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Biogeosciences Discussions

BGD

Interactive comment

Interactive comment on "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" *by* Kristin Doering et al.

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We highly appreciate the valuable comments and suggestions by the anonymous reviewer on our manuscript, especially the approval of our cross-plot approach to compare silicon and nitrogen isotope signatures. According to the reviewers suggestions we added more detailed information about factors potentially affecting the silicon isotope compositions in the introduction and methods section, namely the influence of a changing diatom assemblages and dissolution effects on the downcore record. Furthermore, one major comment addressed a discrepancy between the text in the results

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and the discussion concerning figure 3. Some statements have been rephrased, however, the main issue was a mistake in figure 3, in which the grey bars indicating humid conditions were accidentally shifted by 50 years. The figure has been revised accordingly. In the following each comment is answered in detail in the order of the comments provided by the reviewer.

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 δ30SiBSi 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 225-228: 'The δ30Si records follow a similar trend of lower mean δ30SiBSi 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 311-317:'To evaluate the impact of changes in 30ε on the δ30Si 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 δ30SiBSi 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 30ε 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 δ30Si data (added to fig.3). In the Methods section a paragraph was added to explain the diatom abundances, Line 180-193:

2.3 Diatom assemblage data Diatom analysis of cores M/7/2-024-5TC, 005-3TC and 003-2TC was 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 five groups representing different environmental conditions: 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 δ30SiBSi 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 ïĄď30SiBSi was measured on the 11-32μm. 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 δ30SiBSi record (Ehlert et al., 2012; 2013).

Additional text concerning the diatom assemblages has been added: Line 239-243: '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 247-248: '. . ., as δ30SiBSi analysis do not cover all short events ($\sim$50 years) of reductions in the abundance of upwelling diatom species (Fig. 3f).' Line 260-268:'Furthermore, the diatom assemblages (Fig. 3f-h; based on Fleury et al., 2015) show a close correspondence of the amount of upwelling

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species and δ30SiBSi signatures, with decreases of up to 20% in upwelling species often linked to a reduction of δ30SiBSi by about 0.5 -1‰. However, not every decrease in δ30SiBSi is mirrored by a change in the diatom assemblage and vice versa (e.g. Fig. 3g at 350 yrs BP). 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 from lower abundance of upwelling species (~50%) to higher values during the CWP (~70%) is found at 15° S (003-2TC) in accordance with the strongest changes in BSi and δ30SiBSi at this location.'

We further refer to the interpretation of the Doering et al., (2016), that the d30Si 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 71-76: 'Accordingly, downcore records of δ30SiBSi 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‰ $Suttonetal., 2013).'$

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.

δ30Si 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 lamina-

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tions was interpolated to 1cm resolution. This information was added in Line 149 to 154 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 δ15Nbulk values are based on samples from single laminations these were averaged to 1 cm resolution when directly compared to the δ30Si 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 δ30Si records and compare them to previously published δ30Si and δ15N 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 42-45: While a potential fractionation of δ30Si signatures of biogenic opal during dissolution of -0.55‰ has been reported previously (Demarest 2009), subsequent investigations of dissolution on diatom material from sediments have so far indicated that δ30Si signatures of diatoms within the sediments are generally unaffected by dissolution (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 NO3- are now given in brackets. Line 101-102: 'Along the Peruvian margin the main source for the high amounts of upwelled nutrients (30 μmol L-1 for both Si(OH)4 and NO3-; Bruland et al., 2005)'

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

For the δ30Si the +/- always indicates the 2SD external reproducibility, only for the δ15NO3- 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 108 and 109.

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 125-126.

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

'study of' was 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 209-216) 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).

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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 ïĄď15Nbulk 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 342: 'The shift towards a higher 1:2 NO3-:Si(OH)4 utilization during both the CWP and LIA (arid) indicates enhanced utilization of Si(OH)4 over NO3- leading to Si(OH)4 limitation as indicated by high Si(OH)4 utilization rates between 40% and 90%, and lower NO3- 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 377) was changed accordingly: 'horizontal alignment of the δ15Nbulk versus δ30SiBSi 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 δ15N and δ30Si 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.

Figure 3: Downcore records of BSi (wt%), δ30SiBSi (‰ 2 SD error bar of repeated sample measurements) and δ15Nbulk (‰ records of cores: (a) M77/1-470 (Ehlert et al., 2015), (b) M77/2-024-5TC, (c) M77/2-005-3TC and BO405-13 (δ15Nbulk Gutiérrez et al., 2009), (d) BO405-6 (Ehlert et al., 2015; Gutiérrez et al., 2009) and (e) M77/2-003-2TC. Records are sorted by latitude from left (11°S) to right (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). The cumulative diatom assemblages are compared to δ30Si for core g.) M77/2-024-5TC, h.) M77/2-005-3TC and f.)) M77/2-003-2TC: Upwelling species - light gray; Coastal planktonic – gray; Other species – white; Chaetoceros sp. – red dashed line; δ30SiBSi – black dots; the black line indicates the transition between the LIA and the CWP.

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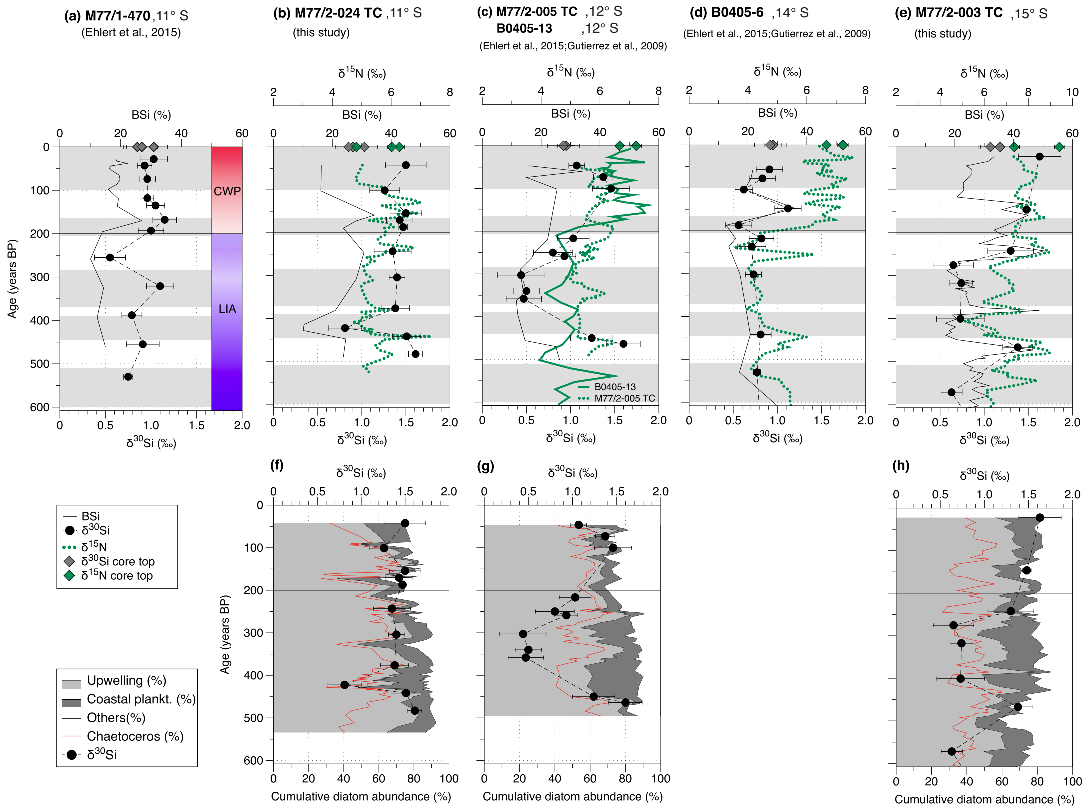
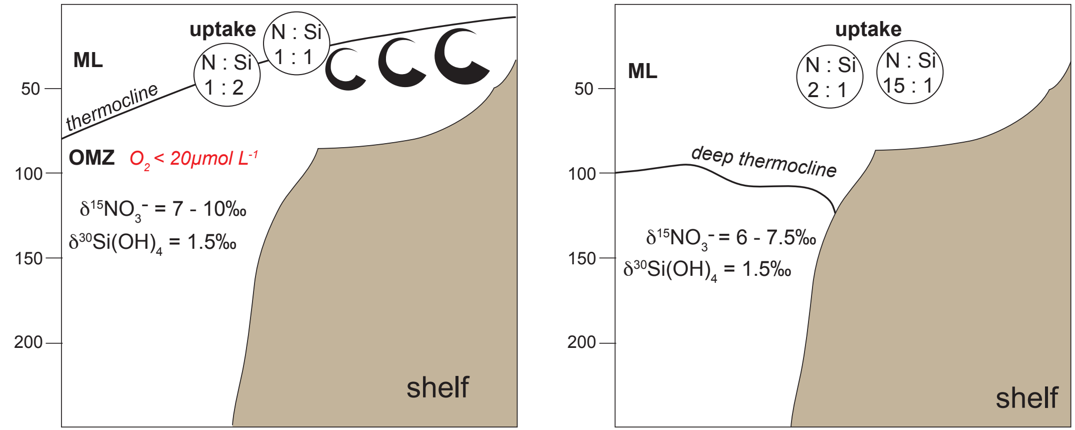

(a) M77/1-470 ,11° S
(Ehlert et al., 2015)
(b) M77/2-024 TC ,11° S
(this study)
(c) M77/2-005 TC ,12° S
B0405-13 ,12° S
(Ehlert et al., 2015;Gutierrez et al., 2009)
(d) B0405-6 ,14° S
(Ehlert et al., 2015;Gutierrez et al., 2009)
(e) M77/2-003 TC ,15° S
(this study)
δ15N (‰)
BSi (%)
Age (years BP)
δ30Si (‰)
CWP
LIA
B0405-13
M77/2-005 TC
(f)
(g)
(h)
Cumulative diatom abundance (%)
BSi
δ30Si
δ15N
δ30Si core top
δ15N core top
Upwelling (%)
Coastal plankt. (%)
Others(%)
Chaetoceros (%)
δ30Si

Fig. 1.



	Si	N
utilization	40 - 80%	40 - 80%
isotope signature	0.8 - 1.5‰	6 - 8‰

Today, CWP and LIA (arid) : La-Niña-like conditions, strong upwelling, high productivity

siliceous phytoplankton (diatoms)
anoxic subsurface condition
N-loss (denitrification + anammox)

	Si	N
utilization	<50%	70 - 100%
isotope signature	0.5 - 1‰	5 - 7‰

LIA (humid) : El-Niño-like conditions, deep thermocline, low productivity

non-siliceous phytoplankton
no nutrient-rich upwelling
suboxic subsurface waters → reduced N-loss

Fig. 2.

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