus indicating a high degree of NO_3^- utilization (70-80%; Fig. 2b; Mollier-Vogel et al., 2012).

In contrast, the $\delta^{30}Si_{BSi}$ signatures north of 10°S are highly variable (0.3-0.9‰) reflecting an overall lower degree of utilization (20-40%; Doering et al., 2016; Ehlert et al., 2012) (Please note that all Si and N utilization calculations are based on an open steady-state system, which was shown to more accurately reflect the natural system off Peru, see Ehlert et al., (2012). At the central Peruvian shelf (10-12°S), where subsurface $[O_2]$ is <20 µmol L^{-1} (Fig. 2a), the subsurface source value of $\delta^{15}NO_3^-$ increases to 8.6‰ due to denitrification (Mollier-Vogel et al., 2012). The $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ values both increase to 0.9 ± 0.1‰ and 6.1 ± 0.8‰, respectively, reflecting higher $Si(OH)_4$ utilization (20-60%) but a decrease in~~lower~~ NO_3^- utilization compared to the northern part of the study area (15-65%, Fig. 2b) associated with increased upwelling intensity, high nutrient re-supply and higher consumption via diatom productivity. In the southernmost part of the shelf (13-16°S) highest productivity and upwelling intensity prevail, leading to a further increase in the subsurface $\delta^{15}NO_3^-$ signature of up to 12.5‰ at 15°S (southernmost surface sediment station of the study area), whereas surface sediment mean $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ values further increase to 1.1 ± 0.1‰ and 8.9 ± 1.4‰ reflecting moderate $Si(OH)_4$ utilization of 50-70% ($\delta^{30}Si_{BSi}$) and NO_3^- utilization of 20-70% ($\delta^{15}N_{bulk}$). The supply for dissolved $Si(OH)_4$ strongly increases from the northern shelf to the southern shelf area (Fig. 2c), reflecting the strongest upwelling conditions. This increase in upwelling and productivity between 10-15°S is reflected by the high accumulation ~~concentrations~~ of BSi (0.4-0.6 g/cm^2/yr ~~10-17%~~; calculated after Ehlert et al., (2012)) and total nitrogen (TN, 0.026-0.035 g/cm^2/yr ~~0.8-1.2%~~; calculated after Mollier-Vogel et al., (2012)) in the sediment (based on accumulation rates of Gutierréz et al., 2009). However, the NO_3^- supply, as indicated by subsurface (50-150 m) NO_3^- concentrations, slightly decreases from North to South, reflecting the loss of NO_3^- via denitrification and anammox.

2. Material and Methods

2.1 Core locations and age models

The new data in this study were obtained from three short, fine-laminated trigger cores retrieved from the main upwelling region off the Peruvian margin during the German R/V Meteor cruise M77/2 in 2008 as part of the Collaborative Research Center (SFB) 754. New records of $\delta^{30}Si_{BSi}$ and BSi concentrations were generated for cores M77/2-024-5TC (024-5TC; 11°05'S, 78°00'W, 210 m water depth), M77/2-005-3TC (005-3TC; 12°05'S, 77°40'W, 214 m water depth) and core M77/2-003-2TC (003-2TC; 15°06'S, 75°41'W, 271 m water depth). One cm slices of the sediment cores were sampled for BSi and silicon isotope measurements to ensure the availability of sufficient amounts of diatoms for silicon isotope analysis (Tab. 1). For core 003-2TC additional BSi concentration measurements of material the extracted from individual laminations was possible (Fleury et al., 2015). As previously published $\delta^{15}N_{bulk}$ values are based on samples from single laminations these were averaged to 1 cm resolution when directly compared to the $\delta^{30}Si$ data in the following. Core locations are shown in Fig. 1b. The age models were published before in ~~study of~~ Fleury et al. (2015). The age models for all cores are given years AD ~~BP, with BP relating to 2008~~.

2.2 Biogenic opal and silicon isotope analyses

The amount of BSi in the sediments was measured following an automated leaching method using sodium hydroxide (DeMaster, 1981; Müller and Schneider, 1993) with a precision of 1-2% (1SD). Unfortunately, no material was left of the cores studied to estimate dry bulk densities to calculate mass accumulation rates (MAR), therefore values were used from cores BO413 (12 °S) and BO406 (14 °S; Gutierréz et al. 2009) which were generally close to 0.02 (g cm^{-2} yr^{-1}) during the LIA and 0.03 (g cm^{-2} yr^{-1}) during the CWP. The exact bulk MAR values (g cm^{-2} yr^{-1}) for each time period were multiplied by the fractional concentration of BSi and TN (Fleury et al., 2015) to calculate the MAR BSi and MAR TN (Figs. 2 and 5).

For the silicon isotope measurements diatoms were extracted from the sediment by chemical and physical cleaning (11 and 32 µm sieve; heavy liquid separation with a sodium polytungstate solution set at 2.15 g mL^{-1}) as described in detail in Ehlert et al. (2012; 2013) and Doering et al. (2016). For all samples the purity of the small diatom fraction (11-32 µm) was evaluated via light microscopy prior to dissolution and only pure (>95%) diatom samples were treated further. All samples were dissolved in 1 mL 0.1 M NaOH and treated with 200 µL concentrated H_2O_2 (Suprapur). Sample solutions were diluted with 4 mL MQ water and neutralized with 0.1 mL 1 M HCl (Reynolds et al., 2008), followed by a chromatographic purification using 1 mL pre-cleaned AG50W-X8 cation exchange resin (BioRad, mesh 200-400) (de Souza et al., 2012). The Si isotopic compositions were determined in 0.6 ppm sample solutions on a *NuPlasma HR* MC-ICPMS at GEOMAR applying a standard-sample bracketing method (Albarède et al., 2004). Silicon isotopic compositions are reported in the δ-notation relative to the reference standard NBS28 in parts per thousand: $\delta^{30}Si = ((R_{sample}/R_{standard})-1)*1000$, where R_{sample} is the $^{30}Si/^{28}Si$ ratio of the sample and $R_{standard}$ is the $^{30}Si/^{28}Si$ ratio of the NBS28. All $\delta^{30}Si$ measurements were run at least in triplicates, with uncertainties ranging between 0.05‰ and 0.27‰ (2 SD). Repeated measurements of an in-house matrix standard gave average δ^{30}Si values of 1.03 ± 0.21‰ (2 SD n=15). Long-term repeated measurements of the reference materials NBS28, IRMM018, and Big Batch gave average δ^{30}Si values of 0.00 ± 0.24‰ (2 SD), -1.40 ± 0.21‰ (2 SD, n=15) and -10.60 ± 0.24‰ (2 SD, n=15), respectively, in good agreement with literature values (Reynolds et al., 2007).

2.3 Diatom assemblage data

Diatom analysis of cores M77/2-024-5TC, 005-3TC and 003-2TC were published previously based on three slides per sample and counting of a minimum of 300 valves for each sample (for details see Fleury et al., 2015). The diatom abundances are presented here for three groups representing different environmental conditions (Fig. 3): Upwelling species – Chaetoceros sp., Skeletonema costatum, Thalassionema nitzschioides var. nitzschioides; Coastal planktonic – Actinocyclus spp., Atinoptychus spp, Asteromphalus spp., and Coscinodiscus sp.; Other diatom species – Nitzschia spp., Rhizosolenia spp. and Thalassiosira spp., Cyclotella spp., Cocconeis sp.;

The diatom assemblage abundance is compared to $\delta^{30}Si_{BSi}$ compositions for cores M77/2-024-5TC, 005-4TC and 003-2TC to investigate if changes in the assemblage have influenced the isotopic record. While diatom counts have been performed on bulk sediment samples $\delta^{30}Si_{BSi}$ was measured on the 11-32µm size fraction. However, it was shown previously that this size range closely resamples the main assemblage, which allows studying the influence of changes in the diatom assemblage on the $\delta^{30}Si_{BSi}$ record (Ehlert et al., 2012; 2013).

2.4 Nutrient utilization

The degree of nutrient utilization can be described assuming either Rayleigh-type (single input followed by no additional nutrients newly supplied to a particular parcel of water followed by fractional loss as a function of production and export) or steady-state (continuous supply and partial consumption of nutrients causing a dynamic equilibrium of the dissolved nutrient concentration and the product) fractionation behavior (Mariotti et al., 1981). For means of simplification we will only provide the values derived from steady state fractionation, which was shown to better reflect upwelling conditions off Peru (Ehlert et al., 2012).

(1) $\%Si(OH)_{4\,consumed} = 1 - \left(\left(\delta^{30}Si - \delta^{30}Si(OH)_{4\,source}\right)/{}^{30}\varepsilon\right) * 100$ ~~or~~

$\%NO_3^{-}{}_{consumed} = [1 - (\delta^{15}N - \delta^{15}NO_3^{-})/{}^{15}\varepsilon] * 100$

with $\%Si(OH)_{4\,consumed}$ or $\%NO_3^{-}{}_{consumed}$ being the percentages of the supplied $Si(OH)_4$ and NO_3^- that have been utilized. For this calculation we apply enrichment factors of −1.1‰ $^{30}\varepsilon$ (δ^{30}Si, De La Rocha et al., 1997) and −5‰ $^{15}\varepsilon$ (δ^{15}N) and assume a constant source water signature of 1.5‰ for $\delta^{30}Si(OH)_{4\ source}$ (i.e. the mean $\delta^{30}Si(OH)_4$ of the PCUC). To evaluate the impact of changes in $^{30}\varepsilon$ on the δ^{30}Si signatures the potential influence of species-specific fractionation was tested based on the impact of a -2.1‰ enrichment factors of *Chaetoceros brevis* (Sutton et al., 2013). However, the estimated impact on past $\delta^{30}Si_{BSi}$ records due to a change in the amount of *Chaetoceros* sp. present in the sediment was less than 5% for all cores (M77/2-024-5TC, 005-3TC and 003-2TC) and thus did not alter the assumed $^{30}\varepsilon$ of -1.1‰ substantially (based on calculations presented in Doering et al., (2016); not shown). The impact of denitrification on the $\delta^{15}NO_3^-$ signatures of the past is assessed in the following section before calculating past NO_3^- utilization for the respective latitudes.

2.5 Calculation of the $\delta^{15}NO_3^-$ source signatures

~~To disentangle denitrification and relative nutrient utilization we apply a correlation comparison of $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ values (Fig. 4a) based on the observations from today's water column and surface sediments (Fig. 2). Despite that denitrification strongly increases the $\delta^{15}NO_3^-$ values in subsurface waters ultimately upwelled to the surface and incorporated into phytoplankton, modern sediment values of $\delta^{15}N_{bulk}$ are mainly controlled by the degree of surface water NO_3^- utilization (Ehlert et al., 2015; Mollier-Vogel et al., 2012). Particularly between 10°S and 17°S, where the subsurface $\delta^{15}NO_3^-$ source value increases southward due to increasing O_2 deficit and increasing denitrification, the $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ values are plot generally close to the 1:1 utilization line indicating a similar uptake efficiency of both NO_3^- and $Si(OH)_4$, respectively (Fig. 4a).~~

Based on modern observations from the water column it is known that NO_3^- and $Si(OH)_4$ are incorporated in a 1:1 ratio when diatoms dominate the phytoplankton assemblage (Brzezinski, 1985; Ragueneau et al., 2000) this ratio, however, can vary between 2:1 and 1:2 on the shallow Peruvian shelf (Grasse et al., 2016). Assuming this is true for the past as well, a change in relative uptake will be visible in the $\delta^{15}N_{Bulk}$ versus $\delta^{30}Si_{BSi}$ relationship in surface sediments. We therefore applied a direct comparison of both isotope signatures in the surface sediments, following an approach of Ehlert et al. (2015). To evaluate how modern sediments record the relative nutrient utilization of both NO_3^- and $Si(OH)_4$, surface sediment values were sorted by latitude (9, 11, 12 and 15ºS) and compared to their respective $\delta^{15}NO_3^-$ and $\delta^{30}Si(OH)_4$ source and utilization relationship at each location.

First, based on the known $\delta^{30}Si(OH)_4$ and NO_3^- source signatures of subsurface waters we can calculate a theoretical utilization assuming 1:1 incorporation ratios of both $Si(OH)_4$ and NO_3^-. There are several factors that may cause $\delta^{15}N$: $\delta^{30}Si$ ratios to deviate from this 1:1 utilization uptake ratio of both nutrients: 1) under iron-limitation more $Si(OH)_4$ relative to NO_3^- will be taken up resulting in heavier silicified diatoms and shifting to a 1:4 N:Si uptake ratio (Hutchins and Bruland, 1998; Franck et al., 2000); 2) under prevalence of non-siliceous phytoplankton groups more NO_3^- than $Si(OH)_4$ is incorporated (Conley and Malone, 1992; Wilkerson and Dugdale, 1996), the ratio might shift up to 15:1 (Grasse et al., 2016). Therefore, the deviation from the 1:1 NO_3^- to $Si(OH)_4$ ratio can serve as an indicator for the degree of relative utilization of NO_3^- over $Si(OH)_4$ (Grasse et al., 2016; see utilization schematic indicated in Figure 4a).

The surface samples from 9ºS (Fig. 4) indicate low to moderate utilization of both nutrients. The sample values, however, plot beneath the 1:1 utilization line, reflecting higher NO_3^- than $Si(OH)_4$ utilization, which is supported by the calculated NO_3^- and $Si(OH)_4$ utilization as based on a steady state calculation (Fig. 2b). The data from 11ºS (Fig. 4a) all plot close to the middle of the respective 1:1 utilization line at about the middle indicating about 50% utilization for both NO_3^- and $Si(OH)_4$, agreeing with the calculated utilization values shown in Fig. 2b. For 15º S the sample values plot further to the left of the 1:1 utilization, indicating higher utilization of $Si(OH)_4$ than NO_3^- (Fig. 4a, 2b). This displacement to the left supports a NO_3^-:$Si(OH)_4$ ratio of 1:2 or 1:4, which agrees with direct observations from the surface waters in areas of strong upwelling (Grasse et al., 2016).

For the past time periods of the CWP and LIA conditions are thought to shift between two states (1) high upwelling intensity, high productivity and strong N-loss processes and (2) low productivity and N-loss intensity. For either state we assume that ~~T~~he ~~linear~~ relationship between $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ signatures should thus also be a direct indicator of the $\delta^{15}NO_3^-$ source signatures. ~~in the past during the CWP and the LIA~~. Depending on the exact conditions the uptake of NO_3^- to $Si(OH)_4$ might be in a ratio of for example 1:1, 2:1 or 1:2. If the conditions remain stable over the time periods samples should represent a linear relationship similar to the utilization lines indicated in Fig. 4. Assuming such a linear relationship of $\delta^{15}N_{bulk}$ to $\delta^{30}Si_{BSi}$ samples for past periods, it is possible to first calculate the respective $\delta^{15}NO_3^-$ source values and then further quantify the amount of NO_3^- utilization.

In order to estimate past changes in the $\delta^{15}NO_3^-$ source values the $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ values for both time periods, CWP and arid and humid periods during the LIA, were separately plotted against each other (Fig. 4c-e) and $\delta^{15}NO_3^-$ was calculated based on the linear function assuming that the source $\delta^{30}Si(OH)_4$ signature always remained stable at 1.5‰ over time:

(2) $\delta^{30}Si(OH)_4 = a * \delta^{15}NO_3^{-} + b$, or

(3) $\delta^{15}NO_3^{-} = \left(\delta^{30}Si(OH)_4 - b\right)/\, a$

with a indicating the slope of the line and b the intercept. For $\delta^{30}Si(OH)_4$ we used the value of 0.4‰ representing near-0% utilization (= source water $\delta^{30}Si(OH)_4$ of 1.5‰ of the PCUC – 1.1‰ fractionation during uptake) to estimate the $\delta^{15}NO_3^-$ source. Accordingly, the values estimated by equation (3) represent the $\delta^{15}NO_3^-$ source value assuming also near-0% utilization of NO_3^-. The final $\delta^{15}NO_3^-$ source values given in Fig. 4 are representing the 100% utilization of NO_3^- resulting in $\delta^{15}N$ within the sediment to be equal to the $\delta^{15}NO_3^-$ source (assuming steady state).

~~Accordingly,~~ We calculated the linear regression based on all samples of the different cores from the different latitudes (11°S, 12° S, 14°S and 15°S) during the CWP and LIA. We also further differentiated between short-term productive phases (arid phases) and the generally prevailing humid El-Niño like conditions during the LIA (grey shadings in Fig. 3), and resolved the resulting equation based on eq. (2) to estimate $\delta^{15}NO_3^-$. For all time periods and latitudes, the linear regressions as well as correlation coefficient (r^2) are given in the supplements (Fig. S1). The results are presented in the following as the resulting $\delta^{15}NO_3^-$ source values and the theoretical ratio of nutrient utilization (i.e. 1:1 or 2:1, 15:1, etc.; Fig. 4. b-d) for each latitudinal range to compare the latitudinal trends between the CWP and LIA

2.6 Calculation of Nutrient supply

Based on these calculated subsurface $\delta^{15}NO_3^-$ values we further calculated the change in nutrient utilization as well as nutrient supply for the different latitudes. Past nutrient utilization was calculated following equation (2). Given the estimate of nutrient demand and export productivity it is further possible to estimate changes in the supply with the relationship Δsupply = Δdemand/Δutilization by applying the equation of (Horn et al., 2011) given by:

$$(4)\quad \mathit{Nutrient\ supply} = \frac{F^{sample}_{BSi/TN} / F^{present}_{BSi/TN}}{\%nutrient^{sample}_{consumed} / \%nutrient^{present}_{consumed}}$$

$F_{opal/TN}$ is the flux of BSi or TN and $\%nutrient_{consumed}$ is the percent of the $Si(OH)_4$ or NO_3^- supply consumed (i.e. nutrient utilization). Given that there are no accumulation rates available for either the surface sediment samples or for any of the cores studied here to determine the export productivity directly, we used mass accumulation rates (g cm^{-2} yr^{-1}) for cores BO406-13 and 406-5 from Gutierréz et al. 2009 to calculate the accumulation rates for BSi and TN (MAR; g/cm^2/yr) ~~(wt%) values for calculation and not flux values~~. ~~This may lead to an overestimation of nutrient supply, but should reflect the correct trends~~. For the different time periods mean values for MAR BSi and MAR TN were calculated and the respective nutrient supply was calculated based on equation (4), indicating changes in the nutrient supply compared to modern values.

3. Results

3.1 Biogenic opal and silicon isotope signatures

The data of the sediment cores from the shelf area between 12°S and 15°S presented here show an increase in BSi content from mean values of 13-23% during the LIA to values of 21-29% during the CWP. The $\delta^{30}Si$ records follow a similar trend of lower mean $\delta^{30}Si_{BSi}$ values of 0.8 ± 0.2‰ (2SD, 12°S), 0.8 ± 0.1‰ (14°S) and 1 ± 0.2‰ (15°S) during the LIA to more variable and higher mean values of 1.3 ± 0.4‰ (12°S), 0.8 ± 0.4‰ (14°S) and 1.5 ± 0.2‰ (15°S) during the CWP. ~~This indicates that diatom productivity and $Si(OH)_4$ utilization, reconstructed via BSi concentrations and $\delta^{30}Si_{BSi}$ values, most of the time were lower during the LIA than during the CWP (~~Fig. 3 a-d; Table 1).

The diatom assemblages (Fig. 3e-g; based on Fleury et al., 2015) show a strong association of the amount of upwelling species and $\delta^{30}Si_{BSi}$ signatures, with decreases of up to 20% in upwelling species often accompanied by a reduction of $\delta^{30}Si_{BSi}$ by about 0.5-1‰. However, not every decrease in $\delta^{30}Si_{BSi}$ is mirrored by a change in the diatom assemblage and vice versa (e.g. Fig. 3f at 1650 AD). Overall the diatom assemblage data indicates little changes in the mean conditions at 11°S (024-5TC) and a slight reduction of upwelling strength at 12°S and 15°S during the LIA in comparison to the CWP. The most distinct shift of lower abundances of upwelling species (~50%) to higher values during the CWP (~70%) is found at 15°S (003-2TC) corresponding to the strongest changes in BSi and $\delta^{30}Si_{BSi}$ at this location.

As previously shown the $\delta^{15}N_{bulk}$ values of the three cores (M77/2-024-5TC, 005-3TC and 003-2TC) presented in this study were on average 0.8‰ lower during the LIA than during the CWP (Fleury et al., 2015; Fig. 3 h,i, k). The $\delta^{15}N_{bulk}$ values reported for core 005-3TC (12°S) are close to values of nearby core B0406-13 (Gutiérrez et al., 2009; Fig. 3i). Similarly, the $\delta^{15}N_{bulk}$ values of core 003-2TC (15°S) agree well with previously published $\delta^{15}N_{bulk}$ record of core B0405-6 (14°S, Fig. 3 j, k; Gutiérrez et al., 2009); Overall, productivity and nutrient utilization proxies (BSi and $\delta^{30}Si_{BSi}$) varied in phase with $\delta^{15}N_{bulk}$ signatures at all core locations (Fig. 3).

3.2 $\delta^{15}NO_3^-$ source signatures, nutrient utilization and supply

~~The isotopic compositions of samples from all cores generally plot close to the 1:1 utilization lines indicating a $\delta^{15}NO_3^-$ source value of 8 to 9‰, similar to present day subsurface waters between 10°S and 15°S (Fig. 4a, b). Furthermore, the $\delta^{15}N_{bulk}$ values and calculated subsurface $\delta^{15}NO_3^-$ source values indicate a similar southward increase from 7‰ to 10‰ between 11°S and 15°S during the CWP (Fig. 4b).~~

During the CWP the calculated $\delta^{15}NO_3^-$ source signatures based on eq. (2) and (3) result in values of 7.6‰ at 11ºS, 8.6‰ at 12ºS and 10.4‰ between 14ºS and 15ºS during the CWP (Fig. 4b; S1 a-c), which reflects a southward increase in $\delta^{15}NO_3^-$source signatures as observed today (Fig. 2a). Based on these $\delta^{15}NO_3^-$ values the nutrient utilizations estimated based on eq. (1) range between 30-90% for NO_3^- and 40-100% for $Si(OH)_4$ (Fig. 5a). During the LIA (arid) similar values are calculated $d^{15}N$ 8‰ between 11ºS and 12ºS and 9‰ between 14ºS and 15ºS. The respective nutrient utilization ranges between 2 to 70% for NO_3^- and 20 to 85% for $Si(OH)_4$. During the humid phases of the LIA the ~~data indicate a lower~~ calculated $\delta^{15}NO_3^-$ source values were lower reaching ~~at around~~ 6‰ ~~for samples~~ between 11°S and 12°S and 7.5‰ ~~further south~~ between 14°S and 15°S (Fig. 4d). ~~Additionally, the $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ data plot below the 1:1 utilization line and between the utilization lines representing ratios of 2:1 and 15:1 for NO_3^-:$Si(OH)_4$, as supported by an increase in~~ The calculated NO_3^- utilization ~~(to~~ ranges between 70 and 90%~~)~~ and ~~a decrease in~~ ~~The calculated~~ $Si(OH)_4$ utilization ~~is lowered (to~~ ranges between 6 and 60%~~) and increased~~ (Fig. 5c). ~~Also, while $\delta^{30}Si_{BSi}$ values remain remarkably stable (around 0.5‰ at 14°S; 0.7-1‰ at 11°S, 12°S and 15°S; with the exception of one higher data point at 11°S), $\delta^{15}N_{bulk}$ values show a wide range between 4.8‰ and 6.7‰ potentially reflecting enhanced NO_3^- limitation prevailing during these humid phases.~~

~~Generally,~~ The mass accumulation rates of TN (MAR TN) were lower by around 0.02 (g/cm^2/yr) ~~slightly~~ lower during the CWP than today and lowest (<0.02 g/cm^2/yr) during the LIA, with little difference between humid and arid phases. The MAR BSi values ~~concentrations~~ were generally higher by about ~~5%~~ 0.1 - 0.35 (g/cm^2/yr) during the CWP and LIA (arid) than today with highest values at 15°S, and more similar values to today during the LIA (humid) (Figs. 2, 5).

~~3. Results and discussion~~

4. Discussion

The climate of the last 600 years is divided into two climatic phases consisting of the CWP (since 1800 AD~~200 years BP to present~~) and the LIA (ca. 1400 to 1800 AD~~600-200 years BP~~). Off Peru, the CWP has been characterized by dry (arid) conditions, high upwelling intensity, as well as high productivity and strong N-loss processes, reflecting overall dominant La-Niña conditions (Fleury et al., 2015; Salvatteci et al., 2014b; Sifeddine et al., 2008). In contrast, the LIA has been shown to be characterized by lower productivity and low denitrification intensity for the present day main upwelling area between 10°S and 15°S (Díaz-Ochoa et al., 2009; Salvatteci et al., 2014b; Sifeddine et al., 2008). Such conditions are more similar to modern El-Niño events in the area and thus generally referred to as El-Niño-like conditions (Clement et al., 2000). Previous paleo-reconstructions agreed that the latter conditions were a consequence of larger scale climatic changes induced by weakening of the Walker circulation and reduction of the South Pacific subtropical High (SPSH), as well as by a southward shift of the mean position of the Intertropical Convergence Zone (ITCZ) and the associated precipitation belt (Fleury et al., 2015; Sachs et al., 2009; Salvatteci et al., 2014b; Sifeddine et al., 2008). This was inferred to result in a deepening of the nutricline and reduced surface productivity and more oxygenated subsurface waters, as indicated by lower BSi and TOC concentrations (*this study*; (Ehlert et al., 2015; Gutiérrez et al., 2009; Salvatteci et al., 2014a) and Si/Fe ratios (Fleury et al., 2015). ~~Conditions which are~~ This scenario is supported by a marked reduction in the concentrations of sedimentary redox sensitive trace metals such as molybdenum and rhenium (Salvatteci et al., 2014b; Sifeddine et al., 2008). However, these conditions were not constant ~~at all.,~~ instead ~~S~~short-term variations during both ~~periods~~ the LIA and the CWP are ~~reflected~~ for example mirrored by changes in diatom abundances, productivity sensitive element~~s~~ ratios (Br/Fe) and $\delta^{15}N_{bulk}$ values (Fleury et al., 2015). These proxy records ~~probably~~ indicate multidecadal shifts between arid/humid conditions during the CWP and particularly the LIA during which marked short-term periods of arid conditions occurred (Fleury et al., 2015) (Fig. 3).

The well-studied biogeochemical evolution of the Peruvian shelf over the last 600 years and the significant differences in productivity and subsurface oxygenation between the CWP and the LIA are the basis for our study to gain new insights into the relationship between nutrient utilization and denitrification via $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ records.

4.1 Changes in BSi production and $\delta^{30}Si_{BSi}$ during the last 600 years

~~Overall~~ The BSi concentrations and $\delta^{30}Si_{BSi}$ signatures at 12°S (005-3TC) and 15°S (003-2TC) are lowest during the LIA (Fig. 3c,e), in agreement with previously published records from 11°S (M77/1-470; Fig. 3a) and 14°S (Ehlert et al., 2015; Fig. 3d). An exception is core 024-5TC (Fig. 3a) from 11°S, where $\delta^{30}Si$ mean values of the LIA (1.3 ± 0.4‰) are similar to CWP mean values (1.4 ± 0.1‰). Furthermore, both the BSi concentrations and $\delta^{30}Si_{BSi}$ of core 024-5TC are significantly higher during the LIA than at nearby core M77/1-470 (Fig. 2a; Ehlert et al. 2015). Such consistently high BSi and $\delta^{30}Si$ values reflect a high~~er~~ degree of $Si(OH)_4$ utilization–generally associated with strong upwelling conditions ~~may be explained by limited $Si(OH)_4$ supply~~ at site 024-5TC during the LIA ~~resulting in a higher degree of $Si(OH)_4$ utilization~~. This is, however, not supported by other productivity proxies such as the Si/Fe ratio and the total diatom abundance for core 024-5TC, which do not indicate similarly high BSi production during the LIA and the CWP (Fleury et al., 2015). However, comparison with the cumulative diatom assemblage indicates overall little difference in the amount of upwelling and coastal planktonic diatom species between the LIA and the CWP at 11°S (Fig. 3f), with intervals of reduced abundances of upwelling species of generally less than 50 years, much shorter than the 100 to 150 years intervals observed at 12 and 15°S. Furthermore, the finely laminated sediments do indicate short periods of higher productivity during the LIA in phase with more arid conditions (Fig. 3, grey shadings; for details see (Fleury et al., 2015). Accordingly, the high mean BSi and $\delta^{30}Si_{BSi}$ values obtained from core 024-5TC may be an artifact of the low sampling resolution with only two $\delta^{30}Si_{BSi}$ samples between 1700 and 1800 AD~~ 200 and 350 years BP~~, as $\delta^{30}Si_{BSi}$ analysis do not cover all short events (~50 years) of reductions in the abundance of upwelling diatom species (Fig. 3f). Alternatively, the increase in $Si(OH)_4$ utilization decoupled from an increase in diatom abundance (Fleury et al., 2015) not shown here) may indicate stronger silicification of the diatom frustules, as often observed under iron (Fe)-deficient conditions further associated with an increase in the $Si(OH)_4$:NO_3^- incorporated by the diatoms (De La Rocha et al., 2000; Takeda, 1998; Wilken et al., 2011).

4.2 Impact of denitrification versus nutrient utilization on the records

4.2.1 Disentangling nutrient utilization and N-loss processes: Changes in the source water nitrate isotopic composition

Given the significant changes in upwelling intensity, productivity and subsurface oxygenation (and thus N-loss) between the LIA and CWP (Fig. 3), we first investigated if and how the preformed $\delta^{15}NO_3^-$ signal changed with latitude (between 11°S and 15°S), and then used this information to reconstruct how nutrient supply and utilization changed during these time periods.

~~This reduced NO_3^- versus Si utilization between 10 and 17°S agreesis in agreement with observations from modern water samples, for which nutrient ratios (NO_3^-:$Si(OH)_4$) near the shelf were found to be close to 1:1 (varying between 1:2 and 2:1) (Grasse et al., 2016). Accordingly, the direct comparison surface sediment $\delta^{30}Si_{BSi}$ versus $\delta^{15}N_{bulk}$ signatures illustrate the southward increase in source $\delta^{15}NO_3^-$ signatures (Fig. 4a; stars), but remain close to the respective 1:1 utilization line for NO_3^-:$Si(OH)_4$. To study the importance of utilization and denitrification during the CWP and LIA we reconstructed nutrient utilization at the different core sites by assessing the deviation from 1:1 (NO_3^-:$Si(OH)_4$) utilization over time based on the direct comparison of $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ values. Under the influence of denitrification (N-loss) the isotopic value of NO_3^- in the source waters will be shifted to higher values.~~

Our results show that the correlation of $\delta^{30}Si_{BSi}$ to $\delta^{15}N_{bulk}$ during the CWP is comparable to modern values between 10°S and 15°S (Figs. 4a,b). The isotopic compositions of samples from all cores generally plot close to the 1:1 utilization lines indicating a $\delta^{15}NO_3^-$ source value of 8 to 9‰, similar to present day subsurface waters between 10°S and 15°S (Fig. 4a, b). Furthermore, the $\delta^{15}N_{bulk}$ values and calculated subsurface $\delta^{15}NO_3^-$ source values indicate a similar southward increase from 7‰ to 10‰ between 11°S and 15°S during the CWP (Fig. 4b). Thus, we suggest that the net increase in $\delta^{15}N_{bulk}$ from North to South during the CWP resembles the increase observed in modern surface sediments (Figs. 2 and 5a). However, unlike todays surface sediment data, the cores at 11°S and 12°S show substantially higher $\delta^{30}Si_{BSi}$ values during the CWP. According to the steady state calculations (3) this reflects high $Si(OH)_4$ utilization of up to 100%, whereas the NO_3^- utilization only reaches 80% at maximum (Fig. 5a).

Based on the classification of Fleury et al. 2015, we further distinguished between samples from humid periods (El Niño-like conditions) and arid periods (La Niña-like conditions) for the LIA (Figs. 4 and 5). This differentiation clearly highlights that samples from LIA (arid) phases are similar to samples from the CWP with $\delta^{15}NO_3^-$ source signatures of 8‰ to 9‰ between 11°S and 15° S, respectively. The shift towards a higher 1:2 NO_3^-:$Si(OH)_4$ utilization during both the CWP and LIA (arid) indicates enhanced utilization of $Si(OH)_4$ over NO_3^- leading to $Si(OH)_4$ limitation as indicated by high $Si(OH)_4$ utilization rates between 40% and 90%~~, whereas~~ and lower NO_3^- utilization rates ~~were a bit lower around~~ between 25% and ~~to~~ 80% (Fig. 5b). Such a decoupling of Si and N within diatoms can be caused by biogeochemical changes, such as iron availability altering the Si:N uptake dynamics (Hutchins and Bruland, 1998; Takeda, 1998) whereby elevated Si:N ratios are characteristic for Fe-limited diatom communities (Takeda, 1998). Accordingly, increased uptake of Si over N can lead to a $Si(OH)_4$ limitation as found during the CWP and LIA arid phases at 11°S to 12°S. The reason may have been that less Fe was upwelled at the narrow shelf between 11°S and 16°S, which led to Fe-limitation during progressing diatom blooms (Doering et al., 2016).

~~During the humid phases of the LIA the data indicate a lower $\delta^{15}NO_3^-$ source values around 6‰ for samples between 11°S and 12°S and 7.5‰ further south between 14°S and 15°S (Fig. 4d). Additionally, the $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ data plot below the 1:1 utilization line and between the utilization lines representing ratios of 2:1 and 15:1 for NO_3^-:$Si(OH)_4$, as supported by an increase in the calculated NO_3^- utilization (to 70-90%) and a decrease in The calculated $Si(OH)_4$ utilization is lowered (to 6-60%) and increased (Fig. 5c). Also, while $\delta^{30}Si_{BSi}$ values remain remarkably stable (around 0.5‰ at 14°S; 0.7-1‰ at 11°S, 12°S and 15°S; with the exception of one higher data point at 11°S), $\delta^{15}N_{bulk}$ values show a wide range between 4.8‰ and 6.7‰ potentially reflecting enhanced NO_3^- limitation prevailing during these humid phases.~~

During the humid phases of the LIA the $\delta^{15}NO_3^-$ source signatures decrease to 6‰ (11-12 ºS) and 7.5‰ (14-15 ºS) further indicating increased NO_3^- over $Si(OH)_4$ utilization (ratios of 2:1 and 15:1; Fig. 4 d) as supported by increased NO_3^- utilization and decreased $Si(OH)_4$ utilization (Fig. 5c). While $\delta^{30}Si_{BSi}$ values remain remarkably stable, $\delta^{15}N_{bulk}$ values show a wide range between 4.8‰ and 6.7‰ potentially reflecting enhanced NO_3^- limitation prevailing during these humid phases. Such a ~~The~~ shift towards increasing $\delta^{15}N_{bulk}$ values with consistently low $\delta^{30}Si_{BSi}$ values can be caused by weaker denitrification due to the higher subsurface oxygenation (only suboxic and not anoxic conditions) reconstructed for the area together with decreased upwelling conditions at the time (Salvatteci et al., 2014b; Sifeddine et al., 2008). Unfortunately, to date there are no isotopic measurements available for either present day El-Niño $\delta^{15}NO_3^-$ or $\delta^{30}Si(OH)_4$ signatures of Peruvian water masses in order to better evaluate the effects of these significant changes in climatic forcing. Overall, our results indicate much higher NO_3^- utilization over $Si(OH)_4$ utilization (Fig. 5c), which is in agreement with phytoplankton assemblage analyses during El-Niño events indicating dominating productivity of non-siliceous phytoplankton groups (Sanchez et al., 2000). Accordingly, primary productivity dominated by non-siliceous phytoplankton leads to enhanced NO_3^- over $Si(OH)_4$ uptake. Although similar conditions are found offshore the Peruvian shelf today, these surface waters originate from the shelf area where diatom blooms prevail, thus being already depleted in $Si(OH)_4$ and not providing an adequate analogue for the conditions observed during the LIA.

However, while NO_3^- limitation seems to have prevailed at all latitudes during the LIA (humid) (i.e. all sample fall between the 2:1 and 15:1 utilization lines), only the data at 11-12°S indicate a $\delta^{15}NO_3^-$ source value close to 6‰. In contrast samples from 14-15°S show~~ slightly~~ higher $\delta^{15}N_{bulk}$ values up to 7.3 ~~± 0.1~~‰, potentially indicating a slight increase in $\delta^{15}NO_3^-$ to up to 7.5‰ due to ongoing but decreased denitrification at 14 to 15°S during this time. It should be noted that it was not possible to calculate $\delta^{15}NO_3^-$ values based on the linear function (eq. (2)) during this period, due to near horizontal alignment of the $\delta^{15}N_{bulk}$ versus $\delta^{30}Si_{BSi}$ values. Alternatively, we cannot exclude that under El-Niño-like conditions, the hydrodynamic conditions off Peru may be better described by a Rayleigh-type model (closed system) instead of the steady state model, which was reported to better describe the modern conditions (Ehlert et al., 2012). Applying a Rayleigh-type model calculation, $\delta^{15}N_{bulk}$ values of 7.3‰ during the LIA (humid) would reflect approximately 75% utilization assuming the $\delta^{15}NO_3^-$ source value remaining at 6‰ and an enrichment factor of -5‰. As upwelling of nutrient-rich water masses was diminished during this time, a closed system scenario is possibly to be more appropriate to interpret the isotopic signatures and would be in agreement with a more oxygenated (suboxic) water-column at the time reducing subsurface denitrification (Briceño-Zuluaga et al., 2016; Gutiérrez et al., 2009; Salvatteci et al., 2014b; Sifeddine et al., 2008). However, due to the lack of modern data for comparison with El-Niño events for comparison we assume a decrease to a $\delta^{15}NO_3^-$ source value of 6‰ between 11°S and 12°S and 7.5‰ between 14°S and 15°S during the LIA (humid) for the following discussion, still indicating a ~~slight~~ southward increase given that denitrification was not shut down completely (suboxic conditions as indicated by trace metal studies; Salvatteci et al., 2014b; Sifeddine et al., 2008) .

4.2.2 ~~Latitudinal variation~~ The effects of changes in the nutrient supply ~~during the CWP and LIA~~

Comparison of $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ values for the past ~600 years indicates that the $\delta^{15}NO_3^-$ source values between 11°S and 15°S during the CWP and LIA (arid) were comparable to today yielding southward increasing values of 7‰ to 10‰ caused by subsurface denitrification under oxygen-depleted conditions (Fig. 2; Fig. 5a, b). For both the CWP and LIA (arid) calculated nutrient utilization indicates higher $Si(OH)_4$ utilization (ranging between 30 and 100%) over NO_3^- utilization (ranging between 20 and 90%), ~~similar to modern utilization at 10-15°S~~ (Figs. ~~2,~~ 5). ~~However,~~ These estimates indicate higher $Si(OH)_4$ utilization ~~was even higher~~ and lower NO_3^- utilization ~~lower~~ than observed today ~~modern values~~. The calculated Si and N supplies both indicate a slight increase compared to today with Si supply increasing and N supply decreasing towards 14°S and 15°S. The latter agrees~~is in agreement~~ with continuous denitrification in the southern area causing loss of NO_3^-.

In contrast, during the LIA (humid) the decrease in productivity and upwelling has led to more oxygenated waters and subsequent reduction in denitrification devoid of a strong increase in subsurface $\delta^{15}NO_3^-$, which was presumably closer to 6‰ and similar to that of the PCUC reaching the northern shelf area today. Only at 14°S and 15°S the subsurface $\delta^{15}NO_3^-$ signal may have been ~~slightly~~ increased by 1.5‰ due to denitrification if assuming that NO_3^- fractionation in the hydrographic system of the area was continuously consistent with a steady-state type model over time (Fig. 5c).

~~Generally, AR TN values are by 0.02 (g/cm²/yr) slightly lower during the CWP than today and lowest (<0.02 g/cm²/yr) during the LIA, with little difference between humid and arid phases. The AR BSi values concentrations are generally higher by about 5% 0.1 - 0.35 (g/cm²/yr) during the CWP and LIA (arid) than today with highest values at 15°S, and more similar values to today during the LIA (humid) (Figs. 2, 5). When comparing modern (Fig. 2a) with mean~~ ~~$\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$~~ ~~values for the CWP (Fig. 5a) we observe a similar southward increase of both~~ ~~$\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$~~ ~~values, with~~

~~generally slightly higher (0.1-0.2‰) $\delta^{30}Si_{BSi}$ values and with slightly lighter (0.5-1‰) mean $\delta^{15}N_{bulk}$ values than today. A similar trend is observed during the LIA (arid) where $\delta^{15}N_{bulk}$ also reach values of up to 7.9‰ at 15°S, while $\delta^{30}Si$ values are more variable and are even higher (0.4-0.5‰) at 11°S and 12°S than modern values.~~

~~During the LIA (humid) $\delta^{30}Si_{BSi}$ values were consistently lower (0.3-0.5‰) than modern values at all latitudes with the only higher values (0.2‰) found at 11°S. The $\delta^{15}N_{bulk}$ values remain close to 5‰, only increasing up to 6.7‰ at 15°S, representing lighter values (0.6-0.3‰) than today, in agreement with the assumption of weakened N-loss processes during this time.~~ The calculated nutrient utilization shows a shift to high NO_3^- utilization (70-90%) and strongly diminished $Si(OH)_4$ utilization (~~6-60%;~~ Fig. 5c). These values are comparable to modern ones from the northern shelf (EQ-10°S), where less nutrients are upwelled and productivity is lower (Ehlert et al., 2012). The calculated NO_3^- supply was lowest during the LIA (humid) with little change over latitude in accordance with prevalence of more oxygenated waters, whereas the Si supply strongly increased especially at 12°S (Fig. 5c). However, the calculated increased $Si(OH)_4$ supply reflects the change in nutrient uptake (i.e. nutrient ratio) due to stratification and potentially Fe limitation rather than an actual increase in $Si(OH)_4$ supply reaching surface waters. Accordingly we observe a high $Si(OH)_4$ supply but low utilization, thus indicating a low $Si(OH)_4$ demand at the time. In contrast NO_3^- supply appears to be lower than today but the strongly enhanced NO_3^- utilization indicates a higher NO_3^- demand. This shift towards a decreased $Si(OH)_4$ but an increased NO_3^- demand further supports a change in the nutrient uptake ratio by phytoplankton (NO_3^-: $Si(OH)_4$ = 2:1 or 15:1, Fig. 4d). This is in agreement with observations from modern El-Niño events, which show a shift in surface productivity from siliceous (diatoms) to non-siliceous (dinoflagellates) phytoplankton (Sanchez et al., 2000).

Overall we find that the CWP, characterized by high upwelling intensity, productivity and N-loss processes (Fleury et al., 2015; Salvatteci et al., 2014b; Sifeddine et al., 2008), is associated with southward increasing $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ values, reflecting moderate NO_3^- utilization and moderate to high $Si(OH)_4$ utilization (Fig. 6, left). Highest $\delta^{30}Si_{BSi}$ and utilization values at 15°S are potentially caused by progressive Fe limitation during diatom blooms, causing a NO_3^-:$Si(OH)_4$ ratio of up to 1:2. Southward increasing $\delta^{15}N_{bulk}$ values and calculated $\delta^{15}NO_3^-$ demonstrate the consistent incorporation of higher isotopic compositions due to subsurface denitrification under anoxic subsurface conditions in agreement with decreasing NO_3^- supply illustrating the N-loss process. Similar conditions prevailed during the sporadic periods of arid conditions observed during the LIA.

In contrast, most of the LIA i.e., the humid phases, was characterized by low productivity and weak denitrification intensity between 10°S and 15°S (Díaz-Ochoa et al., 2009; Salvatteci et al., 2014b; Sifeddine et al., 2008), with no significant southward increase in the source value of $\delta^{15}NO_3^-$ (Fig. 6, right). Accordingly, high $\delta^{15}N_{bulk}$ and little change in NO_3^- supply indicate more complete NO_3^- utilization during the LIA, while $\delta^{30}Si_{BSi}$ signatures and utilization remained low and Si supply high. This indicates a shift towards a dominance of non-siliceous phytoplankton productivity causing NO_3^- limitation and low uptake of Si similar to observations during modern El-Niño events, which are characterized by a deepening of the thermocline and thus decreased nutrient delivery to surface waters.

Conclusions

Based on a compilation of new and previously published $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ records of several short sediment cores from the southern Peruvian shelf (11-15°S) we present a new evaluation of the impact of denitrification on the isotopic source signature of NO_3^- and subsequent utilization. As denitrification increases southward along the shelf today, we applied a latitudinal ~~correlation~~ comparison between $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ signatures in modern surface and latest Holocene sediments. Given that ~~the correlation of~~ both proxies during the last 600 years ~~is~~ have mainly been influenced by nutrient utilization we performed a novel calculation of subsurface $\delta^{15}NO_3^-$ based on the linear regression~~correlation~~ of $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ signatures ~~from~~for the CWP and LIA (arid ~~and~~versus humid conditions). Our results show that during the CWP and sporadic arid conditions during the LIA the isotopic compositions of NO_3^- have increased southward from 7‰ to 10‰ due to subsurface denitrification, similar to modern conditions. Furthermore, enhanced $Si(OH)_4$ characterized nutrient utilization over NO_3^- uptake, reflecting strong diatom blooms as observed today, potentially leading to progressive Fe limitation increasing the Si:N uptake ratio of diatoms to 2:1.

Low productivity and higher subsurface oxygenation (suboxic conditions) during the humid phases of LIA were associated with low $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ signatures. The latitudinal comparison of $\delta^{30}Si_{BSi}$ versus $\delta^{15}N_{bulk}$ signatures supports decreased influence of subsurface denitrification on the NO_3^- isotope distribution with lower and more uniform $\delta^{15}NO_3^-$ source signatures between 6 and 7.5‰. However, NO_3^- utilization was significantly higher, while $Si(OH)_4$ utilization was lower and the Si supply was higher compared with the demand. This change in nutrient utilization is reflected by a $NO_3^-:Si(OH)_4$ uptake ratio of 2:1 to 15:1, suggesting a shift from a diatom-dominated regime to one dominated by non-siliceous phytoplankton. This agrees ~~is in agreement~~ with El-Niño-like conditions prevailing during most of the LIA accompanied by a deepening of the thermocline and lower nutrient availability.

~~Overall, we are able to further improve~~ In summary, our results constitute an improvement of the application of combined $\delta^{30}Si_{BSi}$ and $\delta^{15}N_{bulk}$ signatures as a powerful tool to differentiate between past changes in subsurface denitrification, nutrient utilization and supply but also changes in the nutrient ratio caused by either micro-(Fe) or macro-nutrient limitation.

Data availability

All data will be uploaded at www.pangea.de upon publication

Author contributions

S. Fleury and K. Doering conducted the sampling of the sediment cores at Bordeaux University. K. Doering prepared the samples and performed the isotope measurements. K. Doering wrote the manuscript with contributions from all co-authors.

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Figure captions

Figure 1: (a) Subsurface (100 m) oxygen concentration and current directions in the Eastern Equatorial Pacific. (b) Inset map shows locations of cores M77/2-024-3 TC, M77/2-005-3 TC, M77/2-003-2 TC (this study) and M77/1-470, B0405-13 and B0405-6 (Ehlert et al., 2015; Gutiérrez et al., 2009) in more detail. The bathymetry is given for 0 to 1000 m water depth in 50 m increments.

Figure 2: Latitudinal overview of present day (a) mean $\delta^{15}N_{bulk}$ (‰, black diamonds, 2 SD error bars) and $\delta^{30}Si_{BSi}$ (‰, white circles, 2SD error bars), the black dashed line indicates the subsurface $\delta^{30}Si(OH)_4$ source value of 1.5 ‰, the green solid line marks the $\delta^{15}NO_3^-$ source value, increasing southwards from 6‰ (EQ-8°S), to about 8‰ (10-12°S) and 12.5‰ (15°S). The red bar indicates the area of suboxic conditions in subsurface waters. The black rectangle marks the study area for downcore reconstruction (see also Fig.1). (b) Nutrient utilization for NO_3^- (%, dark grey area) and $Si(OH)_4$ (%, dashed area). (c) MAR BSi (g/cm^2/yr, black dashed line), MAR TN (g/cm^2/yr, green dashed line) and subsurface nutrient concentrations (= supply; in µmol L^{-1}, $Si(OH)_4$: black line; NO_3^-: green line) (modified from Doering et al., 2016; Ehlert et al., 2012; Mollier-Vogel et al., 2012).

Figure 3: Downcore records of BSi (wt%), $\delta^{30}Si_{BSi}$ (‰, 2 SD error bar of repeated sample measurements) records of cores: (a) M77/2-024-5TC and, M77/1-470 (Ehlert et al., 2015)~~, (b)~~, (b) M77/2-005-3TC ~~and~~ (c) BO405-6 (Ehlert et al., 2015~~; Gutiérrez et al., 2009~~) and (d) M77/2-003-2TC.

The cumulative diatom assemblages are compared to $\delta^{30}Si$ for core e.) M77/2-024-5TC, f.) M77/2-005-3TC and g.) M77/2-003-2TC: Upwelling species - light gray; Coastal planktonic – gray; Other species – white; *Chaetoceros* sp. – red dashed line; $\delta^{30}Si_{BSi}$ – black dots; the black line indicates the transition between the LIA and the CWP. For comparison previously published $\delta^{15}N_{bulk}$ (‰) are shown for cores h.) M77/2-024-5TC (Fleury et al., 2015), i.) M77/2-005-3TC (Fleury et al., 2015) and BO405-13 (Gutiérrez et al., 2009), j.) BO405-6 (Gutiérrez et al., 2009) and k.) M77/2-003-2TC (Fleury et al., 2015).

All records are sorted by latitude from top (11°S) to bottom (15°S). The time intervals for the CWP (red) and the LIA (blue) are highlighted in (a); the horizontal grey shading indicates humid periods (Fleury et al., 2015).

Figure 4: (a) ~~Correlation~~ Direct comparison of $\delta^{15}N_{bulk}$ versus $\delta^{30}Si_{BSi}$ for modern surface sediments (modified from (Ehlert et al., 2015): The dashed lines indicate 1:1 utilization of different $\delta^{15}NO_3^-$ source values (7‰, 7.9‰, 8.35‰ and 11.3‰) between 9°S and 15°S (based on Mollier-Vogel et al., 2012), the rectangle marks the respective range of isotope values that can be expected in sediment samples for nutrient utilization with source values of 1.5‰ ($\delta^{30}Si(OH)_4$) and 8.35‰ ($\delta^{15}NO_3^-$); (inset) Schematic overview of nutrient utilization associated with changes in the isotopic compositions of both $\delta^{15}N$ and $\delta^{30}Si$: the black star marks the source signature (or 100% utilization) for $\delta^{15}N$ and for $\delta^{30}Si$, the grey star marks the respective isotopic compositions for 0% utilization, the black dashed line indicates the 1:1 utilization for NO_3^-:$Si(OH)_4$, respectively. Ratios that plot above the utilization lines reflect $Si(OH)_4$ limitation, as indicated by the dark grey and light grey dotted line representing ratios of 1:2 and 1:4, whereas data points below record stronger NO_3^- limitation, as indicated by the dark grey and light grey dashed lines representing ratios of 2:1 and 15:1. The rectangle indicates the total range of possible isotopic values. (~~c e~~b-d) Downcore ~~correlation~~ comparison of $\delta^{15}N_{bulk}$ and $\delta^{30}Si_{BSi}$ for cores 024TC (diamonds), 005TC (grey stars), 003TC (grey squares) and BO405-6 (grey triangles; (Ehlert et al., 2015), for the CWP and the LIA. For the LIA the sample values are separated into arid (~~d~~c) and humid periods (~~e~~d).

Figure 5: Latitudinal comparison of (left) mean $\delta^{15}N_{bulk}$ (‰, black diamonds) and $\delta^{30}Si_{BSi}$ (‰, white circles) and the calculated $\delta^{15}NO_3^-$ source values (green line), (middle) the respective nutrient utilization of NO_3^- (grey, solid line) and $Si(OH)_4$ (dashed area and line) and (right) MAR TN (g/cm^2/yr~~%~~) and MAR BSi (g/cm^2/yr ~~%~~) and nutrient supply relative to today for (a) the CWP, (b) the arid phases of the LIA and (c) the humid phases of the LIA. Please note that for $\delta^{15}N_{bulk}$ values the mean was calculated for all available values for each time period and not only for samples, for which also $\delta^{30}Si_{BSi}$ values are available. Error bars mark the 1 SD of the mean values.

Figure 6: Schematic nutrient ($Si(OH)_4$ and NO_3^-) cycle models for the Peruvian shelf area (0-200m water depth) during the last 600 years. The NO_3^-:$Si(OH)_4$ (N:Si) indicates the ratio in which both nutrients are taken up during biological production~~vity~~ in surface waters.

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Table 1: Downcore record of core M77/2-024-5TC, M77/2-005-3TC and M77/2-003-2TC for $\delta^{30}Si_{BSi}$ (‰) and BSi content (wt%). The 2 SD represents the external reproducibilities of repeated sample measurements.

Core	Age yrs BP	Depth (mm)	BSi (wt%)	$\delta^{30}Si_{BSi}$ (‰)	2SD
24-5TC	42	0	16.2	1.50	0.23
	101	42	16.1	1.26	0.17
	154	104	34.3	1.50	0.18
	170	134	29.3	1.43	0.15
	187	161	23.7	1.47	0.05
	243	213	30.7	1.35	0.21
	304	264	28.1	1.40	0.09
	376	301	21.0	1.38	0.16
	422	390	10.1	0.81	0.19
	441	432	24.6	1.51	0.16
	483	473	23.8	1.61	0.08
005-3TC	46	0	15.9	1.07	0.09
	73	35	15.0	1.37	0.11
	95	69	25.4	1.46	0.21
	217	128	18.8	1.03	0.18
	250	165	17.3	0.80	0.22
	259	185	15.1	0.93	0.13
	303	241	13.1	0.44	0.27
	340	296	14.0	0.50	0.15
	358	323	11.6	0.47	0.20
	450	369	14.5	1.24	0.24
	464	389	25.0	1.60	0.19
003-2TC	22	0	39.2	1.63	0.24
	146	97	40.5	1.48	0.05
	245	174	41.9	1.30	0.26
	288	208	20.8	0.65	0.23
	327	239	23.9	0.74	0.13
	411	304	19.4	0.73	0.27
	474	353	46.7	1.38	0.17
	581	437	29.1	0.63	0.12