

Interactive comment on “Latitudinal variations of $\delta^{30}\text{Si}$ and $\delta^{15}\text{N}$ signatures along the Peruvian shelf: quantifying the effects of nutrient utilization versus denitrification over the past 600 years” by Kristin Doering et al.

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Response to the reviewers comments

We thank the reviewer (Patrick Rafter) for his helpful suggestions to improve the manuscript. According to his comments we restructured the manuscript and established separate Results and Discussion sections. Further, all equations have now been included in the Methods sections. For Figure 4a a more detailed and comprehensive description and explanation was added to the main text. Also, we added the

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linear regression equations and respective correlation coefficient (r^2) for figure 4 in a new supplementary figure S1. In the following each comment is answered in detail in the order of the comments provided by the reviewer. The changes were added to the previous changes applied to the manuscript following suggestions of reviewer 1.

In the following references for lines are always given for the revised manuscript version (not shown).

First, I think the d30Si and d15N 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.

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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

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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 11°S at the top to 15°S 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 15°S 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 12°S and 14°S, 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 d30Si signatures of core 24 are higher by about 0.5‰ at all times. From line 204 onwards it is discussed how this difference in d30Si 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 °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).

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 r² used for the calculations of the d15NO₃-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 NO₃- 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 d15NBulk versus d30SiBSi relationship in surface sediments. We therefore ap-

plied 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 15°S) and compared to their respective $\delta^{15}\text{NO}_3^-$ and $\delta^{30}\text{Si(OH)}_4$ source and utilization relationship at each location. First, based on the known $\delta^{30}\text{Si(OH)}_4$ 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 $\delta^{15}\text{N}:\delta^{30}\text{Si}$ 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 9°S (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 11°S (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 15°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 $\text{NO}_3^-:\text{Si(OH)}_4$ 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 $\delta^{15}\text{NO}_3^-$ source based on linear regression was also moved to the Methods (now section 2.4; Lines 266-274). This paragraph was also

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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 The linear relationship between $\delta^{30}\text{SiBSi}$ and $\delta^{15}\text{Nbulk}$ signatures should thus also be a direct indicator of the $\delta^{15}\text{NO}_3^-$ source signatures. in the past during the CWP and the LIA. Depending on the exact conditions the uptake of NO_3^- to $\text{Si}(\text{OH})_4$ 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 $\delta^{15}\text{Nbulk}$ to $\delta^{30}\text{SiBSi}$ samples for past periods, it is possible to first calculate the respective $\delta^{15}\text{NO}_3^-$ 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 $\delta^{15}\text{NO}_3^-$ 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 $\delta^{15}\text{NO}_3^-$ 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 rele-

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vant 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 $\delta^{15}\text{NO}_3^-$ 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 $\delta^{15}\text{N}$, 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 Guiterrez 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

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estimate dry bulk densities to calculate mass accumulation rates (MAR), therefore values were used from cores BO413 (12 °S) and BO406 (14 °S; Gutiérrez 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).'

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2018-118/bg-2018-118-AC2-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2018-118>, 2018.

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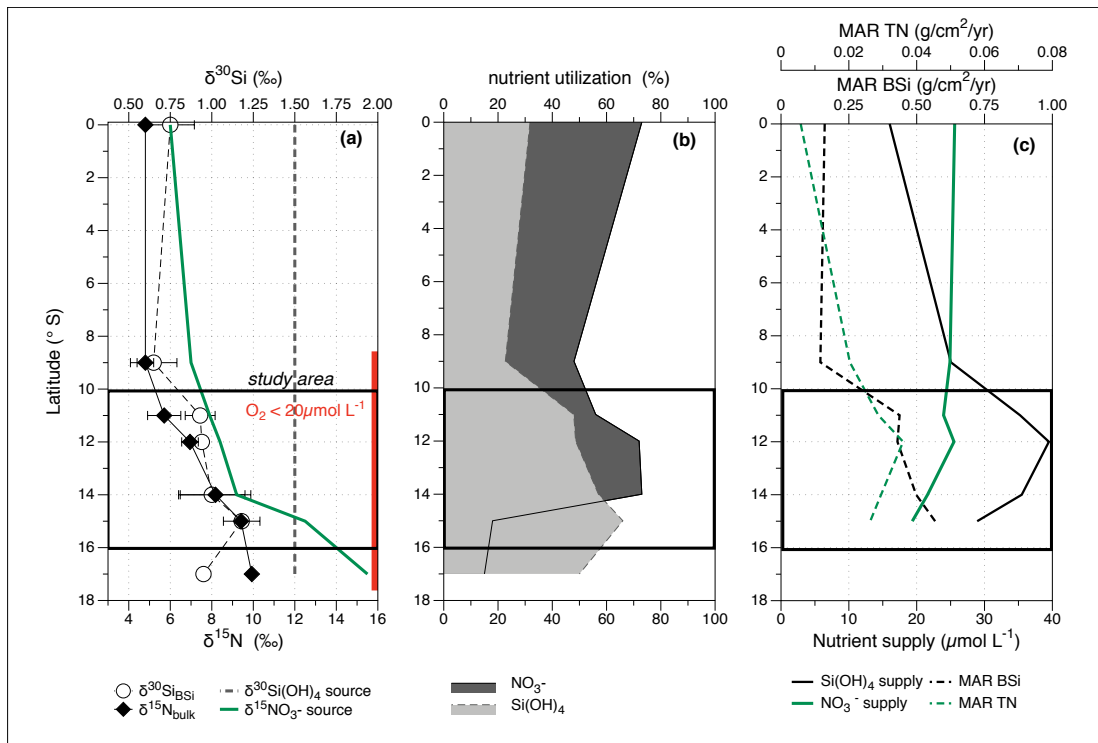


Fig. 1. Figure 2 (revised)

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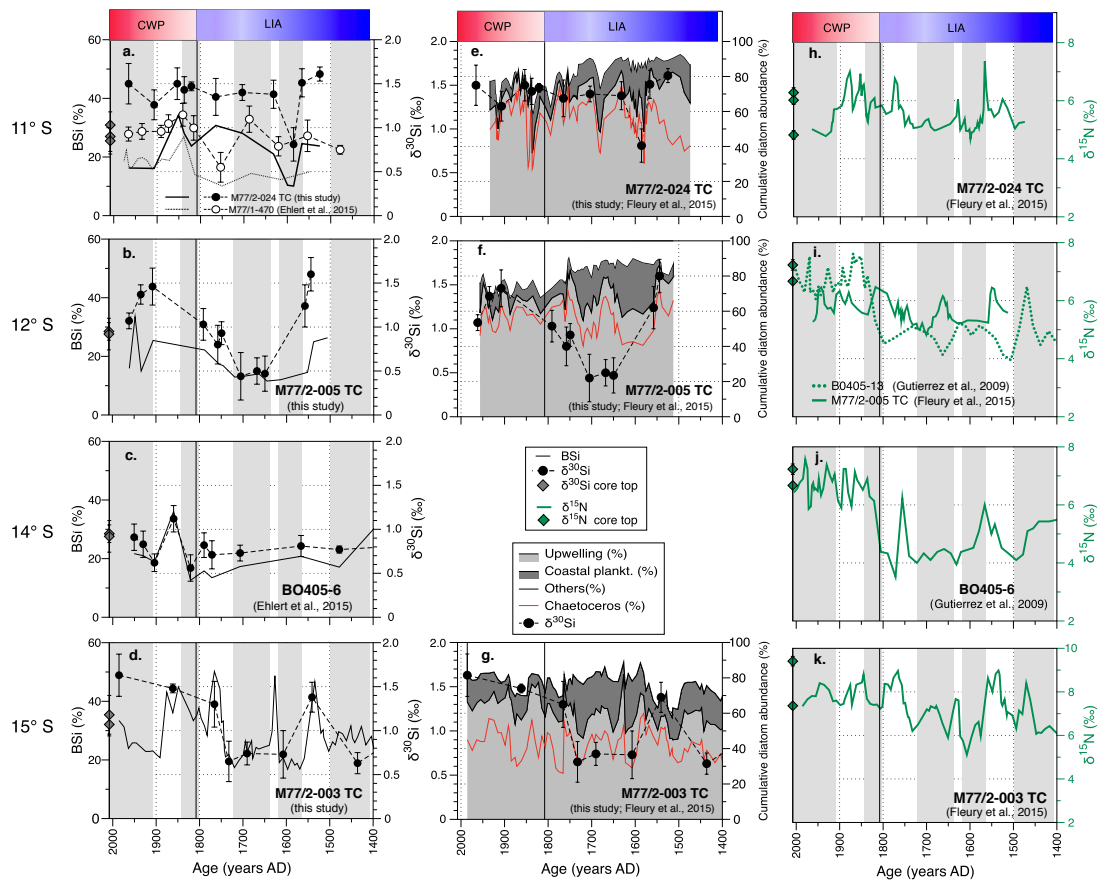


Fig. 2. Figure 3 (revised)

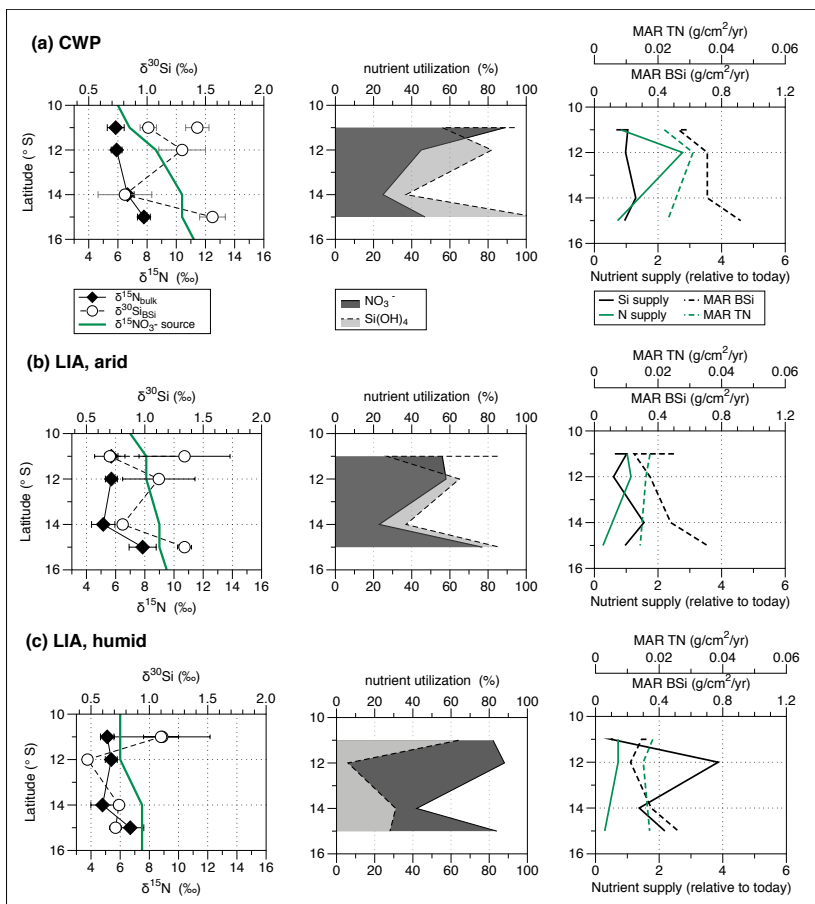


Fig. 3. Figure 5 (revised)