

# Response to reviewers

## Submission cp-2018-88 to *Climate of the Past*

*Editor:*

Dear Dr. de Bar and co-authors,

5 Thank you for your substantial efforts in responding to the comments of the three reviewers. The reviewers provided extensive but constructive comments on your manuscript, and there is general consensus that the dataset is interesting and the conclusions are relevant to the paleoceanography and organic geochemistry readership of *Climate of the Past*.

10 My sense is that your responses address the main technical, interpretive, and clarity concerns of the three reviewers, without overly broadening the scope the manuscript. Thus, I encourage you to formally submit a revised manuscript that incorporates the changes indicated in your detailed responses to the reviewers.

Sincerely,

Alberto Reyes

15 **We thank the editor for the positive assessment of our manuscript. We have revised the manuscript and below we provide point-to-point answers to the comments of the reviewers: when applicable, we indicated where adjustments were made in the text (note: when we refer to line numbers in which we have made adjustments, we refer to the line numbering of the revised manuscript with “track changes” in this document). The reviewers’ comments are in regular font; our replies are in bold font.**

Sincerely, also on behalf of all co-authors,

20 **Marijke de Bar**

*Editor:*

After assessing the reviewer comments, I have a few small suggestions too:

25 1. Perhaps some of the criticisms from Rev 1 and 3 about lack of clarity in parts of the discussion in p.12-14 could be partially resolved by breaking some of your longer paragraphs into shorter, more focused paragraphs.

**We agree, and we have now structured the discussion in a clearer way.**

2. Reviewer 1 suggested several topics for expanded discussion, but I’m convinced by your responses that extensive additions run the risk of overly broadening the scope of the manuscript.

30 3. ka vs kyr: It seems you’ve used ka = “thousands of years \*ago\*” and kyr = “thousand years”. This is a useful distinction so I suggest sticking with it.

**We have followed these suggestions.**

## Response to Referee 1

Comments: de Bar and co-authors use biomarkers (long chain diols, TEX<sub>86</sub> and U<sup>K'</sup><sub>37</sub>) to reconstruct sea temperature variations in the river-influenced upwelling ecosystem off southern Chile during the past 150,000 years. They also compare the Diol Index and the nutrient dial index with other paleoproductivity indicators, including bulk organic matter total organic carbon (TOC), organic matter stable carbon isotopes ( $\delta^{13}\text{C}$ ), as well as phytoplanktonic lipid biomarkers. The data set is interesting for a broad audience and the technical aspects of the manuscript are correct. In general, the manuscript is well organized. However, (i) there are a several assumptions, which need strong re-thinking and (ii) the MS would have greatly benefited from a quick read by native speaker before submission (several sentences are convoluted and difficult to understand, more a grammar than a scientific problem.) Below I list major comments.

**We thank the referee for the positive assessment and for the comments, which we have seriously considered.**

Abstract:

all abbreviations should be first fully written. Readers less familiar with them have no clue what the authors are referring to.

**We have adjusted this.**

Introduction:

1. 15-20: The statement “*Proboscia* diatoms grow in the early stages of upwelling when nutrients strongly increase in concentration (Koning et al., 2001)” is wrongly interpreted and does not support the authors’ interpretation that *Proboscia* is a diatom indicative of high productivity in the Chilean coastal upwelling system. If you keep reading Koning et al. (2001), these authors also mention that “The dominance of these pre-upwellers before the onset of the upwelling season was probably caused by their ability to adjust their buoyancy, which allows them to migrate to deeper levels below the euphotic zone to obtain the nutrients trapped there before the actual upwelling starts (Villareal, 1988).” Moreover, “The upwelling period was characterized by the successive dominance of three diatom species, *Th. nitzschioides*, *N. bicapitata* and *Chaetoceros* resting spores. *T. nitzschioides* dominated the assemblage in July, when the two-gyre upwelling system was firmly established, temperatures were the lowest and H<sub>4</sub>SiO<sub>4</sub> concentrations in the surface waters were high”

**We do not state that *Proboscia* is indicative of high productivity along the Chilean margin. Instead we refer to Tarazona et al. (2003) and Herrera and Escribano (2006) who both describe *Proboscia alata* as being dominant when upwelling is less intense, and thus when general productivity is likely to be lower. Moreover, we suggest that the Diol Index should perhaps be considered more as an indicator of *Proboscia* productivity, rather than general productivity.**

**Concerning the reference to Koning et al. (2001), we have rephrased the sentence as follows (P. 2, lines 19-20): “*Proboscia* grows during the early stages of upwelling since they need relatively little silica and they are able to migrate to deeper waters to obtain nutrients.”**

Specimens of *Proboscia* spp. are hardly found in sed traps samples (Romero et al., 2001, Deep-Sea Res. 48, 2673), and in surface and/or downcore sediments along the Chilean margin, and have never been associated with high productivity along the Chilean margin (Romero and Hebbeln, 2003, Mar. Micropal. 48, 71; Mohtadi et al., 2004, J. Quater. Sci., 19, 347; Romero et al., 2006, Quat Res. 65; Mohtadi et al., 2007, Quaternary Sci. Rev. 26, 1055).

**This is correct. However, the main reason for its rare occurrence in sediments and sediment trap is likely the weak preservation potential (Jordan and Priddle, 1991; Koç et al., 2001; Jordan and Ito, 2002). Furthermore, we also do not claim that *Proboscia* is a dominant diatom genus along the Chilean margin, and as stated above, we do not claim that *Proboscia* is indicative of high productivity in this region.**

P. 3, l. 13: "...several glacial and interglacials periods". Several can be four, but can also be 15. Your study extends only the past 150 kyr, be more concrete.

**We have removed "several".**

Results

P. 9, l. 10-15: (i) "The average TOC content varies between 0.4 and 2.6%." average is not the same as range!; (ii) "The TOC content is significantly higher during the interglacial periods (MIS 1, 3 and 5) compared to glacial periods (MIS 2, 4 and 6)": not quite true, values for MIS 3 are hardly distinguishable from MIS2 and 4. (iii) "During Termination 2. . .": Terminations should be accordingly identified in Figs 3-5; (iv) "the TOC and TN contents increase rapidly (within < 1 kyr) towards interglacial values": is the sampling resolution high enough to state that the increyase occurred within less than 1,000 years?

**(i) We have corrected this.**

**(ii) We agree that this is not formulated clearly, and we will adjust this. However, the average TOC levels (taken together for MIS 1, 3 and 5) of ca 1.4% are in fact significantly higher as compared to the average level for MIS 2, 4 and 6 which is ca. 0.7%. However, we have now added the following (P. 9, lines 24-27):**  
***"The TOC content is significantly higher during the interglacial periods (MIS 1, 3 and 5) compared to glacial periods (MIS 2, 4 and 6; two-tailed  $p < 0.001$ ): the average TOC concentration is 1.4% for the interglacial periods and 0.7% for the glacial intervals (Fig. 3d), although TOC levels for MIS 3 are quite similar to those of MIS 1 and 2."***

**(iii) We have indicated the terminations in Figures 3-5.**

**(iv) We thank the reviewer for pointing this out, as this should indeed be "within < 2 kyrs". We have corrected this.**

P. 9, l. 16-20: very convoluted sentence. Revise

**We have revised this sentence as follows (P. 10, lines 5-8):**

***"The organic matter  $\delta^{13}C$  record ( $\delta^{13}C_{OM}$ ) also reveals a glacial-interglacial variation (Fig. 3c), corresponding to slightly  $^{13}C$ -enriched values during interglacial times ( $\delta^{13}C_{average} = -21.2\%$ ) as compared to the glacials ( $\delta^{13}C_{average} = -21.8\%$ ). Although small, these changes are statistically significant (5% significance level, two-tailed  $p < 0.001$ )."***

P. 10, l. 11-25: much of this information is related to Methods. It should be placed accordingly.

**We have moved the following sentence to the Methods section (P. 9 lines 17-18): “Additionally, we quantified dinosterol, a biomarker for dinoflagellates (Boon et al., 1979; Volkman et al., 1998), as well as loliolide, an indicator of diatom abundance (Klok et al., 1984; Repeta, 1989).”**

P. 11, l. 26: see my comment above for the sampling resolution.

**We have corrected this.**

10

P. 11, l. 26-31: this needs more accurate description. Revise.

**Since we merely want to compare our LDI record with the  $U^{K'}_{37}$ ,  $TEX^H_{86}$  and  $\delta^{18}O$  records to assess whether the LDI is suitable as SST proxy in this region, we believe that our result description is sufficient.**

15

Discussion

P. 12, l. 20-32: this part of the Discussion is very intricate and unclear. Please rephrase.

**We agree that this part is difficult to read, and we have tried to improve the readability.**

P. 13, l. 5-10: why was no *Chaetoceros* peak during MIS4 when the MAR TOC was high?

**We thank the reviewer for this comment, as we should indeed discuss this. As can be seen in Fig. 3, the high MAR TOC during MIS 4 is linked to high sedimentation rates, whereas the peak in MAR TOC during MIS 5 is not. This would suggest that the MAR TOC maximum during MIS 5 actually resulted from increased primary productivity, whereas during MIS4 the high MAR TOC resulted from the increased sedimentation rate. This would in turn explain that there is no peak in *Chaetoceros* counts for this age. We have added the following (P. 14, lines 4-8)**

**“During MIS 4 we also observe a peak in  $MAR_{TOC}$  (Fig. 3a) but there is no corresponding peak in *Chaetoceros* abundance (Fig. 4c). However, the high  $MAR_{TOC}$  during MIS 4 is linked to high sedimentation rates (Fig. 3c), whereas the peak in  $MAR_{TOC}$  during MIS 5 is not, confirming that the  $MAR_{TOC}$  maximum during MIS 5 indeed likely resulted from increased primary productivity, whereas during MIS 4 the high  $MAR_{TOC}$  did not.”**

P. 13, l. 17-18 & l. 25-26: since *Proboscia* is not a secondary component of diatom assemblages in coastal upwelling systems not it is not associated with high productive waters along the Chilean margin, these statements should be thoroughly revised. See my comments above for Introduction.

**We feel that the reviewer might have misunderstood our conclusions. As explained above, we argue that *Proboscia* is likely less abundant during intense upwelling in this region, and is therefore in fact not indicative of high productivity. In the introduction we explain that initially the Diol Index was proposed as an upwelling indicator since in general *Proboscia* is often associated with upwelling conditions. However, the actual conditions during/under which the species is abundant is often described as post-bloom, stratification, early upwelling season and/or the oceanic side of the upwelling front (e.g., Hart, 1942; Takahashi et al., 1994; Katsuki et al., 2003; Moita et al., 2003; Tarazona et al., 2003; Herrera and**

Escribano, 2006; Sukhanova et al., 2006; see references in Table 1 of Rampen et al., 2014b), likely because *Proboscia* is only able to compete with other diatoms when silicate concentrations are low.

5 P. 14, l. 2-5: This statement needs appropriate references/lab studies. Have different species of *Proboscia* been cultured the biomarker content measured in living cells?

10 **We have clarified that Sinninghe Damsté et al. (2003) cultured these *Proboscia* species and measured the lipid composition. Moreover, we have added the results of Rampen et al. (2007) who assessed the long-chain diol composition of *Proboscia inermis*, which also consisted for more than 90% of the C<sub>28</sub> 1,14-diol: “In fact, Sinninghe Damsté et al. (2003) found that 98% of the diols *P. alata* consisted of the saturated and mono-unsaturated C<sub>28</sub> 1,14-diol, whereas *P. indica* produces similar amounts of the C<sub>30</sub> and C<sub>28</sub> 1,14-diol and *P. inermis* also mainly produced the C<sub>28</sub> 1,14-diol (Rampen et al., 2007).”**

15 P. 14, l. 7: It is not correct stating that “*P. alata* needs little Si to build its frustule”. For diatom standards, frustules of *Proboscia* are long and build long chains (see Jordan et al., 1991, Diatom Research 6, 63).

20 **Indeed, *Proboscia* diatoms have long chains but this is not the issue. Both Goering and Iverson (1981) and Sakka et al. (1999) suggest that *Proboscia* is capable of living under very low silicic acid concentrations because of weakly silicified frustules. Moreover, Jordan et al. (1991) state: “The valves of modern *Proboscia* spp. are lightly silicified and thus their distribution in Antarctic sediments is restricted to regions of good preservation”. Thus, though the chains might be long, they are thin and weak.**

25 P. 14, 4.3. Sea surface temperature evolution: the discussion in this section jumps back and forth between different time windows. This is not reader-friendly. Revise  
**To be honest, we do not really see how we jump back and forth between different time windows. However, we have divided the paragraph into smaller sections now and restructured the section a bit.**

30 P. 14, l. 22-25: Does your SST record following “global climate pattern” refers to MIS5 or the entire record? Please clarify

**We refer to the entire record, and we have clarified this.**

35 P. 15, l. 3: A correlation test helps to supports this statement.

**We have performed correlation tests and we plotted these in Fig. 6.**

40 P. 15, l. 7-8: This should be more rigorously discussed.

45 **We show here that our temperature proxies seem to accurately reflect past SST since the absolute difference between the proxy estimate are for most of the record within the maximal possible discrepancy that can be explained by the combined calibration errors. Further discussion of the proxy discrepancies is outside the scope of this paper in which we want to test the applicability of the diol proxies, and not that of the U<sup>K</sup><sub>37</sub> and TEX<sup>H</sup><sub>86</sub>.**

P. 15, l. 26-27: Looking at your Fig 7, several mismatches in the SST behavior of compared records are recognizable. This should be more critically and rigorously discussed (see for instance ODP1241 and GeoB3327-5 vs ODP1234).

5 We merely wanted to show here that our  $U^{K'_{37}}$  record overall agrees with other records in the vicinity of our site, but that in fact these records also show many discrepancies which is likely linked to the latitudinal movement of the ACC. For instance, site GeoB 3327-5 is located at the northern extent of the ACC, and thus largely influenced by its latitudinal movement (Ho et al., 2012), whereas for ODP 1234 this influence might be less. The  $U^{K'_{37}}$  record of ODP 1241 is especially hard to compare with our record since this site is  
10 low-latitudinal ( $6^{\circ}\text{N}$ ) whereas our site is located at  $36^{\circ}\text{S}$ , and thus the glacial-interglacial variability is much weaker at ODP 1241 as compared to our site. More extensive discussions are also a bit outside the scope of this paper as our main focus is to test the applicability of the proxies based on long-chain diols. We have added the following (P. 17, lines 9-14):  
15 *“Regional differences in timing of deglacial warming have previously been related to the southward shift of the SWW, which directly and indirectly influences local paleoproductivity and upwelling intensity, and thereby potentially leaving site-dependent, unique signatures in the SST records (Mohtadi et al., 2008). This may partially explain the discrepancies that we observe between our  $U^{K'_{37}}$  record and the other records. For instance, site GeoB 3327-5 is located at the northern extent of the ACC, and thus largely influenced by its latitudinal movement which is closely related to the migration of the SWW (Ho et al., 2012), whereas for ODP  
20 1234 this influence might be less.”*

The authors should comments and discussed on: - “The production/export depth of TEXH86 is not well constrained, thus complicating the comparison of TEXH and SST (for example, UK ) based records.” (e.g., Kim et al., 2012, EPSL 339, 95-102.; Ho & Laepple, 2018, Nat. Geosc. 9, 606).  
25

On page 16 we already mention that the  $\text{TEX}_{86}$  might potentially reflect a subsurface signal, but that for this region it has been shown earlier that it likely reflects SST: *“For the  $\text{TEX}_{86}$ , it has been shown to potentially reflect subsurface rather than surface water temperatures (Huguet et al., 2007; Kim et al., 2010; 2015; Schouten et al., 2013; Chen et al., 2014) due to the production of isoprenoid GDGTs below the surface mixed layer. Overall, the  $\text{TEX}^{\text{H}}_{86}$  record agrees reasonably well with the  $U^{K'_{37}}$  record for ODP 1234, suggesting that it mainly reflects SST. Also, Kaiser et al. (2015) who established a regional  $\text{TEX}^{\text{H}}_{86}$  calibration suggested that this proxy mainly reflects SST.”*  
30

35 - “glacial–interglacial amplitude of TEXH86- derived SST change in the tropics is overestimated relative to other proxy evidence, a result also independently found by a multi-proxy study in the subpolar region“ (Ho & Laepple, 2015, Earth Planet. Sci. Lett. 409, 15–22; Seki, O. et al. 2014. Prog. Oceanogr. 126, 254–266).

We do not see why this is relevant as ODP 1234 is a subtropical site, and we do not see a larger  $\text{TEX}^{\text{H}}_{86}$  glacial-interglacial amplitude as compared to the  $U^{K'_{37}}$  and LDI. Furthermore, Zhang and Liu (2018) recently showed that core-top  $\text{TEX}_{86}$  data between  $30^{\circ}\text{N}$  and  $30^{\circ}\text{S}$  strongly correlate to SST, which is in contrast with Ho and Laepple (2015) who proposed that  $\text{TEX}_{86}$  data potentially reflect subsurface water temperatures which would cause the overestimation in glacial-interglacial SST change. Moreover, as our primary focus is to test the long-chain diol proxies we suggest that such a discussion is outside the scope of  
40 this manuscript.  
45

## Response to Referee 2

5 de Bar at al. test the applicability of different paleoenvironmental proxies based on long chain diols (LDI, Diol  
Index, and NDI ) by studying the ODP Site 1234 located within the Peru-Chile upwelling system and covering  
the last 150 kyrs. They compare LDI-derived SSTs with other temperature proxies ( $\text{TEX}_{86}^{\text{H}}$ ,  $\text{U}_{37}^{\text{K}}$ ) and with the  
Diol index and NDI with other phytoplankton production proxies (accumulation rates of TOC and lipid  
10 biomarkers). Their results suggest that the Diol Index should not be considered as an upwelling proxy per se, and  
that the NDI might not be suitable as a more general paleonutrient proxy. I find this is an interesting study. I  
particularly appreciated the multi-proxy comparison for SST and productivity reconstructions. The overall  
manuscript is well structured and well written, even though some parts would need clarification. The data are  
robust and in general the conclusions are well supported by the data. I however think that some points in the  
discussion could be clarified/more detailed, as it is sometimes difficult to understand. Please find my comments  
15 below.

**We thank the referee for the positive assessment and for the comments, which we have used to improve the manuscript.**

20 P. 2, l. 12: “mean annual sea surface temperature” instead of “annual mean sea surface temperature”.

**We have corrected this.**

P. 4, l. 16: throughout the text you use either “ka” or “kyr”. I would be consistent and choose one or another.

25

**After suggestion of the editor, we keep this distinction.**

P. 9, l. 10: delete “average” as you talk about ranges.

30 **We have corrected this.**

P. 9, l. 13: it would be good to indicate the Terminations on the figures.

**We have indicated the Terminations in Figs. 3-5.**

35

P. 10, l. 8-9: the alkenone AR does not show this decrease around the boundary of MIS 4 and 5.

**Yes, this indeed true, and we have now added this. This difference between the concentration and AR is likely caused by the increase in sedimentation rate around the MIS 4-5 boundary.**

40

P. 12, l. 16-19: this sentence is not very clear and in contradiction. Please clarify.

**We agree that this sentence is not clear and seems contradictory; we have rephrased this sentence.**

P. 12, l. 19-32: this part is not really clear and relatively difficult to follow. Please rephrase.

**Referee 1 provided a similar comment. We have tried to describe this section more clearly.**

5 P. 13, l. 1: “individual lipid biomarkers” instead of “individual biomarker lipids”.

**We have corrected this.**

10 P. 13, l. 1-12: How do you explain the peak of MARTOC in MIS 4 which does not correspond to a peak in loliolide concentration/Chaetoceros abundance? There is also no peak for the other lipid biomarkers, except for the 1,13 and 1,15-diols. Who are the potential producers of the 1,13 and 1,15-diols?

**We thank the reviewer for this comment, since this part indeed requires discussion; a similar comment was also given by reviewer #1.**

15 **Fig. 3 shows that the increase in MAR<sub>TOC</sub> in MIS 4 is concomitant with an increase in sedimentation rate, whereas during MIS 5 this is not the case. Therefore it is likely that whereas the peak in MAR<sub>TOC</sub> during MIS 5 is mainly caused by increased primary productivity (as also indicated by the other records), the MAR<sub>TOC</sub> maximum during MIS 4 is the result of enhanced particle settling due to the increase in sedimentation rate. Henceforth, we also do not observe any phytoplankton lipid biomarker peaks during this period.**

20 **The reason for the increase in both the concentration and AR of 1,13- and 1,15-diol around this period is unclear, as is the potential producers of these biomarkers. As explained in the Introduction, 1,13- and 1,15-diols have been observed in cultures of Eustigmatophyte algae, but these distributions do not agree with the distributions we observe in the marine realm, and thus the producer is still elusive.**

25 **We have added the following (P. 14, lines 4-8):**

30 ***“During MIS 4 we also observe a peak in MARTOC (Fig. 3a) but there is no corresponding peak in Chaetoceros abundance (Fig. 4c). However, the high MARTOC during MIS 4 is linked to high sedimentation rates (Fig. 3c), whereas the peak in MARTOC during MIS 5 is not, confirming that the MARTOC maximum during MIS 5 indeed likely resulted from increased primary productivity, whereas during MIS 4 the high MARTOC did not”***

P. 15, l. 12-15: this sounds surprising as you state in P. 4, l. 2 that ODP 1234 “lies in the vicinity of two large Andean river systems”. Has the influence of terrestrial input on diols been observed for recent times in this site?

35 **Yes, the core is located relatively close to the coast of Chile (~65 km) and the river mouths of the Río Bio-Bio and Río Itata, which both drain large basins. However, this distance is likely still too large to detect riverine influence in the organic matter deposited in the sediment. For instance, in the study of de Bar et al. (2016), the BIT index and the fractional abundance of the C<sub>32</sub> 1,15-diol was assessed in surface sediments along the river-influenced Iberian margin. High BIT and C<sub>32</sub> 1,15-diol values were only**  
40 **observed for stations which were located < 15 km from the coast.**

P. 15, l. 25-30: you could provide more details on the comparison with the other sites. Even though the general trend agrees well, there are clear differences with sites at proximity of ODP 1234 (GIK 17748-2; GeoB 3302-1).

45 **We thank reviewer #2 for this comment. Reviewer #1 has a comparable comment which we answer here in a similar way. We merely wanted to show here that our U<sup>K'</sup><sub>37</sub> record overall agrees with other records in**



the vicinity of our site, but that in fact these records also display many discrepancies that are likely linked to the latitudinal movement of the ACC. For instance, site GeoB 3327-5 is located at the northern extent of the ACC, and thus largely influenced by its latitudinal movement (Ho et al., 2012), whereas for ODP 1234 this influence might be less. Moreover, we believe that this is somewhat outside the scope of this paper as our main focus is to test the applicability of the proxies based on long-chain diols. However, we have added the following (P. 17, lines 9-14):

*“Regional differences in timing of deglacial warming have previously been related to the southward shift of the SWW, which directly and indirectly influences local paleoproductivity and upwelling intensity, and thereby potentially leaving site-dependent, unique signatures in the SST records (Mohtadi et al., 2008). This may partially explain the discrepancies that we observe between our  $U^{K'}_{37}$  record and the other records. For instance, site GeoB 3327-5 is located at the northern extent of the ACC, and thus largely influenced by its latitudinal movement which is closely related to the migration of the SWW (Ho et al., 2012), whereas for ODP 1234 this influence might be less.”*

P. 28, l. 8: a bracket is missing.

**We have corrected this.**

Figures 3, 4, 6, A1: the tick marks on the axes (especially the axis with the Age) are missing. Please add them so the reader can associate more easily the values with the data points.

**We have added these.**

### **Response to Referee 3**

The authors of “A Late Quaternary climate record based on long chain diol proxies from the Chilean margin” analyzed a suite of organic biomarkers in a marine sediment core from the coast of Chile to a) assess glacial-interglacial dynamics in marine productivity (ie. upwelling) and associated climate change, and b) to establish the efficacy of long-chain diols in paleoenvironmental reconstruction, particularly with regards to the recently proposed Nutrient Diol Index (NDI) as a metric for marine productivity. They compared diol-based indices to independent records of SST (alkenones and GDGTs) and productivity (algal lipid fluxes, total organic carbon fluxes, etc.) and show that NDI is distinctly different than other upwelling proxies and so is not widely interpretable as an upwelling indicator, suggesting instead that the principal C28 1,14-diol producer, Proboscia alata, occurs more commonly in non-upwelling settings. Furthermore, the Diol Index appears to reflect all Proboscia productivity, but still does not capture the upwelling signature expressed in other paleoproductivity proxies. The dataset seems robust and these topics are of broad interest to the paleoceanography and organic geochemistry communities. In general, I think the paper could be published after addressing issues regarding the clarity of the paleoclimate implications and the writing structure.

**We thank the referee for the positive assessment and for the comments, which we discuss below and have used to improve our manuscript.**

Please include the full name for each abbreviation the first time abbreviations are mentioned. Likewise, provide the diol-specific equations in the introduction because it would help the reader follow the introduction section easier without flipping through the paper to find the equations.

5 **We have included the full names. However, we do not think that including the diol equations in the introduction will improve the clarity of the text, and we already describe specifically on which LCDs the equations are based.**

The goal stated in the first sentence of the abstract stands in contrast with the goal of the title.

**We agree with the referee, and we have changed the first sentence of the abstract.**

10 Page 12-13: The relationship between temperature and productivity should be discussed more explicitly. I think this section relating the broader climate system and the productivity regime needs clarification. A plot showing the temperature and the nutrient/upwelling indicators together is warranted, given that the paper is drawing links between these two variables. Can either 'northward migration of the SWW' or 'southward migration of the subtropical high' or global cooling induce more upwelling and is there a way to distinguish between these factors in the paleoceanographic record?

15 **We are not sure on how to more explicitly discuss the relation between productivity and temperature. We start the discussion by illustrating the general idea on how the latitudinal movement of the ACC and SWW linked to the transition of the Last Glacial Maximum to the Holocene might affect productivity. In short, different studies suggest that during the LGM productivity was likely stimulated by greater nutrient input deriving from the ACC (being in the north) and enhanced river runoff due to the northern position of the**  
20 **SWW. Accordingly, productivity would be lower during the Holocene due to the southern position of the ACC and SWW. However, during the Holocene, the winds associated with the subtropical high pressure system might induce upwelling. Moreover, there are also studies that propose that the northern position of the SWW during the LGM might in fact prevent upwelling and thus inhibit productivity despite the**  
25 **greater input of nutrients. Hence, we discuss coastal productivity in light of the main current and wind regimes linked to glacial-interglacial variability. However, most studies have focused on the last ~30 kyrs, and therefore little is still known about upwelling and productivity during for instance the Last Interglacial. Nevertheless, we discuss our biomarker records in light of the knowledge that we have of the LGM and Holocene.**

30 Page 14: Many ideas are put forward about *P. alata* ecology, but I am left with an uncertain idea of what NDI (aka *P. alata* productivity) variations signify in a specific climatic or ecological sense. Is there a suggestion of why *P. alata* varies so dramatically during some periods, but not during MIS 1/2/3/4? I think the discussion on the modern observations of *P. alata* blooms and distributions are helpful, but should be related more explicitly to the paleoceanographic record if possible. Is the author's suggestion that reduced NDI around 100 ka is an indication that upwelling occurred continuously, rather than on a seasonal basis, thereby eliminating the "early- or post-  
35 upwelling nutrient conditions"?

**Both the NDI and the Diol Index reflect the relative abundance of *Proboscia* diatoms as the 1,14-diols are specific for this group of diatoms. Since along the Chilean margin *Proboscia alata* has been observed, we propose that for our location the NDI reflects *P. alata* productivity. However, in other regions the C<sub>28</sub> 1,14-**

diol might be produced by other *Proboscia* species and the NDI might thus not reflect solely *P. alata* productivity. In this light we have also partly adjusted our hypothesis that the NDI potentially reflects *P. alata* productivity; it is merely more species-specific as compared to the Diol Index since it excludes the C<sub>30</sub> 1,14-diol from the numerator. We have added the following (P. 15, lines 16-18):

5 “*In other regions, the C<sub>28</sub> 1,14-diol might be produced by other Proboscia species (e.g. P. inermis) and the NDI might thus not reflect solely P. alata productivity. In summary, we suggest that the NDI at the Chilean margin likely reflects Proboscia productivity, and may therefore not be suitable as paleo-nutrient tracer.*”

10 As for the question why the NDI/*Proboscia* activity is relatively constant during MIS 1/2/3/4 but shows large variation during MIS 5: this is one of the main issues we have addressed in the manuscript. We propose, based on the maximum in MAR<sub>TOC</sub> during MIS 5 concurrent with e.g. the highest abundances of preserved *Chaetoceros* valves, that around 100 ka the upwelling intensity was likely to be strong and primary productivity was stimulated. What we know from the modern-day *Proboscia* ecology, is that this diatom genus proliferates when nutrients increase, i.e. during upwelling. However, it is particularly able of

15 dominating the diatom community during early upwelling conditions when silicate concentrations are still low, and the nutrients are still in the deeper waters. When actual upwelling occurs, and the nutrients are transported to the surface and silicate concentrations increase, *Proboscia* is likely outcompeted by for instance *Chaetoceros* which is more heavily silicified. Accordingly, we think this might explain the relatively low Diol Index and NDI around 100 ka, as the relative abundance of *Proboscia* was likely to be

20 low. However, before and after this event, i.e. around ca. 120 and 90 ka, upwelling was likely less intense, and conditions were more favorable for *Proboscia*.

As for the referee’s last question: the reduced NDI around 100 ka does not indicate that upwelling occurred continuously throughout the year and thus does not eliminate the seasonal basis of upwelling. However, the NDI and Diol Index reflect integrations of multiple years and thus an averaged signal of

25 *Proboscia* productivity over these years. We believe that the minimum in the NDI around 100 ka, suggesting that phosphate and nitrate concentrations were around 0 µmol/L, is not realistic, because the “mean annual nutrient concentrations” were not likely to be ~0 during this upwelling interval. Even though nutrients can be used up at the end of an upwelling season, mean annual nutrient concentrations are likely to be relatively high.

30 There is an increase in TOC-MAR and importantly, 1,13- and 1,15-diols in MIS 4. Please comment on if this is an indication of specific upwelling or nutrient conditions that might promote the eustigmatophyte but not other algal groups.

Yes, this is true, and we have included this in the revised manuscript. Moreover, similar comments were put forward by referees 1 and 2. We believe that the increase in MAR<sub>TOC</sub> during MIS 4 is likely linked to

35 the evident increase in sedimentation rate during this period (Fig. 3a). During MIS 5, the maximum in MAR<sub>TOC</sub> corresponds to elevated TOC levels and a constant sedimentation rate, suggesting an increase in primary productivity. However, during MIS 4, the TOC levels are almost twice as low, but the sedimentation rate is clearly higher, suggesting that the increased MAR<sub>TOC</sub> is a result of enhanced particle settling. We have added the following:

40 “*During MIS 4 we also observe a peak in MAR<sub>TOC</sub> (Fig. 3a) but there is no corresponding peak in Chaetoceros abundance (Fig. 4c). However, the high MAR<sub>TOC</sub> during MIS 4 is linked to high sedimentation rates (Fig. 3c),*

*whereas the peak in MAR<sub>TOC</sub> during MIS 5 is not, confirming that the MAR<sub>TOC</sub> maximum during MIS 5 indeed likely resulted from increased primary productivity, whereas during MIS 4 the high MAR<sub>TOC</sub> did not”*

5 P. 15 Starting line 31: Regional differences in the timing of deglacial warming might be expected, but this does not address the different timing among proxies at Site 1234. Please elaborate on the significance of the LDI versus UK37 difference during ~10 kyr around the LGM.

10 **Yes, we completely agree with referee 3, however, we are not certain on how to explain this ±10 kyr time lag between the deglacial warming as recorded by the LDI and the U<sup>K</sup><sub>37</sub> and TEX<sup>H</sup><sub>86</sub>. The LDI-temperatures are also considerably lower as compared to the other proxy temperatures. Although the producers of the 1,13- and 1,15-diols are unknown, they are likely to be phototrophs living in the upper part of the photic zone (e.g., Rampen et al., 2012; Balzano et al., 2018), and therefore we would expect similar temperature estimates for the LDI and U<sup>K</sup><sub>37</sub>. We have added the following (P. 16, lines 24-27)**  
**“Potentially, the production of the 1,13- and 1,15-diols shifted to a colder season due to regional climatic change associated with the southward migration of the ACC and SWW upon the deglacial warming. Finally, we observe an early onset of the deglacial warming for the LDI compared to the U<sup>K</sup><sub>37</sub> and TEX<sup>H</sup><sub>86</sub> (ca. 6 kyrs; Fig. 5b), the reasons for which are elusive ”**

Some points need grammatical correction:

P1. L. 11: Change “proxies” to “indices” because the Diol Index is stated to be an indicator rather than a proxy in Line 12.

**We have adjusted this.**

20 P1. L.12: “. . .the NDI as a quantitative proxy. . .”

**We have rephrased as follows: “... the NDI index as proxy for...”.**

P1. L. 15: Either specify the number of glacial/interglacial periods or just remove this clause.

**We have removed this.**

P2. L. 16:: Provide the equation for DI, or rephrase, because it is not simply the ratio, but rather the percentage.

25 **We agree that this formulation is unclear, and we have rephrased as follows (P. 2, lines 16-17):**  
**“The Diol Index, which is an indicator for past upwelling/high nutrient conditions, is defined as the fractional abundance of 1,14-diols with respect to 1,13-diols (Willmott et al., 2010) or the C<sub>30</sub> 1,15-diol (Rampen et al., 2008)...”**

30 P2. L 24: Remove “sea”, or change to “marine”?

**We have changed this into “marine”.**

P2. L 24-25: If possible, specify if the change in saturation is related to changing species or interspecies diol adjustments.

This is not known. In sediments, mono-unsaturated 1,14-diols are generally lower in abundance as compared to the saturated 1,14-diols. However, culture data show that *Proboscia* diatoms often produce more unsaturated diols, and that the degree of unsaturation is strongly affected by temperature (Rampen et al., 2009; OG). This temperature relationship was however not observed in marine surface sediments  
5 (Rampen et al., 2014) and the low abundance of unsaturated 1,14-diols might be the result of preferential degradation. However, the regional differences in 1,14-diol distributions are likely also the result of different species producing different 1,14-diols.

P2. L. 27: Remove “Preliminary”

10 **We have removed this.**

P2. L28: “paleo-upwelling” could be used instead of past upwelling. Remove “as”. Also, change “proxies” to “indicators” unless the reconstruction of upwelling rates is a quantitative transfer function.

**We have corrected this.**

P3. L. 10: The Holocene is part of the Quaternary – no need to mention separately. orzet

15 **We have removed “and Holocene”.**

P3. L. 10: “large climate cycle” is kind of arbitrary

**We have removed “covering the last large climate cycle of the Pleistocene”**

P3. L. 10: remove “bulk organic matter”

**We will have removed this.**

20 P3. L. 29: Can you include more specifics about the connection – namely, specify if stronger ACC and Westerlies result in warmer or cooler climate.

**The relationship between the ACC and Westerlies with productivity and upwelling is described in section 4.1, but we agree that we should elaborate more on the link between the ACC/Westerlies and temperature, which we have done as follows (P. 3 line 32 – P. 4 line 4):**

25 ***“Lamy et al. (2002) showed that long-term Holocene trends in temperature and productivity are linked to latitudinal shifts of the ACC and the Westerlies. On a millennial- to multidecennial-scale, paleotemperature variations are strongly connected to millennial-scale climate variations in Antarctica. When the ACC migrates northward, potentially associated with an expansion of Antarctic sea ice, cold, subantarctic waters are advected into the southern hemisphere midlatitudes, including the Chilean margin (e.g., Lamy et al., 2004; Kaiser et al., 2005).”***  
30

P. 3 L. 30-33. Does not follow from previous part of paragraph. I think it needs a segue from climate to upwelling/sedimentation dynamics, because this statement isn’t about climate like the rest of paragraph. Also, please describe the subtropical high pressure system clearly because it is referred to later as a possible explanation.

**We agree that this structure was not optimal, and we have moved these lines to the second part of the paragraph (P. 4, lines 11-14). We have now included one sentence on the subtropical high-pressure system in the ‘Study site’ section. However, we have now removed the sentence in which we suggest that the subtropical high-pressure system might potentially be related to the upwelling event during the Last Interglacial, since this is rather speculative.**

P. 4 L. 2: There might be some variation in this, but I think a better spelling is Biobío

**We have corrected this.**

P. 4, L. 3: remove “both” and “large” to read “. . .which drain basins of 24,000 km<sup>2</sup>. . .”

**10 We have corrected this.**

P. 4 L. 13: Remove “providing the potential for high-resolution records” because it’s not necessary and I don’t think the author’s did that kind of sampling.

**We have removed this.**

P. 5 L. 5: If these benthic foraminifera data are already published, I don’t think this paragraph is necessary, is it?  
**15 Are any adjustments made to the McManus and Heusser paper? For brevity, this could be folded into the age model paragraph because it provides the basis for the correlations of the cores. This change is not critical for publishing the paper.**

**The correction of 0.64‰ is new information and therefore relevant. Since the planktonics are described in this paragraph, we prefer to keep the information on the benthic data also in this section.**

**20 P. 6 L 9: Specify that the GDGT naming scheme in the following descriptions relates to the structures in Castañeda and Schouten, or some other appropriate reference**

**We refer to Sinninghe Damsté et al. (2002).**

P. 6 L. 28: Remove “in this case” and clarify that the BAYSPAR refers to the Tierney and Tingley citation.

**25 We believe that “in this case” is relevant here, since the core-tops on which the calibration is based, is different for every paleo-reconstruction; it depends on the assumed prior mean temperature and search tolerance. We used a prior mean of 13 °C and a search tolerance of 0.2 TEX<sub>86</sub> units, resulting in the 62 high latitudinal grid boxes on which in this case the calibration is based. We now refer to Tierney and Tingley (2014, 2015).**

P. 6 L. 31-32. Awkward phrasing because of passive voice.

**30 We have rephrased this sentence in present sense.**

P. 7. “Conductive”?

**We thank the referee for remarking this typo: it should be “conducive”.**

P. 7, L. 7: “isomers can indicate these types of environments in the past. . .” should be rephrased because it is confusing as written.

**We have rephrased this.**

P. 7 L. 8: Include a reference suggesting 0.3 is acceptable threshold for Methane Index.

- 5 **We refer here to Zhang et al. (2011): “*Combined GDGT distribution and isotopic evidence suggest that 0.3 to 0.5 of the MI might be a reasonable threshold for distinguishing gas hydrate impacted and/or methane-rich environments from normal marine realm.*”**

P. 7 L 34: What was the injector configuration?

- 10 **On-column injection, we have now clarified this.**

P. 8 L. 8: Helium does not need to be capitalized.

**We have corrected this.**

- 15 P. 8 L. 23: The first part of this sentence should be rephrased because it is confusing as written.  
**We have rephrased this.**

P. 8 L. 27: “..potentially riverine derived. . .” should be rephrased for grammar.

**We have rephrased as follows: “*which is potentially derived from rivers*”.**

20

P. 8 L. 30: Given that you are testing the effectiveness of the NDI index, insert: “..The NDI index, a proposed proxy for PO43-. . .”

**We have corrected this.**

25

P. 10 L 34: Insert a comma after “In all sediments”

**We have corrected this.**

- 30 P. 10: It seems strange that crenarchaeol is the first biomarker presented when it has only been mentioned as a standard in the first part of the paper, and is never discussed or interpreted in any details. Could remove statement about crenarchaeol, else it should be discussed. Similarly, figures 4f and 4g and 4h come before 4a, 4b, etc. in the text. I recommend rearranging this so that diol results come first and things don’t seem out of order, or just refer to them as figure 4.

**We have clarified that crenarchaeol is a specific biomarker for Thaumarchaeota (P. 10, line 18):**

- 35 **We agree that the order in Figure 4 is in contrast with the results, and we have rearranged the panels in this figure, as well as some paragraphs in the methods section.**

P 10 L 4: The reported accumulation rate for crenarchaeol does not match what is shown in figure 4f.

- 40 **We thank the referee for noticing this; we have corrected this.**

P. 10 L. 16: Figure “4i”, not figure 4j. Also, the data are labeled pg g-1, but the text states µg g-1. Likewise ng versus mg for the 1,14-diol accumulation rates.

**We thank the referee for pointing out these inaccuracies, and we have corrected these.**

P. 11 L 26-27: State on which proxies these estimates are based.

5 **We agree that this was unclear, and we have clarified that this is based on all three proxies.**

P. 11, L 28: The spline curves show a decrease of 4-6°C not 6-7°C. Smallest change is for iGDGTs.

**We have corrected this, as all proxies show a ca. 4-6°C temperature decrease.**

10 P. 12 L 27: “. . .since neither opal concentration nor opal or TOC-MAR increased simultaneously with TOC concentration” might help clarify this sentence.

**We have changed accordingly.**

P. 13, L 16: Intervals of enhanced upwelling are not explicitly labeled in Figs 3b and 3c.

15 **We agree that this is unclear and we have changed this as follows: “... with enhanced upwelling (i.e., around 100 ka; purple band in Fig. 3)”.**

P. 13, L 27. Rephrase “As for the diol index and the . . .” because this phrase has another common meaning than as it is used.

**We have rephrased this.**

P. 14 L 10: "during/under" could just be "in"

20 **We have corrected this.**

Figure 4: How can there be sometimes more chaetoceros counts than total diatom counts?

**This is because the counts are not quantitative, but descriptive: F=few; C=common; A=abundant; VA=very abundant. However, we now realize that we did not clarify this in the caption, which we have now corrected.**

25 Figure 5: What are the orange versus blue lines in the Site 1234 Benthic oxygen isotopes? It is not mentioned in the figure caption.

30 **We thank the referee for noticing this, and we have now clarified this in the caption. The color scheme is similar to Fig. 2, where the two colors reflect the two separate age models. The blue data reflect the benthic  $\delta^{18}\text{O}$  dated by correlation to Atlantic core MD95204, whereas the orange data represent the  $\delta^{18}\text{O}$  data correlated to the Vostok ice core chronology.**





# A Late Quaternary climate record based on long chain diol proxies from the Chilean margin

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**Abstract.** ~~The primary focus of this study is to test the applicability of different paleoenvironmental~~In this study we have applied different ~~proxies-indices~~ based on long chain diols, i.e., the Long chain Diol Index (LDI) as proxy for past SST, the Diol Index as indicator of past upwelling conditions and the Nutrient Diol Index (NDI) as ~~quantitative~~ proxy for nitrate and phosphate concentrations in seawater. The proxies were analyzed in marine sediments recovered at ODP Site 1234, located within the Peru-Chile upwelling system, with a ~2 kyr resolution, covering the last 150 kyrs, ~~i.e., encompassing several glacial and interglacial periods~~. We also generated TEX<sup>H</sup><sub>86</sub> and U<sup>K'</sup><sub>37</sub> temperature and planktonic δ<sup>18</sup>O records, as well as total organic carbon (TOC) and accumulation rates (ARs) of TOC and lipid biomarkers (i.e., C<sub>37</sub> alkenones, GDGTs, dinosterol and loliolide) to reconstruct past phytoplankton production. The LDI-derived SST record co-varies with TEX<sup>H</sup><sub>86</sub>- and U<sup>K'</sup><sub>37</sub>-derived SST records as well as with the planktonic δ<sup>18</sup>O record, implying that the LDI reflects past SST variations at this site. TOC and phytoplankton AR records indicate increased export production during the Last Interglacial (MIS 5), simultaneous with a peak in the abundance of preserved *Chaetoceros* diatoms, suggesting intensified upwelling during this period. The Diol Index is relatively low during the upwelling period, but peaks before and after this period, suggesting that *Proboscia* diatoms were more ~~dominant-abundant~~ before and after the period of upwelling. The NDI reveals the same ~~variations-trends~~ as the Diol Index suggesting that the input of nitrate and phosphate was minimal during upwelling, which is unrealistic. We suggest that the Diol Index and NDI should perhaps be considered as ~~an indicators~~ for *Proboscia* (~~multiple species~~) productivity instead of upwelling ~~conditions or nutrient concentrations, per se, whereas the NDI likely reflects *Proboscia alata* productivity, and might therefore not be suitable as a more general paleonutrient proxy.~~

## 1 Introduction

Paleoclimatic reconstructions typically rely on physical, biological, and geochemical proxies from sedimentary archives.

30 Physical proxies include sediment composition, structure, grain size, density, and magnetic susceptibility, which may provide information on the paleodepositional environment. Biological proxies comprise preserved (micro-)organisms such as diatoms,

foraminifera, dinoflagellates, corals, and mollusks, or remnants deriving from higher plants such as pollen and spores. Geochemical proxies are based on the chemical composition of either the sediment or fossilized organisms. Stable isotope and elemental concentrations are inorganic proxies typically measured in shells or skeletons of marine organisms (foraminifera, mollusks, corals) preserved in the sediment, providing insight into the chemistry of the seawater in which the organisms lived.

5 Organic proxies are a relatively newer class of tools, based on fossilized molecules that are unique for a specific organism or group of organisms, referred to as biomarkers. The ratios of specific biomarker molecules are often related to physical parameters of the environment in which the source organism grew, such as temperature, salinity, oxygen availability or productivity, and therefore such organic proxies can also be applied to reconstruct past depositional environments (e.g., Brassell et al., 1986; Prahl and Wakeham, 1987; Schouten et al., 2002; Rampen et al., 2008, 2012; Willmott et al., 2010; Gal et al., 2018).

In the last decade long chain diols (LCDs) have attracted attention as novel proxies to reconstruct past environmental conditions. The Long chain Diol Index (LDI) was proposed, based on the distribution of C<sub>28</sub> and C<sub>30</sub> 1,13- and 1,15-diols in marine surface sediments, which shows a good correlation with ~~annual~~-mean annual sea surface temperature (SST; Rampen et al., 2012). These compounds have been detected in cultures of Eustigmatophyte algae (e.g., Volkman et al., 1992; 1999; Méjanelle et al., 2003; Rampen et al., 2014a), but the LCD distributions observed are different to those observed in the marine realm (e.g., Versteegh et al., 1997; 2000; Rampen et al., 2012; 2014a), and hence, their role as LCD producers in the ocean remains uncertain. The Diol Index, which is an indicator for past upwelling/high nutrient conditions, is defined as the ~~ratio~~ fractional abundance of 1,14-diols ~~versus-with respect to~~ 1,13-diols (Willmott et al., 2010) or the C<sub>30</sub> 1,15-diol (Rampen et al., 2008), where 1,14-diols are biomarkers for *Proboscia* diatoms (Sinninghe Damsté et al., 2003; Rampen et al., 2014b).

20 ~~*Proboscia* grows during the early stages of upwelling since they need relatively little silica and they are able to migrate to deeper waters to obtain nutrients.~~*Proboscia* diatoms grow in the early stages of upwelling when nutrients strongly increase in concentration (Koning et al., 2001) and, therefore, it was proposed that the relative abundance of 1,14-diols can trace past upwelling conditions. C<sub>28</sub>, C<sub>30</sub> and C<sub>32</sub> 1,14-diols have also been observed in the marine Dictyochophyte *Apedinella radians* (Rampen et al., 2011) but its role as 1,14-diol producer in the marine realm is unknown. Recently, a new index based on the saturated and mono-unsaturated C<sub>28</sub> 1,14-diol was proposed as a quantitative proxy for nitrate and phosphate concentrations (Gal et al., 2018), called the ~~nutrient~~-Nutrient diol-Diol index-Index (NDI). The authors found a strong positive correlation between the NDI and phosphate ( $R^2 = 0.85$ ) and nitrate ( $R^2 = 0.80$ ) concentrations for the ~~sea surface-marine~~ sediment data sets of Rampen et al. (2014b) and de Bar et al. (2016). This suggests that the NDI might be a good indicator of past nutrient variations in surface waters.

30 ~~Preliminary a~~Applications in sediment cores of these LCD proxies have shown that the LDI, as well as the Diol Index, are promising ~~as~~-paleotemperature and ~~past-paleo~~-upwelling proxies-indicators (e.g., Pancost et al., 2009; Lopes dos Santos et al., 2012; Rampen et al., 2012; Seki et al., 2012; Rodrigo-Gámiz et al., 2014; Plancq et al., 2015; Jonas et al., 2017). However, a number of uncertainties still exist in the application of these biomarkers. For example, recent studies of surface sediments from coastal regions reveal different 1,13- and 1,15-diol distributions compared to open ocean sediments (de Bar et al., 2016; Lattaud

et al., 2017a; 2017b). Relatively high fractional abundances of the C<sub>32</sub> 1,15-diol along the coast were observed, as a result of riverine input, significantly affecting the LDI signal, likely due to different 1,13- and/or 1,15-diol producers thriving in river outflow waters. Moreover, studies have related high *Proboscia* diatom abundances to stratified instead of upwelling conditions (e.g., Fernández and Bode, 1994). Similarly, Contreras et al. (2010) determined the relative abundance of the C<sub>28</sub> 1,14-diol at ODP Site 1229 located in the Peruvian upwelling system, and observed increased concentrations during the Last Interglacial (LIG; MIS 5e) and related this to enhanced water column stratification. Furthermore, Rodrigo-Gámiz et al. (2015) showed that for sediment traps and surface sediments around Iceland, which were characterized by high concentrations of 1,14 diols (>75% of all LCDs), the LDI did not correspond to SST. This makes application of the LDI at sites with high input of diols from *Proboscia* diatoms (e.g., upwelling sites) uncertain. Finally, due to its recent development no studies have been performed yet to test the applicability of the NDI as a paleo-nutrient proxy.

To constrain the uncertainties in applying the LCD proxies (LDI, Diol Index and NDI) at sites with upwelling and riverine input, we studied the ~~Late Quaternary and Holocene~~ sedimentary record at ODP Site 1234. This site is located along the Chilean margin, within the Chile-Peruvian upwelling system, and near two major river mouths of the Andean river systems Río Bio-Bio and Río Itata, both draining large basins (Muratli et al., 2010a). We sampled the last ~150 kyrs, ~~covering the last large climate cycle of the Pleistocene~~, including ~~several~~ glacial and interglacial periods, and generated LDI, TEX<sub>86</sub> and U<sup>K</sup><sub>37</sub> based temperature records to constrain glacial-interglacial variations in SST throughout this entire interval. Additionally, we compared the Diol Index and the NDI record with other paleoproductivity indicators, including ~~bulk organic matter~~ total organic carbon (TOC), organic matter stable carbon isotopes (δ<sup>13</sup>C), as well as phytoplanktonic lipid biomarkers that are characteristic for certain phytoplankton communities (C<sub>37</sub> alkenones, loliolide and dinosterol).

## 2 Materials and methods

### 2.1 Study site

Marine sediments along the coast of Chile and Peru have been thoroughly studied, as it is a key region in the southern hemisphere for studying climate variability related to both atmospheric and oceanographic circulation (e.g., Lamy et al., 1998, 1999, 2002, 2004; Hebbeln et al., 2000, 2002; Mohtadi & Hebbeln, 2004; Stuut and Lamy, 2004; Heusser et al., 2006; Romero et al., 2006; Mohtadi et al., 2008; Muratli et al., 2010a, 2010b; Verleye & Louwye, 2010; Chase et al., 2014). The main circulation patterns include the Southern Westerly Winds (SWW) and the Antarctic Circumpolar Current (ACC; Fig 1). The ACC approaches the South American continent from the west, and initiates both the Humboldt Current (or Peru Chile Current) flowing northwards along the continental margin and the Cape Horn Current flowing southwards (e.g., Stuut et al., 2006; Fig. 1). The Humboldt Current flows along the Chilean coast and turns westwards as it approaches the equator, forming the South Equatorial Current (SEC). Variations in strength and location of the ACC and Southern Westerlies are thought to be the main

climate controls in this region. Lamy et al. (2002) showed that long-term Holocene trends in temperature and productivity are linked to latitudinal shifts of the ACC and the Westerlies. On a millennial- to multidecadal-scale, paleotemperature variations are strongly connected to millennial-scale climate variations in Antarctica. When the ACC migrates northward, potentially associated with an expansion of Antarctic sea ice, cold, subantarctic waters are advected into the southern hemisphere mid-

5 latitudes, including the Chilean margin (e.g., Lamy et al., 2004; Kaiser et al., 2005). The subtropical high-pressure system is an important climate control north of 33°S, which can enhance coastal upwelling (Mohtadi and Hebbeln, 2004).

However, the continental margin is also under influence of terrestrial input due to rainfall and land erosion (Lamy et al., 2004), and terrestrial material deposited along the coastal margin derive from mainly two mountain ranges, i.e., the Coast Range and the Andes (Lopez-Escobar et al., 1977; Martin et al., 1999).

10 ODP Site 1234 is located in the south east Pacific Ocean (36°13.153'S, 73°40.902'W, 1015 m water depth), ca. 65 km offshore of Concepción, Chile. This site lies in the vicinity of two large Andean river systems: the Río Bio-Bío and Río Itata, which ~~both~~ drain ~~large~~ basins of 24,000 km<sup>2</sup> and 11,200 km<sup>2</sup>, respectively (Muratli et al., 2010a). The continental margin is under influence of terrestrial input due to rainfall and land erosion (Lamy et al., 2004), and terrestrial material deposited along the coastal margin derive mainly from two mountain ranges, i.e., the Coast Range and the Andes (Lopez-Escobar et al., 1977;

15 Martin et al., 1999). Moreover, ODP Site 1234 is located within the Peru-Chile upwelling system, which is one of the most important upwelling regions on Earth (Berger et al., 1987), due to the combination of upwelling-favorable winds (Daneri et al., 2000; Carr and Kearns, 2003) and an eastern boundary current (Humboldt Current). The upwelling regime stretches from 5°S to 38°S, corresponding to ca. 5000 km of coastline. South of 38°S, onshore winds suppress upwelling (Strub et al., 1998), but high productivity is sustained by relatively high nutrient supply from the ACC (Hebbeln et al., 2000), which is typically

20 rich in nitrate and limited in micronutrients such as iron (de Baar et al., 1995). Along the Chilean coast, iron availability (as well as other micronutrients) can increase due to fluvial supply as the precipitation of the Southern Westerlies onshore enhances river runoff (Mohtadi & Hebbeln, 2004).

## 2.2 Age model and sample strategy

The core was drilled as part of Ocean Drilling Program (ODP) Leg 202. Sedimentation rates were relatively high (~80 cm/kyr

25 on average), ~~providing the potential for high-resolution records (~~Mix et al., 2003; Heusser et al., 2006). The age model used is from Heusser et al. (2006) and is based upon radiocarbon dates and correlation of benthic  $\delta^{18}\text{O}$  to deep Atlantic core MD95204 (upper half) and the Vostok ice core chronology (lower half; see Heusser et al., 2006 and references therein). Heusser et al. (2006) switched between the two age models around 69 ka where they overlap, as indicated by the dashed line in Fig. 2a. However, this results in a substantial, and likely unrealistic, dip in the sedimentation rate between ca. 80 and 90 ka

30 in the hiatus between the age models (Fig. 2b). Hence, we chose to use the upper age model (dark blue in Fig. 2) which extends up to ~83 ka, and linearly interpolate between this age and the age of ~90 ka constrained by the other age model for the lower half of the core. This depth-age range of linear interpolation between the two age models is highlighted in green in Fig. 2 and

results in less abrupt changes in sedimentation rates. The core was sampled with a ~2 kyr resolution, covering the last ~150 kyrs. In total, 74 sediment samples were analyzed for bulk and organic geochemistry.

### 2.3 Elemental analysis

5 All 74 sediment samples were freeze-dried and homogenized. Small aliquots (ca. 50 – 100 mg) were used for elemental analysis. For this purpose, all aliquots were acidified with 2 M hydrochloric acid (HCl) to remove all carbonates, and rinsed with distilled water to remove salts. Subsequently, the decalcified sediment samples were analyzed for total organic carbon (TOC), ~~total nitrogen (TN)~~ and stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) by means of a Thermo Scientific Flash 2000 Elemental Analyzer coupled to a Thermo Scientific Delta V Advantage Isotope Ratio Mass Spectrometer. Total nitrogen (TN) was  
10 measured on aliquots which were not acidified. Results are expressed in standard  $\delta$ -notation relative to Vienna Pee Dee Belemnite (VPDB) for  $\delta^{13}\text{C}$ . The precision as determined using laboratory standards calibrated to certified international reference standards, were in all cases  $<0.2\text{‰}$ . TOC mass accumulation rates ARs ( $\text{MAR}_{\text{TOC}}$ ) were calculated by multiplication of the sedimentation rate (linear interpolation between depth points of the age-depth model; see above) with an estimated bulk density of  $1.6\text{ g cm}^{-3}$  (Mix et al., 2003) and subsequent multiplication with the TOC percentage.

15

### 2.4 Foraminiferal stable isotope analysis

Benthic stable isotope data were previously published, and were generated using standard techniques in laboratories at Oregon State University and the Woods Hole Oceanographic Institution (McManus et al., 1999, 2002, 2003; Heusser et al., 2006). Oxygen isotope ratios in *Cibicidoides* and *Uvigerina* were adjusted to each other by  $0.64\text{‰}$  (Shackleton, 1974). Additional  
20 data on the planktonic species *Globigerina bulloides* were generated at Lamont Doherty Earth Observatory (LDEO) of Columbia University using a Thermo Delta V Plus gas-source isotope ratio mass spectrometer (IRMS) equipped with a Kiel IV automated individual acid bath sample-preparation device. Although a recent study found no size-related influence on *G. bulloides*  $\delta^{18}\text{O}$  (Costa et al., 2017) specimens were generally picked from the 250–300  $\mu\text{m}$  size range, with 8-12 individuals selected for analysis. Samples were replicated at ~5–10% frequency and measured isotope ratios were calibrated to the VPDB  
25 isotope scale with NBS-19 and NBS-18. Reproducibility of the in-house standard (1 sigma) is  $\pm 0.06\text{‰}$  ( $\delta^{18}\text{O}$ ) and  $\pm 0.04\text{‰}$  ( $\delta^{13}\text{C}$ ).

### 2.5 Lipid extraction and organic geochemical analysis

The sediment samples (ca. 15 g dry weight) were extracted using accelerated solvent extraction (ASE) using a DIONEX 200,  
30 at  $100\text{ °C}$ , a pressure of  $7\text{--}8 \times 10^6\text{ Pa}$ , and a mixture of dichloromethane (DCM) and methanol (MeOH) (9:1; v:v). The total lipid extracts (TLEs) were dried under a stream of nitrogen ( $\text{N}_2$ ) using a Caliper TurboVap LV. All TLEs were desulfurized

using copper granules activated with 1M HCL. The copper turnings were added to the TLEs and stirred overnight and subsequently dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), in order to remove precipitate and water, and dried down under N<sub>2</sub>. For quantification purposes, three internal standards were added to the TLEs: 10-nonadecanone (C<sub>19:0</sub> ketone) for long chain alkenones, C<sub>22</sub> 7,16-diol for LCDs (Rodrigo-Gamiz et al., 2015) and the C<sub>46</sub> GDGT for GDGTs (Huguet et al., 2006).  
5 The TLEs (aliquots of ~4.5 mg) were separated into apolar, ketone (containing alkenones) and polar (containing LCDs and GDGTs) fractions, by separation over activated (2h at 150 °C) Al<sub>2</sub>O<sub>3</sub> and elution with hexane/DCM (9:1; v:v), hexane/DCM (1:1; v:v) and DCM/MeOH (1:1; v:v), respectively. Polar fractions were split for GDGT (25%) and LCD (75%) analysis.

### 2.5.1 GDGTs

10 Aliquots of the polar fractions were dissolved in hexane:isopropanol (99:1, v:v) to a concentration of ca. 2 mg mL<sup>-1</sup>. The fractions were then filtered through 0.45 µm polytetrafluoroethylene (PTFE) filters. GDGTs were analyzed by means of Ultra High Performance Liquid Chromatography Mass Spectrometry (UHPLC-MS), on an Agilent 1260 HPLC, equipped with automatic injector, coupled to a 6130 Agilent MSD and HP Chemstation software according to Hopmans et al. (2016). The injection volume was 10 µL. Separation of the GDGTs was achieved in normal phase using 2 silica BEH HILIC columns in  
15 series (150 mm x 2.1 mm; 1,7 µm; Waters Acquity) at a temperature of 25 °C. The mobile phases are hexane (A) and hexane:isopropanol (9:1, v:v) (B). Compounds were isocratically eluted for 25 minutes with 18% B, followed by a linear gradient to 35% B in 25 minutes and a linear gradient to 100% B in the 30 min thereafter. The flow rate was kept constant (0.2 mL min<sup>-1</sup>) during the analysis. The conditions for the APCI-MS were identical to Hopmans et al. (2016). GDGTs were detected in single ion monitoring (SIM) mode of the protonated molecules ([M+H]<sup>+</sup>) of the various GDGTs. A standard mixture  
20 of C<sub>46</sub> GDGT (internal standard) and crenarchaeol was analyzed to determine the relative response factor (RFF) between these two compounds (c.f. Huguet et al., 2006), and thereby quantify GDGTs in the sediments.

For reconstruction of past SST we used the TEX<sub>86</sub><sup>H</sup> index as proposed by Kim et al. (2010), which is defined as the logarithmic function of the original TEX<sub>86</sub> (Schouten et al., 2002):

$$\text{TEX}_{86}^H = \log \frac{[\text{GDGT-2}] + [\text{GDGT-3}] + [\text{Cren}']}{[\text{GDGT-1}] + [\text{GDGT-2}] + [\text{GDGT-3}] + [\text{Cren}']} \quad (1)$$

25 where the numbers correspond to the amount of cyclopentane moieties in the isoprenoid GDGTs and where Cren' refers to the later eluting isomer of crenarchaeol (Sinninghe Damsté et al., 2002). We have discarded 13 samples for the TEX<sub>86</sub> calculation due to the partial co-elution of GDGT-2 with an unknown compound.

The TEX<sub>86</sub><sup>H</sup> values were converted to SSTs applying the global core top calibration of Kim et al. (2010):

$$30 \quad \text{SST} = 68.4 \times \text{TEX}_{86}^H + 38.6 \quad (2)$$

There is also a regional TEX<sub>86</sub><sup>H</sup> calibration available, based on Chilean surface sediments between 25 and 50 °S (Kaiser et al., 2015):

$$SST = 59.6 \times \text{TEX}_{86}^H + 33.0 \quad (3)$$

This calibration has a similar slope compared to the global core-top calibration of Kim et al. (2010) but a lower intercept, which results in SSTs that were ca. 2.4 °C lower compared to the  $\text{TEX}_{86}^H$ -SSTs calculated after Kim et al. (2010). Although the outcomes are relatively similar, the calibration of Kim et al. (2010) resulted in SSTs that agreed better with the  $U^{K_{37}}$  and LDI records, and therefore we have used this calibration. In Appendix A, the  $\text{TEX}_{86}^H$  temperatures based on the calibration of Kaiser et al. (2015) are plotted (Fig. A1). Additionally, we plotted  $\text{TEX}_{86}$  temperatures calculated after the Bayesian calibration of Tierney and Tingley (2014, 2015) in Fig S1. These SSTs are on average 4 °C lower compared to the  $\text{TEX}_{86}^H$ -derived temperatures after Kim et al. (2010), which might be due to the relative large number of high latitude core tops on which in this case the BAYSPAR calibration is based (Tierney and Tingley, 2014; 2015), whereas the  $\text{TEX}_{86}^H$  calibration of Kim et al. (2010) excludes (sub)polar core-top data. However, both reconstructions show the same trend.

To assess continental organic matter input into the marine realm, we calculated the Branched Isoprenoid Tetraether (BIT) index, as proposed by Hopmans et al. (2004), ~~was calculated~~, including the 6-methyl brGDGTs as described by de Jonge et al. (2014; 2015):

$$\text{BIT} = \frac{[\text{brGDGT } 1a] + [\text{brGDGT } 11a+11a'] + [\text{brGDGT } 111a+111a']}{[\text{brGDGT } 1a] + [\text{brGDGT } 11a+11a'] + [\text{brGDGT } 111a+111a'] + [\text{Cren}]} \quad (4)$$

where the numbers correspond to different branched GDGTs (Hopmans et al., 2004).

Additionally, we calculated the Methane Index (MI), as a proxy for dissociation of marine gas hydrates conducive to anaerobic oxidation of methane (AOM), as proposed by Zhang et al. (2011):

$$\text{MI} = \frac{[\text{GDGT}-1] + [\text{GDGT}-2] + [\text{GDGT}-3]}{[\text{GDGT}-1] + [\text{GDGT}-2] + [\text{GDGT}-3] + [\text{Cren}] + [\text{Cren}]} \quad (5)$$

The archaea living in hydrate-impacted environments mainly contain GDGT-1, -2 and -3 as their membrane lipids. ~~Therefore, relative high abundances of these GDGTs might indicate and hence relative high abundances of these isomers can indicate~~ these types of environments in the past, and potentially explain erroneous  $\text{TEX}_{86}^H$  results due to high GDGT-1, -2 and/or -3 abundances. For all samples, this index was < 0.3, except for one data point (MI = 0.6), which was therefore removed from further discussion. Additionally, to assess other potential influence on the  $\text{TEX}_{86}^H$ , we determined the %GDGT-0 and Ring Index for all sediments. All values were below the advised thresholds, implying no substantial biases on the  $\text{TEX}_{86}$  (Zhang et al., 2011; Sinninghe Damsté et al., 2012; Zhang et al., 2016).

## 2.5.2 Long chain alkenones

Ketone fractions were dissolved in ethyl acetate to a concentration of ~ 1 mg mL<sup>-1</sup>, and analyzed on an Agilent 6890N gas chromatograph (GC) with flame ionization detection (FID). Separation was achieved on a fused silica column with a length of 50 m and diameter of 0.32 mm, coated with a CP Sil-5 (thickness = 0.12 µm). Helium was used as carrier gas. The flow mode was a constant pressure of 100 kPa. Alkenones were injected on-column at 70 °C at the start of the analysis, increased by 20 °C min<sup>-1</sup> to 200 °C followed by 3 °C min<sup>-1</sup> until the final temperature of 320 °C. This end temperature was held for 25 min.



Quantification of the alkenones was achieved by means of the C<sub>19:0</sub> ketone internal standard. Identification of the long chain alkenones was done on an Agilent 7890B GC system interfaced with an Agilent 5977A MS. Separation was achieved on a CP Sil-5 column with an identical diameter and film thickness as that of the GC-FID, but a length of 25 m. Helium was the carrier gas, maintaining a constant flow rate of 2 mL min<sup>-1</sup>. The MS operated at 70 eV. For both systems, the injection volume was 1  
 5 μL. The long chain alkenones were identified in full scan, scanning between *m/z* 50 and 850, and comparison with literature (de Leeuw et al., 1980; Volkman et al., 1980; Marlowe et al., 1984).

The U<sup>K'</sup><sub>37</sub> index was calculated according to Prahl and Wakeham (1987):

$$U_{37}^{K'} = \frac{[C_{37:2}]}{[C_{37:2}] + [C_{37:3}]} \quad (6)$$

The U<sup>K'</sup><sub>37</sub> values were converted to SSTs using the calibration of Müller et al. (1998):

$$10 \quad SST = \frac{U_{37}^{K'} - 0.044}{0.033} \quad (7)$$

There is also a Bayesian calibration available for the U<sup>K'</sup><sub>37</sub>, called the BAYSPLINE (Tierney and Tingley, 2018), but below ~ 24 °C temperature estimates are similar to that of the calibration of Müller et al. (1998). Since our temperatures are well below 24 °C, we have applied the calibration of Müller et al. (1998).

### 15 2.5.3 LCDs

The LCDs were silylated prior to analysis. Polar fractions were dissolved in 25 μL of pyridine and 25 μL of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and heated at 60 °C for 20 min. Prior to injection, 450 μL ethyl acetate was added. GC-MS analysis was carried out on an Agilent 7890B gas chromatograph coupled to an Agilent 5977A mass spectrometer. Samples were injected at 70 °C. The oven temperature was programmed to 130 °C by 20 °C min<sup>-1</sup>, and  
 20 subsequently to 320 °C by 4 °C min<sup>-1</sup>; this final temperature was held for 25 min. The GC was equipped with an on-column injector and fused silica column (25 m x 0.32 mm) coated with CP Sil-5 (film thickness 0.12 μm). The carrier gas was **Helium helium** at a constant flow of 2 mL min<sup>-1</sup>. The mass spectrometer operated with an ionization energy of 70 eV. The injection volume was 1 μL. Identification of the LCDs was achieved in full scan, scanning between *m/z* 50 to 850, and on basis of their characteristic fragmentation (Versteegh et al., 1997). Quantification of the LCDs and proxy computation was done by analysis  
 25 in SIM mode of the characteristic fragments (*m/z* 299, 313, 327 and 341; Rampen et al., 2012; *m/z* 187 for C<sub>22</sub> 7,16-diol internal standard). We applied the following correction factors for the relative contribution of the selected fragment ions during SIM to the total ion counts: 16% for all saturated diols, 9% for all unsaturated diols and 25% for the C<sub>22</sub> 7,16-diol internal standard. Past SST was reconstructed by means of the LDI index (Rampen et al., 2012):

$$LDI = \frac{[C_{30} \text{ 1,15-diol}]}{[C_{28} \text{ 1,13-diol}] + [C_{30} \text{ 1,13-diol}] + [C_{30} \text{ 1,15-diol}]} \quad (8)$$

30 Subsequently, LDI values were converted to SST values via the following equation:

$$SST = \frac{LDI - 0.095}{0.033} \quad (9)$$

Three samples were discarded for the calculation of the LDI due to partial co-elution of the C<sub>28</sub> 1,13-diol with another unknown compound.

For the reconstruction of past upwelling conditions, the Diol Index as proposed by Willmott et al. (2010) was applied:

$$\text{Diol Index} = \frac{[C_{28} \text{ 1,14-diol}] + [C_{30} \text{ 1,14-diol}]}{[C_{28} \text{ 1,14-diol}] + [C_{30} \text{ 1,14-diol}] + [C_{28} \text{ 1,13-diol}] + [C_{30} \text{ 1,13-diol}]} \quad (10)$$

5 ~~We chose to apply the index of Willmott et al. (2010) as it~~ The Diol Index according to Rampen et al. (2008) was shown to be also affected by variations in SST due to the inclusion of the C<sub>30</sub> 1,15-diol in the ratio (Rampen et al., 2014b; Zhu et al., 2018), and since on a glacial-interglacial timescales ~~s~~ we expect substantial SST differences, we consider the Willmott et al. (2010) ratio more appropriate.

10 Possible fluvial input of LCDs was assessed by the fractional abundance of the C<sub>32</sub> 1,15-diol which is potentially ~~riverine derived~~ derived from rivers (de Bar et al., 2016; Lattaud et al., 2017a; 2017b):

$$F_{C_{32} \text{ 1,15-diol}} = \frac{[C_{32} \text{ 1,15-diol}]}{[C_{28} \text{ 1,13-diol}] + [C_{30} \text{ 1,13-diol}] + [C_{30} \text{ 1,15-diol}] + [C_{32} \text{ 1,15-diol}]} \quad (11)$$

The NDI index, a proposed proxy for PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup> concentrations, was calculated following Gal et al. (2018):

$$\text{NDI} = \frac{[C_{28} \text{ 1,14-diol}] + [C_{28:1} \text{ 1,14-diol}]}{[C_{28} \text{ 1,14-diol}] + [C_{28:1} \text{ 1,14-diol}] + [C_{30} \text{ 1,14-diol}] + [C_{30:1} \text{ 1,14-diol}] + [C_{28} \text{ 1,13-diol}] + [C_{30} \text{ 1,13-diol}] + [C_{30} \text{ 1,15-diol}]} \quad (12)$$

The NDI was then translated to [PO<sub>4</sub><sup>3-</sup>] and [NO<sub>3</sub><sup>-</sup>] concentrations by using the following equations (Gal et al., 2018):

$$15 \quad [\text{PO}_4^{3-}] = \frac{\text{NDI} - 0.015}{0.413} \quad (13)$$

$$[\text{NO}_3^-] = \frac{\text{NDI} - 0.075}{0.026} \quad (14)$$

20 Finally, loliolide, an indicator of diatom abundance (Klok et al., 1984; Repeta, 1989), and dinosterol, a biomarker for dinoflagellates (Boon et al., 1979; Volkman et al., 1998), were identified by GC-MS analysis (simultaneously with the LCDs) of the silylated polar fraction and quantified using the C<sub>22</sub> 7,16-diol standard in full scan, correcting for the molecular weights of the compounds.

### 3 Results

#### 3.1 Bulk parameters and sedimentation rates

25 The ~~average~~ TOC content varies between 0.4 and 2.6%. The TOC content is significantly higher during the interglacial periods (MIS 1, 3 and 5) compared to glacial periods (MIS 2, 4 and 6; two-tailed  $p < 0.001$ ): the average TOC concentration is 1.4% for the interglacial periods and 0.7% for the glacial intervals (Fig. 3d), although TOC levels for MIS 3 are quite similar to those of MIS 1 and 2. Similarly, the average TN levels are 0.2% and 0.1% during the interglacial and glacial intervals, respectively (Fig. 3d). During Termination 2, both the TOC and TN contents increase rapidly (within ~~1-2~~ kyrs) towards interglacial values, and the highest TOC and TN values are observed around 78 ka (2.6 and 0.3%, respectively). The atomic

C/N ratio (Fig. 3b) varies from 4.3 to 10.5 and is on average higher during the interglacial periods (7.2) as compared to glacial times (6.2). ~~The organic matter  $\delta^{13}\text{C}$  record ( $\delta^{13}\text{C}_{\text{OM}}$ ) also reveals a glacial-interglacial variation (Fig. 3c), corresponding to slightly, but significantly (at the 5% significance level, two tailed  $p < 0.001$ ),  $^{13}\text{C}$ -enriched values during interglacial times ( $\delta^{13}\text{C}_{\text{average}} = -21.2\text{‰}$ ) as compared to the glacials ( $\delta^{13}\text{C}_{\text{average}} = -21.8\text{‰}$ ). However, the average difference in  $\delta^{13}\text{C}$  between glacial and interglacial values over the entire record is relatively small (ca. 0.6‰). The organic matter  $\delta^{13}\text{C}$  record ( $\delta^{13}\text{C}_{\text{OM}}$ ) also reveals a glacial-interglacial variation (Fig. 3c), corresponding to slightly  $^{13}\text{C}$ -enriched values during interglacial times ( $\delta^{13}\text{C}_{\text{average}} = -21.2\text{‰}$ ) as compared to the glacials ( $\delta^{13}\text{C}_{\text{average}} = -21.8\text{‰}$ ). Although small, these changes are statistically significant (5% significance level, two-tailed  $p < 0.001$ ).~~

Using the age model modified from Heusser et al. (2006), we estimated sedimentation rates that varied between ca. 0.2 and 1.7  $\text{mm yr}^{-1}$  (Fig. 3a). Sedimentation rates were highest in MIS 4, during which the sedimentation rate reaches values of around 2  $\text{mm yr}^{-1}$ . Sedimentation rates were lowest during the warmest periods (MIS 1 and 5e; ca. 0.3-0.4  $\text{mm yr}^{-1}$ ). The  $\text{MAR}_{\text{TOC}}$  varied between ca. 2 and 32  $\text{g m}^{-2} \text{yr}^{-1}$  and shows a relatively similar pattern as the sedimentation rate, implying that the sedimentation rate strongly controls the AR of TOC (Fig. 3a). Around ca. 100 ka there is a pronounced maximum in the TOC AR, reaching ca. 32  $\text{g m}^{-2} \text{yr}^{-1}$ .

### 3.2 Lipid biomarker concentrations and ARs

In all sediments, long chain alkenones, GDGTs and LCDs were present above the quantification limit. The total concentration of crenarchaeol, ~~produced by a specific biomarker for~~ marine Thaumarchaeota (Schouten et al., 2002; 2003), varies between ca. 2 and 16  $\mu\text{g g}^{-1}$ , with highest values during MIS 5, after MIS 5e (Eemian Interglacial; Fig. 4f4a). Accumulation rates (ARs) range from 1 to ~~6-25~~  $\text{mg m}^{-2} \text{yr}^{-1}$  (Fig. 4f4a).

The summed concentration of the di- and tri-unsaturated  $\text{C}_{37}$  alkenones, a productivity proxy for alkenone-producing haptophytes (e.g., Prahl et al., 1988; Prahl and Muehlhausen, 1989; Rostek et al., 1997; Villanueva et al., 1997), varies between ca. 0.5 and 10  $\mu\text{g g}^{-1}$ . Highest concentrations are observed for MIS 5e (126–116 ka; Fig. 4g4b). Around the boundary of MIS 4 and 5, concentrations decrease from ca. 6 to 2  $\mu\text{g/g}$  sediment, ~~however the alkenone AR does not show this decrease.~~ During the Late Holocene,  $\text{C}_{37}$  alkenone concentrations increase again. The alkenone AR record resembles that of the  $\text{MAR}_{\text{TOC}}$  with a peak around 100 ka of ca. 10  $\text{mg m}^{-2} \text{yr}^{-1}$  (Fig. 4j4b).

~~The main LCDs detected throughout the core are the  $\text{C}_{28}$  and  $\text{C}_{30}$  1,13-,  $\text{C}_{28}$ ,  $\text{C}_{30}$  and  $\text{C}_{30,1}$  1,14- and the  $\text{C}_{30}$  and  $\text{C}_{32}$  1,15 diols. We did not detect the  $\text{C}_{32}$  1,14 diol (characteristic for *Apedinella radians*), but we did identify the  $\text{C}_{30,1}$  1,14 diol and  $\text{C}_{29}$  12-OH fatty acid, which are typical biomarkers for *Proboscidea* diatoms (Sinninghe-Damsté et al., 2003), implying that *Proboscidea* diatoms are most likely the source of the 1,14 diols detected in the sediments. The profile of the summed concentration of 1,14 diols shows four distinct sharp peaks during the MIS 5 (Fig. 4j), reaching concentrations up to 1.4  $\mu\text{g g}^{-1}$ . The 1,14 diol AR shows one distinct peak at 94 ka of ca. 2  $\text{mg m}^{-2} \text{yr}^{-1}$ , whereas throughout the rest of the record the AR varies between 0 and 0.8  $\text{mg m}^{-2} \text{yr}^{-1}$ . Figure 4h shows the ARs of the summed 1,13- and 1,15 diols. The AR of the 1,13 diols ranges between~~

ca. 0.1 and 1.2 mg m<sup>-2</sup> yr<sup>-1</sup> throughout MIS 6 and 5, and peaks (ca. 1.5 mg m<sup>-2</sup> yr<sup>-1</sup>) at the end of MIS 5 revealing highest ARs during MIS 4, followed by a subsequent gradual decrease towards Holocene values of around 0.2 mg m<sup>-2</sup> yr<sup>-1</sup>. The AR record of the 1,15-diols is highly similar to that of the 1,13-diols for MIS 1 to 4, as well as for MIS 6, but shows higher values during the second half of MIS 5 with maxima around 94 and 104 of between ca. 1 and 1.5 mg m<sup>-2</sup> yr<sup>-1</sup>. Additionally, we quantified dinosterol, a biomarker for dinoflagellates (Boon et al., 1979; Volkman et al., 1998), as well as loliolide, an indicator of diatom abundance (Klok et al., 1984; Repeta, 1989). Dinosterol shows highest abundance during the Last Interglacial (MIS 5), peaking just after the Eemian Interglacial (between ca. 116 and 110 ka; Fig. 4e4c) with concentrations of ca. 4 µg g<sup>-1</sup>. This peak is followed by a gradual decrease towards the LGM with values near 1 µg g<sup>-1</sup> sediment. The AR record of dinosterol highly resembles the concentration record but peaks somewhat later, i.e., between ca. 105 and 98 ka. The loliolide concentration shows one maximum during the Late Holocene of ca. 2.3 µg g<sup>-1</sup> sediment (Fig. 4d). Its AR varies between ca. 0 and 1 mg m<sup>-2</sup> yr<sup>-1</sup>, throughout the record, with one pronounced peak around 100 ka of around 2 mg m<sup>-2</sup> yr<sup>-1</sup>.

The main LCDs detected throughout the core are the C<sub>28</sub> and C<sub>30</sub> 1,13-, C<sub>28</sub>, C<sub>30</sub> and C<sub>30:1</sub> 1,14- and the C<sub>30</sub> and C<sub>32</sub> 1,15-diols. We did not detect the C<sub>32</sub> 1,14-diol (characteristic for *Apedinella radians*), but we did identify the C<sub>30:1</sub> 1,14 diol and C<sub>29</sub> 12-OH fatty acid, which are typical biomarkers for *Proboscia* diatoms (Sinninghe Damsté et al., 2003), implying that *Proboscia* diatoms are most likely the source of the 1,14-diols detected in the sediments. The profile of the summed concentration of 1,14-diols shows four distinct sharp peaks during the MIS 5 (Fig 4j-f), reaching concentrations up to 1.42 µg g<sup>-1</sup>. The 1,14-diol AR shows one distinct peak at 94 ka of ca. 2.1.7 mg m<sup>-2</sup> yr<sup>-1</sup>, whereas throughout the rest of the record the AR varies between 0 and 0.86 mg m<sup>-2</sup> yr<sup>-1</sup>. Figure 4h shows the ARs of the summed 1,13- and 1,15-diols. The AR of the 1,13-diols ranges between ca. 0.1 and 1.2.0.8 mg m<sup>-2</sup> yr<sup>-1</sup> throughout MIS 6 and 5, and peaks (ca. 1.5.2 mg m<sup>-2</sup> yr<sup>-1</sup>) at the end of MIS 5 revealing highest ARs during MIS 4, followed by a subsequent gradual decrease towards Holocene values of around 0.2 mg m<sup>-2</sup> yr<sup>-1</sup>. The AR record of the 1,15-diols is highly similar to that of the 1,13-diols for MIS 1 to 4, as well as for MIS 6, but shows higher values during the second half of MIS 5 with maxima around 94 and 104 of between ca. 1 and 1.5.3 mg m<sup>-2</sup> yr<sup>-1</sup>.

### 3.3 Foraminiferal stable isotopic composition

We generated a δ<sup>18</sup>O record of *G. bulloides* for MIS 5, from ca. 70 to 142 ka, as well as for a short interval within MIS 3, from ca. 36 to 41 ka, plotted in Fig. 5b. The δ<sup>18</sup>O of *G. bulloides* varied between ca. 0.3 and 4.2‰ and are most depleted during the Eemian Interglacial around 123 ka (δ<sup>18</sup>O = 0.3‰), and enriched values are observed for MIS 6 and 3.

### 3.4 Organic proxy records

The Diol Index record shows several maxima, of which the most evident one is during MIS 5 (Fig. 4a4g). During MIS 5e, the Diol Index reveals two peaks around 126 and 116 ka (up to 0.7), followed by a sharp drop and a subsequent increase around 110 ka, reaching a maximum value at ~ 86 ka (up to 0.8). After 86 ka, the index gradually decreases. During MIS 2–4 the Diol Index varies between ca. 0.1 and 0.5. During MIS 1, the Diol Index shows a gradual increase from ca. 0.15 to 0.35.

We did not detect the mono-unsaturated C<sub>28</sub> 1,14-diol (C<sub>28:1</sub> 1,14-diol), and therefore this diol could not be included in the calculation of the NDI index. In ~64% of the surface sediments of the datasets of Rampen et al. (2014b) and de Bar et al. (2016) on which the NDI calibration of Gal et al. (2018) is based, the C<sub>28:1</sub> 1,14 was also not detected. The NDI record reveals similar variations as the Diol Index, although more pronounced. During MIS 6 the NDI is close to zero, followed by a small peak at the end of the Eemian Interglacial (NDI = 0.4), coincident with the peak in the Diol Index at 116 ka. NDI-derived [NO<sub>3</sub><sup>-</sup>] and [PO<sub>4</sub><sup>3-</sup>] concentrations around 116 ka are 11 and 0.8 μmol L<sup>-1</sup>, respectively (Fig. 4b4h). Similar to the Diol index, the ratio then decreases after which the NDI shows a broad peak (~ 100–80 ka) with a maximum at 88 ka (NDI = 0.6), which gives concentrations of 20 and 1.4 μmol L<sup>-1</sup> when translated to [NO<sub>3</sub><sup>-</sup>] and [PO<sub>4</sub><sup>3-</sup>], respectively (Fig. 4b4h). Between 80 and 0 ka (i.e., MIS 4–1), the NDI index does not reveal any distinct maxima, and the ratio varies between ca. 0 and 0.2.

Overall the organic SST proxy records broadly follow the same trend, clearly revealing glacial-interglacial temperature variability (Fig. 5b). Indeed, when we cross-correlate the three proxies, all combinations display significant positive correlations ( $p < 0.001$ ; Fig. 6) albeit with some scatter.

Additionally, the SST trends show good correspondence with the planktonic δ<sup>18</sup>O record of *G. bulloides* (Fig. 5c), as well as with the benthic oxygen isotope record for ODP Site 1234 (Heusser et al., 2006; Fig 5a), and the global stack of benthic δ<sup>18</sup>O values (e.g., Lisiecki and Raymo, 2005; Fig. 5d). Termination 2 (around 130 ka) is clearly expressed in all three organic proxy SST records, showing a rise in temperature of approximately 4 °C within ca. 1–2 kyr. During MIS 5e, SSTs were between ca. 16 and 18 °C, based on the three temperature proxies. Then, during MIS 5, the interglacial substages representing alternating cold and warm periods are clearly reflected in all three proxy records. The three records show temperature drops between ca. 6–4 and 7–6 °C during MIS 5a (ca. 70 ka). During MIS 4, 3 and 2, all SST records show a gradual decrease towards the LGM, during which U<sup>K</sup><sub>37</sub> and TEX<sup>H</sup><sub>86</sub> reveal temperatures between 9 to 10 °C, and the LDI between 7 and 8 °C. Around 25 ka, U<sup>K</sup><sub>37</sub> and TEX<sup>H</sup><sub>86</sub> temperatures show a similar steady rise to Holocene temperatures of around 16 and 18 °C. The LDI reveals an approximate 7 °C warming over Termination 1, starting slightly later at around 22 ka. During the last ~20 kyr, LDI-derived SSTs are ~3–4 °C lower as compared to the U<sup>K</sup><sub>37</sub> and TEX<sup>H</sup><sub>86</sub>-derived SSTs.

## 4 Discussion

### 4.1 Productivity

The average bulk organic carbon δ<sup>13</sup>C over the last 150 kyr is -21.4 (±0.6; s.dev.)‰, and the atomic C/N ratio displays an average value of 6.8 (±1.3), both implying a dominant marine organic carbon source (Bordovskiy, 1965; Emerson and Hedges, 1988; Meyers, 1997). Today, the amount of sedimentary organic carbon is a good indicator of export production along the Chilean margin (Hebbeln et al., 2000). Hence, higher TOC levels during the interglacial intervals in the ODP 1234 record may suggest enhanced marine productivity during these intervals for this site. However, enhanced interglacial productivity is in contrast with previous studies that state that coastal productivity on the Peru Margin was highest during the LGM and diminished during the Holocene (e.g., Thomas et al., 1994; Marchant et al., 1999; Thomas, 1999; Hebbeln et al., 2000, 2002;

Lamy et al., 2002, 2004; Romero & Hebbeln, 2003; Mohtadi & Hebbeln, 2004). These studies suggest that during the LGM the ACC migrated northward, supplying nutrients (particularly nitrate and phosphate; Levitus et al., 1994), together with a northward shift of the Southern Westerly belt as main precipitation source onshore, resulting in enhanced micronutrient supply via continental runoff. This combined effect would have stimulated productivity along the Chilean coast during the LGM.

5 Upon deglaciation the climate zones propagated southward resulting in a lowering of productivity, as indicated by pollen, sedimentological and continental studies (e.g., Heusser, 1990; Lamy et al., 1998, 1999, 2001, 2004; Brathauer & Abelmann, 1999; Haberle & Bennett, 2004; Stuetz & Lamy, 2004; Kaiser et al., 2005; Heusser et al., 2006). These studies which suggested a 5° to 6° northward movement of the Southern Westerly belt during the LGM.

In contrast to the hypothesis of stimulated productivity during the LGM, and lower productivity during the Holocene, two

10 studies ~~for core sites at the same latitude as our core (35–36°S)~~ suggested low paleoproductivity during the LGM for core sites at the same latitude as that of our core (35–36°S) (Romero et al., 2006; Mohtadi et al., 2008). Mohtadi et al. (2008) hypothesized that if the climate zones shifted 5 to 6° northward during the LGM, the SWW would be just above the core site (35–36°S), blowing directly onshore thereby preventing coastal upwelling. In turn, during the Early Holocene the subtropical high pressure would have become the dominant atmospheric player according to Romero et al. (2006), favouring upwelling.

15 However, Muratli et al. (2010b), who reconstructed paleoproductivity over the last ~30 kyrs for ODP 1234, suggested that the rise in TOC after the LGM is probably not the result of increased productivity, but of a lower oxygen availability due to decreased Antarctic Intermediate Water ventilation, and thus increased preservation. The authors based these suggestions on the fact that, since both neither opal concentrations and nor opal and or organic carbon TOC MARs do not increase increased simultaneously with TOC concentrations. Chase et al. (2014) support this hypothesis based on the Th normalized organic

20 carbon fluxes. Our (unnormalized) MAR<sub>TOC</sub> support these findings as well since although TOC levels show a steady rise after the LGM, we do not observe this increase in the accumulation of organic carbon, and the MAR<sub>TOC</sub> is higher during the LGM as compared to the Holocene, suggesting higher glacial productivity. In summary, our findings seem consistent with previous studies which suggested that higher TOC levels during the Holocene likely not result from increased productivity, but rather from increased preservation.

25 ~~However, d~~Interestingly, during MIS 3, 4 and 5 we observe even higher MAR<sub>TOC</sub> values, reaching a pronounced maximum around 100 ka during MIS 5, i.e., during an interglacial period. Hence, this record suggests that the general productivity over the last ~150 kyrs was highest around 100 ka. This interpretation is supported by most of the AR records of the individual lipid biomarkers ~~lipids~~ peaking around 100 ka. The C<sub>37</sub> alkenone, crenarchaeol and dinosterol ARs are all at their maximum between ca. 105 and 95 ka (Fig. ~~4g4b~~, ~~4f4a~~ and ~~4e4c~~, respectively), simultaneous with maximal MAR<sub>TOC</sub> (Fig. 4j). The AR of loliolide

30 (indicating diatom abundance) peaks at 100 ka (Fig. 4d), coincident with a maximum in total diatoms and *Chaetoceros* diatom counts (Mix et al., 2003; Fig 4c), and concurrent with the peak in MAR<sub>TOC</sub>. *Chaetoceros* diatoms are generally associated with upwelling (e.g., Abrantes, 1988; Abrantes and Moita, 1999), and also for the Peru-Chile upwelling system, the diatom genus *Chaetoceros* is thought to dominate the diatom community during upwelling conditions (e.g., Anabalón et al., 2007; Schrader and Sorknes, 1991; Romero et al., 2001; Vargas et al., 2004; Abrantes et al., 2007; González et al., 2007; Sanchez et al., 2012).



Therefore, the high abundance of *Chaetoceros* diatoms at ~100 ka suggests that there was a peak in upwelling intensity around this time, ~~possibly related to the southern position of the subtropical high pressure system and associated upwelling inducing winds.~~ This upwelling would have introduced macronutrients from deeper colder waters into the euphotic zone, stimulating several phytoplankton communities, including haptophytes, dinoflagellates and diatoms. During MIS 4 we also observe a peak in MAR<sub>TOC</sub> (Fig. 3a) but there is no corresponding peak in *Chaetoceros* abundance (Fig. 4i). However, the high MAR<sub>TOC</sub> during MIS 4 is linked to high sedimentation rates (Fig. 3c), whereas the peak in MAR<sub>TOC</sub> during MIS 5 is not, confirming that the MAR<sub>TOC</sub> maximum during MIS 5 indeed likely resulted from increased primary productivity, whereas during MIS 4 the high MAR<sub>TOC</sub> did not.

#### 10 4.2 1,14-diols as past upwelling and nutrient indicators

Interestingly, peaks in the Diol Index and 1,14-diol concentrations and accumulation rates occur before and after (around 116 and 88 ka; Fig. 4a and 4j), but not during the time interval with enhanced upwelling (*i.e.*, around 100 ka; purple band in Fig. 3b and 3e). Contreras et al. (2010) also reported high abundances of the C<sub>28</sub> 1,14-diol around 120 ka near the coast of Peru (11°S). This suggests that *Proboscia* diatoms were more abundant before and after this period of intense upwelling, and is in agreement with observations that in the present-day Chile-Peru upwelling region, *Proboscia alata* is more dominant when upwelling is less intense (Tarazona et al., 2003; Herrera and Escribano, 2006). Although the recent time scale is quite different from our long-time record, which represents an integrated signal of several hundreds to thousands of years, it suggests that over the time period 120–80 kyr, on average, upwelling became stronger, reaching a maximum at 100 ka before subsequently decreasing. Shortly before and after the period of maximum upwelling, the conditions (averaged over multiple years) were apparently optimal for *Proboscia* diatoms. As previously suggested by Rampen et al. (2014b), this indicates that the Diol index should perhaps be considered as a specific indicator for *Proboscia* productivity, rather than upwelling strength generally, as the environmental conditions determining *Proboscia* abundance likely differ from region to region.

Recently, the NDI was introduced as a quantitative paleonutrient proxy. ~~As for the~~ The Diol Index and the 1,14-diols AR and the NDI ~~is-are~~ low during the time of most intense upwelling (around 100 ka), suggesting a minimum in annual mean nitrate and phosphate concentrations, which is highly unlikely. The NDI is based on the saturated and mono-unsaturated C<sub>28</sub> 1,14-diol relative to other diols. Whereas we observe a strong correlation between the ARs of the mono-unsaturated and saturated C<sub>30</sub> 1,14-diol ( $R^2 = 0.6970$ ), the correlations between the C<sub>28</sub> 1,14 and C<sub>30</sub> 1,14-diol ( $R^2 = 0.2332$ ), and the C<sub>28</sub> 1,14 and C<sub>30:1</sub> 1,14-diol ( $R^2 = 0.4836$ ) are weak, indicating different source organisms for the C<sub>28</sub> and C<sub>30</sub> 1,14-diols, in agreement with previous studies (Rampen et al., 2014b; de Bar et al., 2016; Gal et al., 2018). In fact, ~~Rampen et al. (2009)~~ Sinninghe Damsté et al. (2003) found that 98% of the diols in *P. alata* consisted of the saturated and mono-unsaturated C<sub>28</sub> 1,14-diol, whereas *P. indica* produces similar amounts of the C<sub>30</sub> and C<sub>28</sub> 1,14-diol and *P. inermis* mainly produced the C<sub>28</sub> 1,14-diol (Rampen et al., 2007). ~~Furthermore,~~ *P. alata* is the *Proboscia* species detected along the modern coast of Chile and Peru (Tarazona et al., 2003; Herrera and Escribano, 2006), and, therefore, it is likely that *P. alata* is the predominant producer of the C<sub>28</sub> 1,14-diol

detected in the ODP 1234 sediments. Consequently, the NDI record likely reflects variations in the abundance of *P. alata* over the last 150 kyrs in the Chilean margin, whereas the Diol Index (which also includes the C<sub>30</sub> 1,14-diol) more likely reflects the abundance of multiple species of *Proboscia*.

Previous studies showed that *P. alata* preferentially blooms over other diatoms when nutrients are high but silica concentrations are low (as *P. alata* needs little Si to build its frustule) (Haake et al., 1993; Sakka et al., 1999; Koning et al., 2001; Smith, 2001). In fact, although *P. alata* is often observed in high-nutrient and/or upwelling regions (Hernández-Becerril, 1995; Lange et al., 1998; Koning et al., 2001; Smith, 2001), the conditions during/underin which the species is abundant, is often described as post-bloom, stratification, early upwelling season and/or the oceanic side of the upwelling front (e.g., Hart, 1942; Takahashi et al., 1994; Katsuki et al., 2003; Moita et al., 2003; Tarazona et al., 2003; Herrera and Escribano, 2006; Sukhanova et al., 2006; see references in Table 1 of Rampen et al., 2014b). Moreover, sediment trap studies from the Arabian Sea showed that the maximum flux of *Proboscia* lipids was at the start of the upwelling season (Prahl et al., 2000; Wakeham et al., 2002; Sinninghe Damsté et al., 2003; Rampen et al., 2007). When silicate concentrations increase (i.e., during upwelling), *P. alata* is likely outcompeted by more heavily silicified diatoms (such as *Chaetoceros*; e.g., Riegman et al., 1996). This suggests that the C<sub>28</sub> 1,14-diol likely reflects early- or post-upwelling nutrient conditions. Hence, the dip in reconstructed [PO<sub>4</sub><sup>3-</sup>] and [NO<sub>3</sub><sup>-</sup>] concentrations at ~ 100 ka is not realistic and likely due to the low abundance of *P. alata* at this time of intense upwelling. In other regions, the C<sub>28</sub> 1,14-diol might be produced by other *Proboscia* species (e.g. *P. inermis*) and the NDI might thus not reflect solely *P. alata* productivity. In summary, we suggest that the NDI at the Chilean Margin likely reflects *Proboscia* productivity, and may therefore not be suitable as paleo-nutrient tracer.

### 20 4.3 Sea surface temperature evolution

The three organic proxy-based SST records broadly follow the trend of the planktonic oxygen isotope record for MIS 5, as well as the benthic oxygen isotope record for ODP Site 1234 (Heusser et al., 2006; Fig 5), and the global stack of benthic δ<sup>18</sup>O (e.g., Lisiecki and Raymo, 2005) for the entire record, suggesting that the evolution of SST at our study location generally follows global climate patterns. The resolution of our record is not high enough to recognize possible millennial-scale SST variations related to climatic events such as the Antarctic Cold Reversal. Nevertheless, the overall SST patterns are similar to other Southern Hemisphere records (e.g., Kaiser et al., 2005; Kaiser and Lamy, 2010; Caniupán et al., 2011; Lopes dos Santos et al., 2013) and Antarctic ice-core stable isotope records (e.g., Blunier & Brook, 2001). The three temperature proxies are all significantly positively correlated and present a coherent view of regional climate variability (Fig. 6).

In principle, we would expect similar reconstructed temperatures from the LDI and U<sup>K'</sup><sub>37</sub> indices, since both proxies are based on biomarkers produced by photosynthetic algae (Prahl and Wakeham, 1987; Rampen et al., 2012). Indeed, Kim et al. (2002) showed that for surface sediments off Chile U<sup>K'</sup><sub>37</sub>-derived temperatures strongly correlated with annual mean temperatures of the sea surface mixed layer. The linear regression for the U<sup>K'</sup><sub>37</sub> vs. the LDI is close to the 1:1 line, suggesting the LDI is reflecting SST. Interestingly, the LDI reveals a greater amplitude over the record as compared to the U<sup>K'</sup><sub>37</sub> and TEX<sup>H</sup><sub>86</sub>, with a



maximum temperature difference between the coldest (LGM) and warmest (Eemian Interglacial) temperature of ca. 10 °C, whereas this is ca. 7 and 8 °C, for the  $U^{K'_{37}}$  and  $TEX^{H_{86}}$ , respectively. Other LDI and  $U^{K'_{37}}$  applications on glacial-interglacial timescales also show somewhat greater amplitudes for the LDI compared to the  $U^{K'_{37}}$ , (Rampen et al., 2012; Lopes dos Santos et al., 2013; Rodrigo-Gámiz et al., 2014; Jonas et al., 2017). This might potentially suggest that the surface sediment calibration of the LDI requires some modification, such as a lower slope. Further analysis of surface sediments should reveal this.

For the  $TEX^{H_{86}}$ , it has been shown to potentially reflect subsurface rather than surface water temperatures (Huguet et al., 2007; Kim et al., 2010; 2015; Schouten et al., 2013; Chen et al., 2014) due to the production of isoprenoid GDGTs below the surface mixed layer. Overall, the  $TEX^{H_{86}}$  record agrees reasonably well with the  $U^{K'_{37}}$  record for ODP 1234, suggesting that it mainly reflects SST. Also, Kaiser et al. (2015) who established a regional  $TEX^{H_{86}}$  calibration suggested that this proxy mainly reflects SST. However, all cross-correlations still reveal relatively large scatter, reflecting the multiple different constraints on the respective proxies, as each one is affected by different parameters and can reflect different seasonal temperatures. Nevertheless, for the largest part of the record, the absolute temperature differences between the three temperature proxies is smaller than the maximal possible discrepancy that can be explained by the combined calibration errors (calibration errors of  $U^{K'_{37}}$ ,  $TEX^{H_{86}}$  and LDI are 1.5 °C, 2.5 °C and 2.0 °C, respectively; Müller et al., 1998; Kim et al., 2010; Rampen et al., 2012, respectively).

The only period during which the offsets are larger than calibration errors, is the last ~25 kyrs, i.e., from the LGM to the Holocene, and the relatively brief interval between 52 and 56 ka. During these timespans, the LDI-derived temperatures are ca. 3 to 6 °C lower than those derived from  $U^{K'_{37}}$ - or  $TEX^{H_{86}}$ . This offset could potentially be related to terrestrial input, however, we have assessed the relative contribution of terrestrial derived organic carbon, by means of the BIT index (Hopmans et al., 2004) and the fractional abundance of the  $C_{32}$  1,15-diol (de Bar et al., 2016; Lattaud et al., 2017a; 2017b), which were both always <0.2, implying that there was no substantial riverine input from terrigenous organic matter. Alternatively, the LDI might be compromised by high input of 1,14-diols (Rodrigo-Gámiz et al. 2015), however, we do not observe a correlation between the LDI (or the SST offset between the LDI and  $U^{K'_{37}}$  or  $TEX^{H_{86}}$ ) and the fractional abundance of the summed 1,14-diols. Potentially, the production of the 1,13- and 1,15-diols shifted to a colder season due to regional climatic change associated with the southward migration of the ACC and SWW upon the deglacial warming. Finally, we observe an early onset of the deglacial warming for the LDI compared to the  $U^{K'_{37}}$  and  $TEX^{H_{86}}$  (ca. 6 kyrs; Fig. 5b), the reasons for which are elusive.

~~Interestingly, overall, the LDI reveals greater amplitude over the record as compared to the  $U^{K'_{37}}$  and  $TEX^{H_{86}}$ , with a maximum temperature difference between the coldest (LGM) and warmest (Eemian Interglacial) temperature of ca. 10.5 °C, whereas this is ca. 7.5 and 8.0 °C, for the  $U^{K'_{37}}$  and  $TEX^{H_{86}}$ , respectively. Interestingly, other LDI and  $U^{K'_{37}}$  applications on glacial-interglacial timescales also show somewhat greater amplitudes for the LDI records as compared to the  $U^{K'_{37}}$ , (Rampen et al., 2012; Lopes dos Santos et al., 2013; Rodrigo-Gámiz et al., 2014; Jonas et al., 2017). This might potentially suggest that the surface sediment calibration of the LDI requires some modification, e.g., a lower slope. Further analysis of surface sediments should reveal this.~~

We can compare our SST records of ODP Site 1234 with those of other SST records along the coast of South America, in particular those generated by the  $U^{K'_{37}}$ , which has been used the most often (Fig. 7). Our  $U^{K'_{37}}$  temperature record agrees well with other records in the vicinity of ODP 1234, both in terms of absolute temperature as well as in glacial-interglacial temperature amplitude. Our  $U^{K'_{37}}$  SST record shows an approximate 7 °C warming over Termination 1, which is in agreement with other past SST records for the central and Southern Chilean margin (Kim et al., 2002; Lamy et al., 2002; 2004; Kaiser et al., 2005; Romero et al., 2006; Kaiser and Lamy, 2010). Although the timing of deglacial warming associated with Termination 2 is comparable to other records, the last deglaciation (Termination 1) reveals an early start (around 26 ka) at Site 1234 as compared to neighboring sites. The  $TEX^H_{86}$  record reveals this same timing, whereas the LDI suggests a timing more comparable to other records in the vicinity (around 20 ka). Regional differences in timing of deglacial warming have previously been related to the southward shift of the SWW, which directly and indirectly influences local paleoproductivity and upwelling intensity, and thereby potentially leaving site-dependent, unique signatures in the SST records (Mohtadi et al., 2008). This may partially explain the discrepancies that we observe between our  $U^{K'_{37}}$  record and the other records. For instance, site GeoB 3327-5 is located at the northern extent of the ACC, and thus largely influenced by its latitudinal movement which is closely related to the migration of the SWW (Ho et al., 2012), whereas for ODP 1234 this influence might be less. Furthermore, the combined regional records show an increase in the magnitude of  $U^{K'_{37}}$  temperature variations over glacial-interglacial timescales towards the south (Fig. 7), which agrees with the idea of greater glacial-interglacial temperature differences at high latitudes as compared to low latitudes (e.g., CLIMAP, 1976; Mohtadi & Hebbeln, 2004; Mohtadi et al., 2008).

## 5 Conclusions

We have ~~tested the applicability of applied~~ long chain diols as tracers for past SST (using the LDI index), upwelling and nutrient conditions (Diol Index), and  $[PO_4^{3-}]$  and  $[NO_3^-]$  (NDI index) at ODP 1234, located within the Peru-Chile upwelling system. The LDI agrees with the  $TEX^H_{86}$  and  $U^{K'_{37}}$  sea surface temperature records, as well as with the planktonic  $\delta^{18}O$ , suggesting that the LDI reflects past SSTs. During the Last Interglacial (MIS 5), increased accumulation of TOC and phytoplankton lipid biomarkers centered around 100 ka indicate enhanced primary productivity. Concurrently, there is a peak abundance in preserved *Chaetoceros* diatoms, suggesting a peak in upwelling intensity. The Diol index peaks before and after this peak in upwelling, agreeing with present-day diatom distributions along the Chile-Peru margin, with *Chaetoceros* diatoms being dominant during upwelling, and *Proboscia alata* thriving in more stable waters. The NDI (based primarily on the  $C_{28}$  1,14-diol) shows the same trend as the Diol Index (based on both the  $C_{28}$  and  $C_{30}$  1,14-diols), i.e., also showing a dip around 100 ka, suggesting low mean annual nitrate and phosphate concentrations during this upwelling interval, which is not realistic. Likely *P. alata* is the main  $C_{28}$  1,14-diol producer at ODP 1234 suggesting that the NDI likely reflects *P. alata* productivity at the core site, and is therefore not suitable as paleo-nutrient tracer, since the species is generally outcompeted when Si concentrations increase, i.e., during upwelling (potentially explaining the minimum in NDI around 100 ka). Overall, these data suggest that the NDI and the Diol Index should perhaps be considered potentially reflects *Proboscia alata* productivity instead

~~of nutrient concentrations, and that the Diol index should perhaps be considered as a specific indicator~~ for *Proboscia* productivity, rather than nutrient concentrations or general upwelling conditions.

**Data availability.** The data can be downloaded from PANGAEA.

5  
**Competing interests.** The authors declare that they have no conflict of interest.

**Author contribution.** Marijke W. de Bar, Jaap Sinninghe S. Damsté and Stefan Schouten designed the experiments and Dave Stolwijk carried them out. Jerry F. McManus analysed the planktonic foraminiferal stable oxygen isotopes. Marijke W. de Bar  
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## Figure captions

**Fig. 1** Maps showing the location of ODP Site 1234. **(a)** A simplified illustration of the present-day atmospheric and oceanographic setting and the site location. SEC = South Equatorial Current; APF = Antarctic Polar Front; STF = Subtropical Front. **(b)** Present-day mean annual SST ( $^{\circ}\text{C}$ ) for the region. Data derived from the World Ocean Atlas 2013; maps were drawn in Ocean Data View (Schlitzer, 2015), and modified manually.

**Fig. 2** Age-depth relations for ODP 1234 derived from Heusser et al. (2006). **(a)** Age-depth constrains based on the correlation of benthic  $\delta^{18}\text{O}$  with Atlantic core MD95204 (dark blue; upper half) and the Vostok ice core chronology (orange; lower half). Heusser et al. (2006) switched between the two different age models at  $\sim 69$  ka/ $\sim 53$  mcd (dashed line). However, we used the full upper age model and then linearly interpolated between the age models from  $\sim 60$  to 64 mcd, as indicated by the connecting green line. **(b)** Sedimentation rates calculated after linear interpolation between the age-depth tie-points of the two age models. The sedimentation rates calculated after the linear interpolation between the age models are presented in green. In transparent orange, the sedimentation rates are plotted when applying the dating strategy of Heusser et al. (2006).

**Fig. 3** Geochemical bulk records for the studied interval of ODP 1234. **(a)** sedimentation rate (blue) and  $\text{MAR}_{\text{TOC}}$  (orange), **(b)** atomic C/N ratio, **(c)** Bulk organic  $\delta^{13}\text{C}$ , **(d)** TOC (red) and TN (green) concentrations. The different color bands indicate different time periods: interglacial stages MIS 1, 3 and 5 in pink, including the MIS 5e in dark pink. The LGM is highlighted in blue. MIS ages are according to Lisiecki and Raymo (2005). The dashed lines indicate the onset ages of Terminations 1 (Pacific age of Stern and Lisiecki, 2014) and 2 (approximate age).

**Fig. 4** Biomarker proxy and accumulations records for ODP 1234. **(a)** ~~Crenarchaeol concentrations and MARs. Diol Index (blue) and biogenic opal concentrations (green; Muratli et al., 2010b) for the last  $\sim 28$  kyrs.~~ **(b)**  ~~$\text{C}_{37}$  alkenone concentrations and MARs. Phosphate (blue) and nitrate (orange) concentrations calculated after the NDI index (blue).~~ **(c)** ~~Dinosterol concentrations and MARs. Total diatom counts (purple) and *Chaetoceros* diatom counts (blue) (Mix et al., 2003). The thick smoothed lines reflects 2-point running averages of the diatom records.~~ **(d)** Loliolide concentrations and MARs. **(e)** ~~1,13- and 1,15-diol MARs. Dinosterol concentrations and MARs.~~ **(f)** ~~1,14-diol concentration and MARs. Crenarchaeol concentrations and MARs.~~ **(g)** Diol Index (blue) and biogenic opal concentrations (green; Muratli et al., 2010b) for the last  $\sim 28$  kyrs.  ~~$\text{C}_{37}$  alkenone concentrations and MARs.~~ **(h)** ~~Phosphate (blue) and nitrate (orange) concentrations calculated after the NDI index (blue).~~ ~~1,13- and 1,15-diol MARs.~~ **(i)** ~~Total diatom counts (purple) and *Chaetoceros* diatom counts (blue) (Mix et al., 2003). The thick smoothed lines reflects 2-point running averages of the diatom records. The counts are descriptive: F = few; C = common; A = abundant; VA = very abundant.~~ ~~1,14-diol concentration and MARs.~~ **(j)** Mass AR of TOC. For panels **(da)** – **(gd)** and **(if)**: concentrations are in grey and MARs are in black. The different color bands indicate different time periods: interglacial stages MIS 1, 3 and 5 in pink, including the MIS 5e, in dark pink. The LGM is highlighted in blue. The purple

band indicates the period of presumed enhanced upwelling. MIS ages are according to Lisiecki and Raymo (2005). The dashed lines indicate the onset ages of Terminations 1 (Pacific age of Stern and Lisiecki, 2014) and 2 (approximate age).

**Fig. 5** Foraminiferal oxygen isotope and organic temperature proxy records for ODP 1234. **(a)** The benthic stable oxygen isotope records for ODP Site 1234 of Heusser et al. (2006), where the blue data reflect the benthic  $\delta^{18}\text{O}$  dated by correlation to Atlantic core MD95204, and the orange data represent the  $\delta^{18}\text{O}$  data correlated to the Vostok ice core chronology. **(b)** The organic geochemical seawater surface temperature records:  $U^{K'_{37}}$  (green),  $\text{TEX}^{\text{H}_{86}}$  (red) and LDI (blue). The thick lines reflect 3-point running averages. **(c)** Planktonic foraminiferal  $\delta^{18}\text{O}$  of the species *Globigerina bulloides* with the 3-point running average. **(d)** Global compilation of benthic stable oxygen isotopes (Lisiecki and Raymo, 2005). The pink colored bands reflect the interglacial periods (MIS 1, 3 and 5). The pink lines within MIS 5 reflect the different substage  $\delta^{18}\text{O}$  minima and maxima. MIS (substage) ages are according to Lisiecki and Raymo (2005). The blue band reflects the Last Glacial Maximum, and the star symbol represents the present-day SST (World Ocean Atlas 2013 version 2). The dashed lines indicate the onset ages of Terminations 1 (Pacific age of Stern and Lisiecki, 2014) and 2 (approximate age).

**Fig. 6** Cross-correlations of sea surface temperature estimates based on the  $\text{TEX}^{\text{H}_{86}}$ ,  $U^{K'_{37}}$  and LDI indices. Linear regressions are indicated by the black solid lines, together with the 95% confidence intervals. All correlations are significant ( $p < 0.001$ ). The orange dashed line represents the 1:1 line.

**Fig. 7** **(a)** Pacific  $U^{K'_{37}}$  SST reconstructions off South America for the last ~160 kyrs (3-point running averages). **(b)** Sea surface temperature ( $^{\circ}\text{C}$ ) map for the region. The colors of the records correspond to the colors of the site symbols in the map. Alkenone-based SST data is from Caniupán et al. (2011) (MD07-3128; 53 $^{\circ}\text{S}$ ), Ho et al. (2012) (GeoB 3327-5; 43 $^{\circ}\text{S}$ ), Kaiser et al. (2005) (ODP1233; 41 $^{\circ}\text{S}$ ), this study (ODP 1234; 36 $^{\circ}\text{S}$ ), Kim et al., 2002 (GeoB 3302-1 and GIK 17748-2; 33 $^{\circ}\text{S}$ ), Bin Shaari (2013) (ODP 1237; 16 $^{\circ}\text{S}$ ), Bin Shaari et al. (2013) (ODP 1239; 1 $^{\circ}\text{S}$ ) and Bin Shaari et al. (2014) (ODP 1241; 6 $^{\circ}\text{N}$ ). Surface temperature data derived from the World Ocean Atlas 2013; map is drawn in Ocean Data View (Schlitzer, 2015), and modified manually.

Figure 1

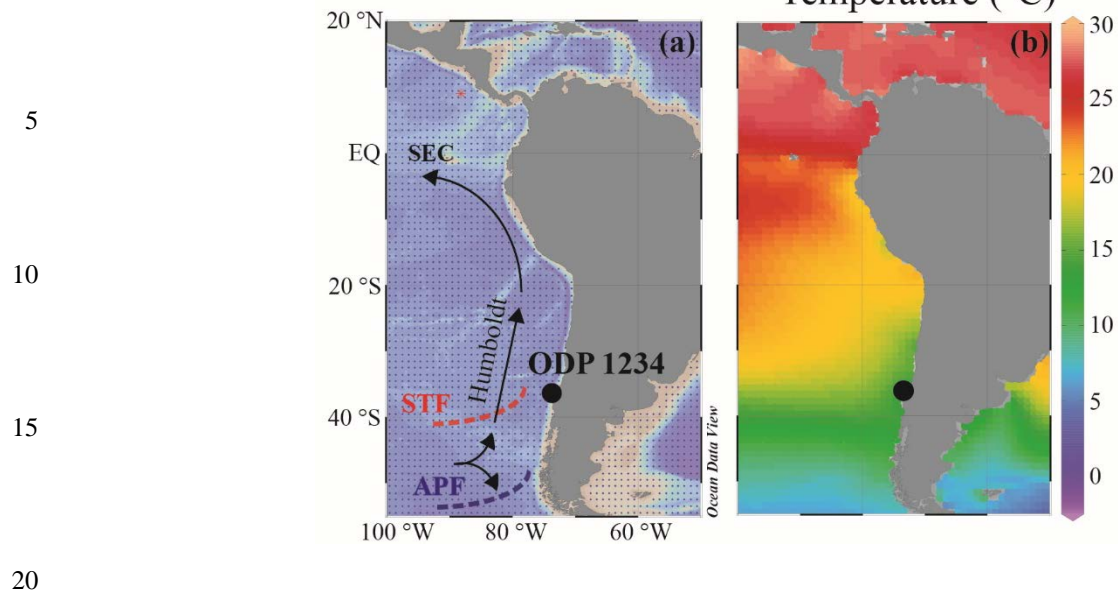


Figure 2

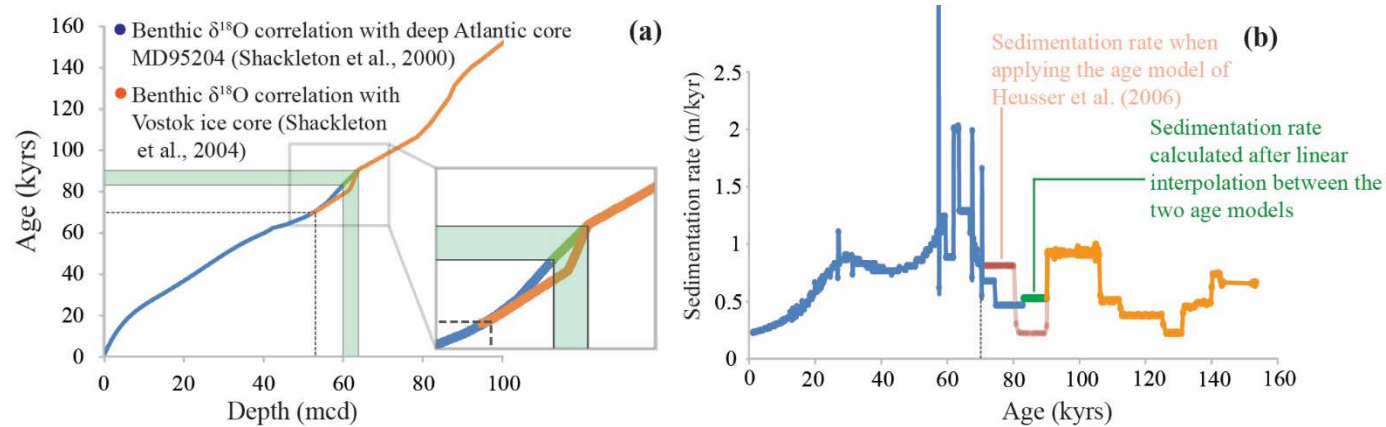




Figure 3

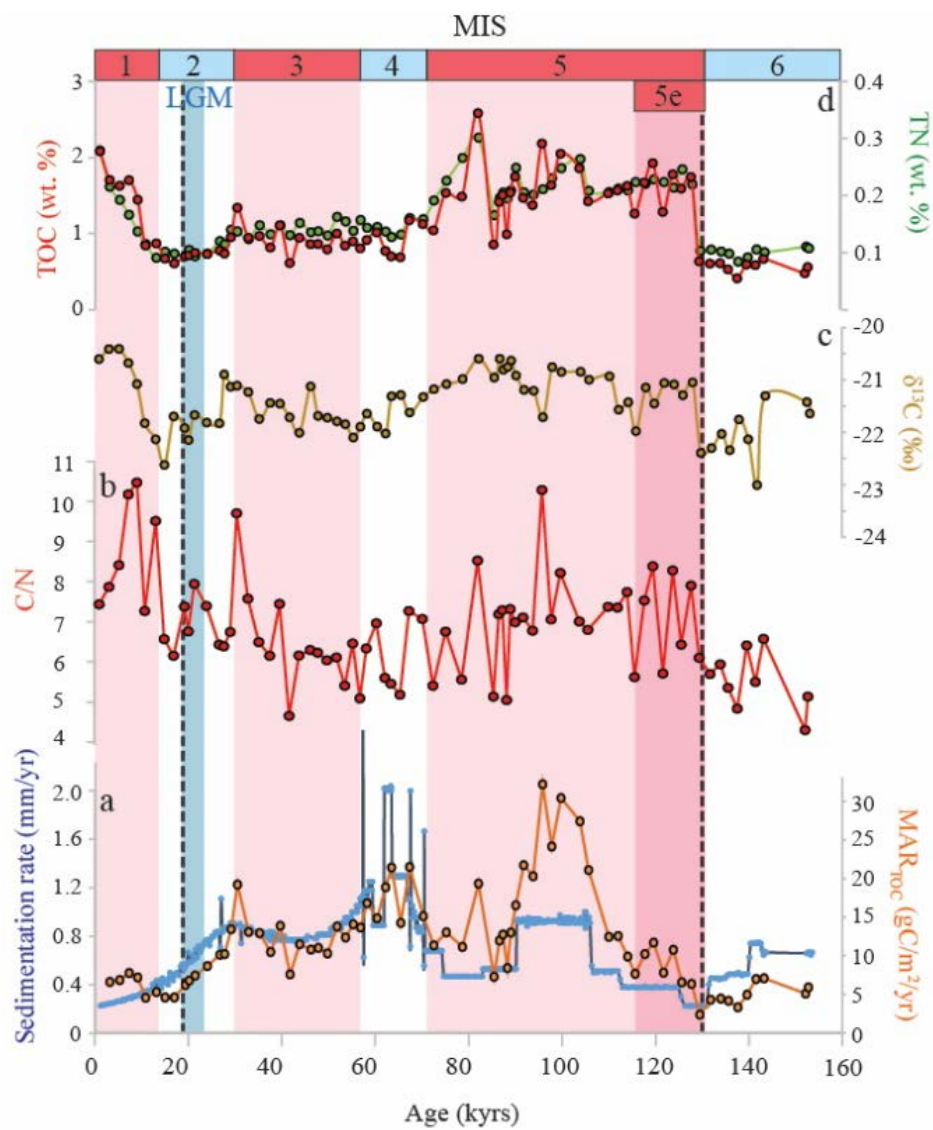


Figure 4

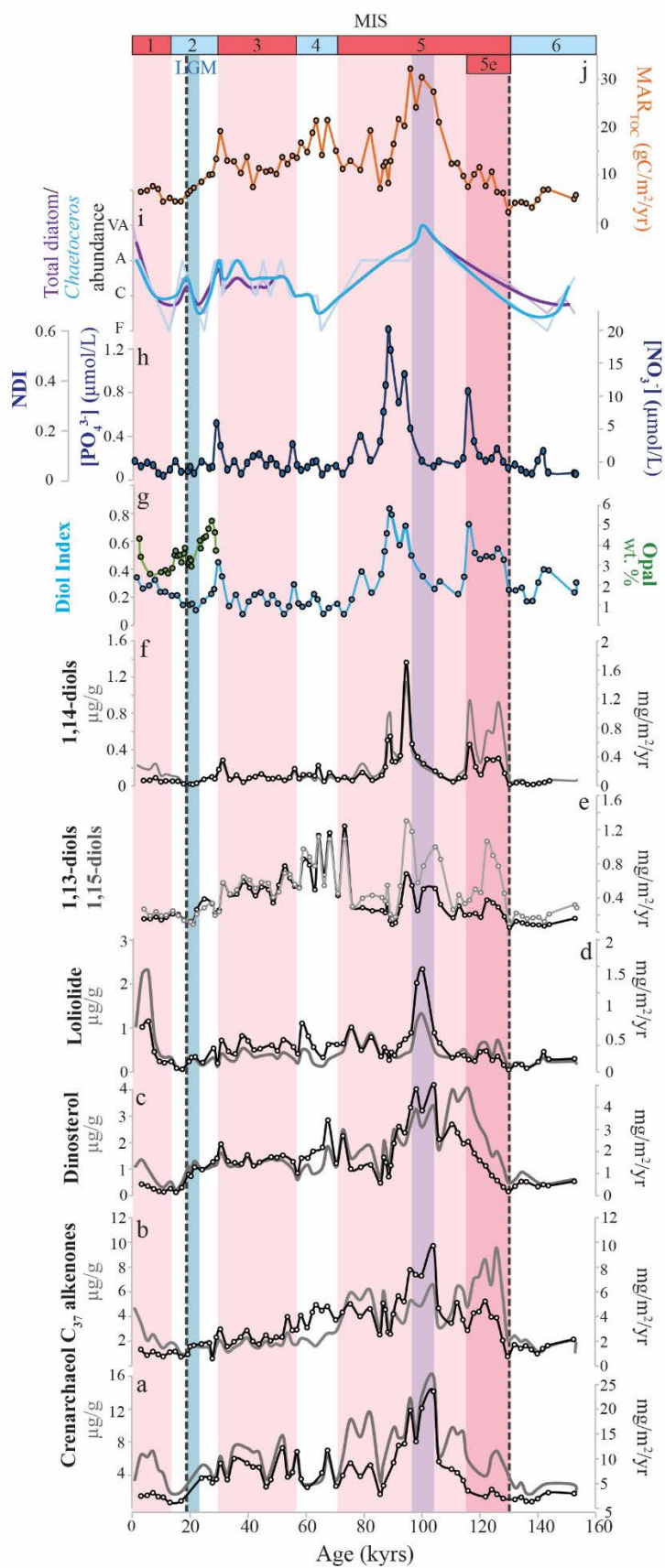
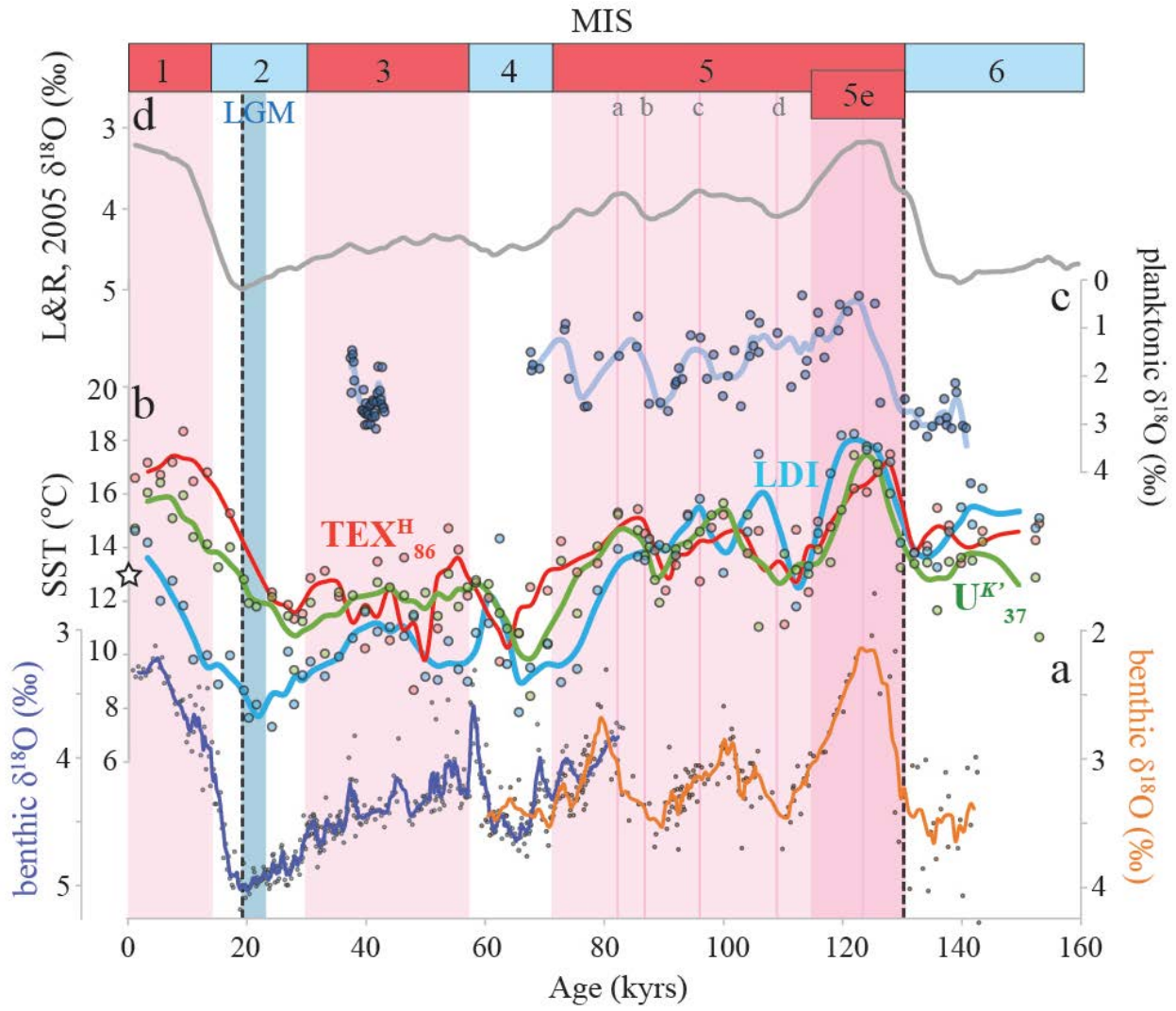


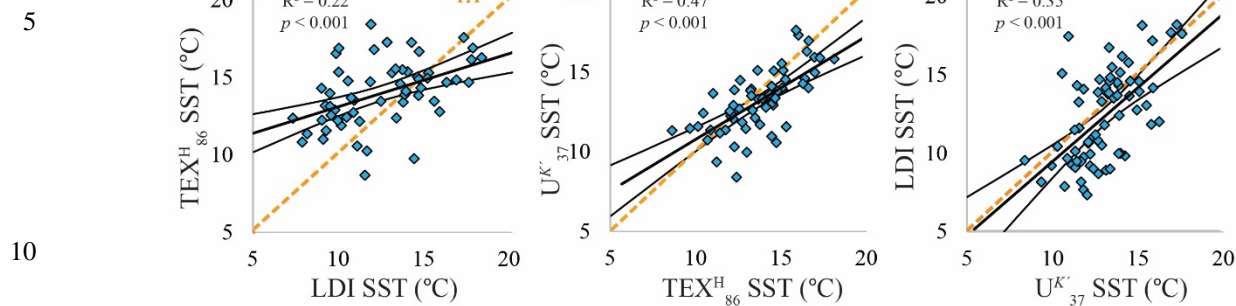
Figure 5



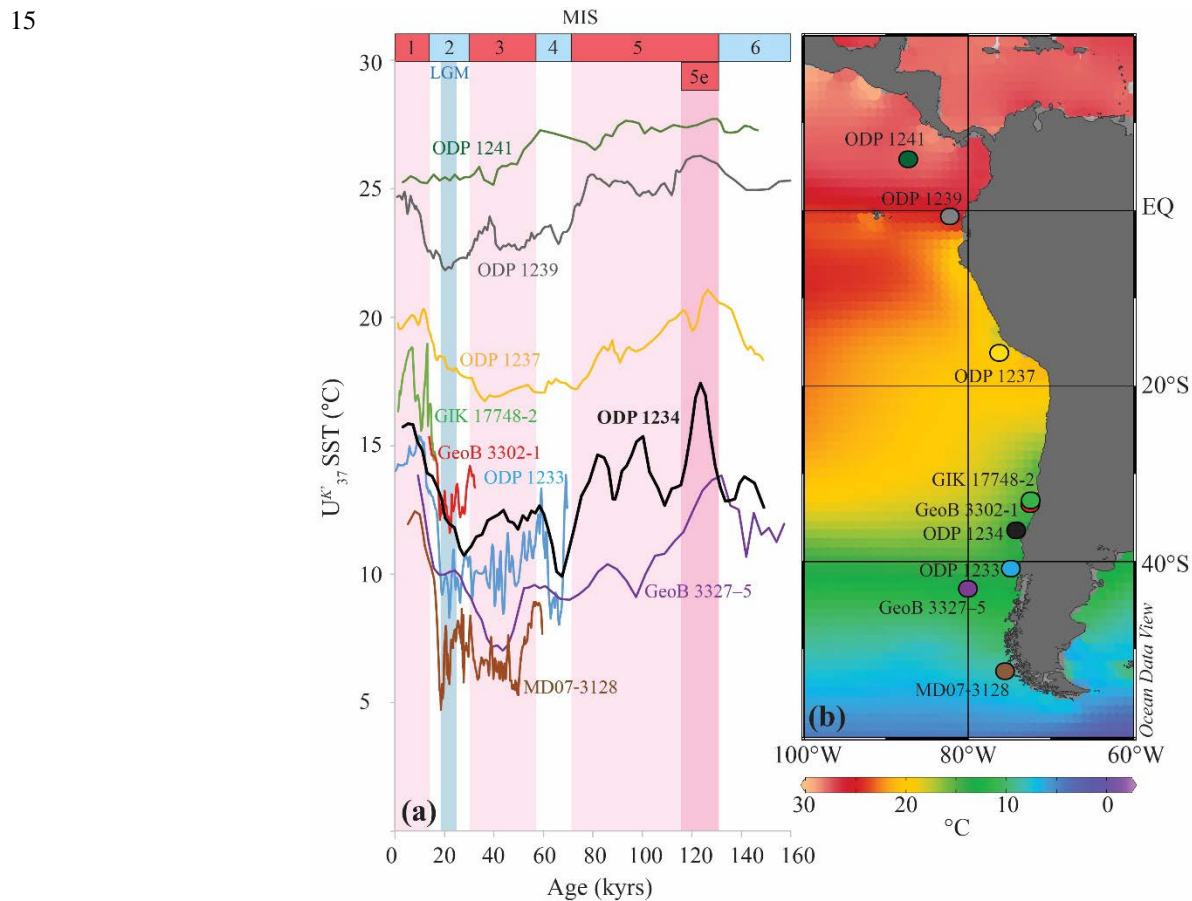
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**Figure 6**



**Figure 7**



## Appendix A

**Figure A1.** TEX<sub>86</sub> records for ODP 1234 applying different calibrations, i.e., the global core-top calibration of Kim et al. (2010) in red (TEX<sup>H</sup><sub>86</sub>), the local core-top calibration of Kaiser et al. (2015) in purple and the Bayesian model of Tierney and Tingley (2014; 2015) in green applying the BAYSPAR tool (<http://bayspar.geo.arizona.edu/>). For the BAYSPAR calculation we have assumed a prior mean 13 °C and a search tolerance of 0.2 TEX<sub>86</sub> units. The calculated values are based on TEX<sub>86</sub> values from 62 20° by 20° latitude-longitude grid boxes.

