

Glacial-interglacial sea water isotope change near the Chilean Margin as reflected by $\delta^2\text{H}$ of C₃₇ alkenones.

Katrin Hättig¹, Devika Varma¹, Stefan Schouten^{1,2}, Marcel T. J. van der Meer¹

¹ Department of Marine Microbiology and Biogeochemistry, NIOZ Royal Netherlands Institute for Sea Research, Texel, the Netherlands.

² Department of Earth Sciences, Faculty of Geosciences, Utrecht University, Utrecht, the Netherlands.

Correspondence to: Katrin Hättig (katrin.haettig@nioz.nl)

Authors response: *We thank both reviewers for their constructive comments on the manuscript, which will help to improve it. Please find a detailed reply to all comments below.*

Reviewer 2:

General Comments

RC2: Hättig et al. present an interesting new collection of paired surface ocean $\delta^2\text{H}_{\text{C}37}$ and benthic $\delta^{18}\text{O}_{\text{FORAM}}$ records from the Chilean Margin for reconstructing changes in ocean isotopic composition ultimately speaking to water mass and/or salinity variability from the LGM.

The data show good agreement with a previously published record from the same locality, and the treatment of sample and data analyses are consistent with those accepted in the literature. The authors' new approach/application of hydrogen isotopic composition of alkenones for reconstructing the hydrogen isotopic composition of surface water (and then ultimately of salinity) is unique and interesting and certainly warrants publication. I believe this body of work is suited to Climate of the Past, following careful revision.

My overall recommendation to the authors would be to carefully consider reviewing the paper for clarity and detail. There are many instances of grammatical errors/sentences that are difficult to follow. In particular, the discussion and even more so the conclusion is not as well organized as it could be. The conclusion should be a thoughtful overview of the major findings of the work and as it is written it is relatively difficult to follow. I strongly encourage the authors to review the organization of this section and to also improve on the overall portrayal of the major conclusions from this work.

- **Authors:** *We thank the reviewer for the positive response. We will carefully go through the text, especially the conclusions, and improve the structure and language.*

Next, if the authors could be clearer and more explicit about the errors that they are reporting throughout, it would be a more powerful reflection of the data. There are of course assumptions that must be made throughout; however, I also wonder if the authors would consider reporting the error in the transfer functions used (i.e., Equations 1 through 8).

- **Authors:** *We agree with the reviewer that clear reporting of data and errors is important. We, therefore, display the dataset of the modern open-ocean seawater isotopes and salinity in figure S2 and S3 of the supplemental information. The root-mean-square errors (RMSE) for the transfer functions (1, 7, 8) give an indication of the possible error range for the reconstructed δ^2H_{sw} from δ^2H_{C37} and δ^2H_{sw} vs $\delta^{18}O_{sw}$ values in ‰VSMOW. We refer to our reply to reviewer's 1 comment where we specify the propagated error, which is ca. 9‰ for the absolute δ^2H_{sw} values and ca. 6‰ for $\Delta\delta^2H_{sw}$.*

RC2: Because much of the discussion and conclusions deal with the offset found between surface and benthic estimations/reconstructions of δ^2H_{sw} , and because the reconstruction specifically of benthic δ^2H_{sw} relies on temperature, which the authors do not model, I wonder if the authors considered running (and then reporting on) an experiment where they vary the bottom temperature estimates for the benthic reconstruction of δ^2H_{sw} to determine a conceivable (appropriate) range (and to demonstrate the sensitivity) of this particular offset (Lines 195-208). It is difficult to follow that the authors assume temperature is consistent at depth when they report a major shift in isotopic/salinity signatures between surface and benthic environments. Whether this can be resolved here or not, I do believe the authors should spend some time in their discussion on this discrepancy. Are there no planktonic foraminifera $\delta^{18}O$ data to use for reconstructing surface salinity?

- **Authors:** *We thank the reviewer for this comment which is identical to a comment made by reviewer 1. We, therefore, refer to our reply to reviewer's 1 comment where we perform a sensitivity analysis which shows that even with unrealistically small bottom water temperature changes, the change in δ^2H_{sw} of bottom waters would still be lower than that of surface waters.*

RC2: Finally, I wonder why the authors did not test the δ^2H_{C37} – salinity calibration models for reconstructing salinity at this site (at the very least plotting their new δ^2H_{C37} data alongside previously published data). The authors mention this calibration in the literature; however, the paper overall might be made more powerful and rigorous by including this evaluation.

- **Authors:** *The δ^2H_{C37} – salinity calibrations based on culture studies (e.g., Schouten et al., 2006), core-top studies (Weiss et al., 2019) and SPOM filters (Gould et al., 2019) have been compared and discussed for the ODP Core Site 1234 at the Chilean Margin in the study of Weiss et al. (2019b). Our hydrogen isotope data from site 1235 is very similar to the last deglaciation δ^2H_{C37} shift reported by Weiss et al. (2019b) and other global sites. Therefore, we did not see the need to repeat this discussion here, though we will briefly summarize it in a revised manuscript.*

Specific Comments:

RC2: Line 9/the overarching argument that the work presented illustrates a 'regional' not 'local' phenomena/record: I suppose it is relatively subjective, however, it is my experience that a regional phenomenon (especially in the vast ocean environment) would require the authors to have evaluated core samples taken from a much larger range of latitude/locations along the Chile margin. In my experience, 12km distance between two cores is showing consistency at one specific local, where the two cores would be treated essentially as replicate records to illustrate a robust finding. I suggest the authors reconsider whether their work presented is truly extending a local record to a regional one with just two cores so close in proximity. Although this does not detract from the importance of their record, nor does it negate the impact two core records has on improving the results.

- **Authors:** *The reviewer is correct that the distance between the two cores is only 12 kilometers, but the water depth from which the cores are retrieved is quite different and therefore still represents somewhat different conditions. Thus, although the cores are from very close proximity, we feel that "local" does not entirely do this study justice, but we agree with the reviewer that "regionally" is perhaps making it too big. However, we do note that a large number of palaeoceanographic studies draw regional conclusions by extrapolating results from a single core to a whole region. Here we extrapolate the results of two replicate records to a whole region which is, in our view, more robust than most other studies. Furthermore, the comparison to other records confirms that the signal is not reflecting local circumstances (e.g. river input) but regional and perhaps global changes.*

RC2: Throughout the manuscript, I would also suggest the authors be very clear and careful about describing isotopic trends/directionality. Whenever a change is indicated in isotopic composition through time, it would be very helpful to the reader to know in which direction the change occurred (i.e., the seawater has becoming enriched in $\delta^{18}\text{O}$ for example). This is an important detail that will aid the reader throughout.

- **Authors:** *We agree that this needs to be clearer.*

RC2: Figure 2 and Table 1: The figure and table headings here are a little bit difficult to follow. I suggest (as was done nicely in Figure 1) the authors start the headings with a more general/overarching statement of what the figure/table are describing/illustrating before describing specific aspects of the figure/table. Ensure that the figure/table titles can be read independently of the main text and be fully understood.

- **Authors:** *We agree with this and will change accordingly.*

Technical Corrections:

RC2: Line 2: subscript on C37 (C₃₇)

- **Authors:** *We will correct it.*

RC2: Line 9 and throughout the work: please determine whether you will spell the word 'seawater' as one word (as in my experience it is often spelled) or as two words 'sea water'. There are many instances of both iterations throughout the manuscript, and this should be cleaned up before publication.

- **Authors:** *We will make it consistent.*

RC2: Line 12: It is important I think to indicate that the second core reported on in this work is indeed a previously reported on/published record - this is good to indicate even in the abstract here and then also throughout.

- **Authors:** *We will make this clearer. However, both in the Abstract and in the Introduction we state that we present a new hydrogen isotope record of ODP core 1235. In the introduction line 76-77, as well as throughout the methods and results (e.g. line 210 and 213), we state clearly that we compare our record to published data of ODP site 1234 (i.e. de Bar et al., 2018 and Weiss et al., 2019b).*

RC2: Line 16: Make it clear here that "this suggests a shift of ca. 5 per mil in benthic/deep water".

- **Authors:** *We will make this clearer but, as stated in the reply to the comments of reviewer 1, we prefer to use the term bottom water, rather than deep or benthic.*

RC2: Line 21: again be clear about how you spell seawater – perhaps here the parentheses are not necessary and just spell out 'seawater'.

- **Authors:** *Thank you for pointing this out, we intend to spell it consistently as "seawater".*

RC2: Line 22: the phrasing 'which could improve' is a bit weak, perhaps just 'which improve our understanding'...

- **Authors:** *We will change it.*

RC2: Line 28: Be sure the use of the colon ":" throughout is necessary. For instance, this sentence could instead read: "... isotopes of seawater, where during glacial periods large amounts of water...."

- **Authors:** *We will correct it.*

RC2: Line 28: "Low oxygen and hydrogen isotope values" is not clear, do you mean more negative? It may be helpful to include/define the equations for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ here. Since $\delta^2\text{H}$ especially is a relatively 'new' proxy for seawater salinity, defining the hydrogen isotopes explicitly could be informative.

Authors: *Yes, we mean more negative. We discuss the updated equations for $\delta^2\text{O}$ and δH in the Material and Methods section.* **RC2:** Line 29: You might consider removing the word "the" in this sentence: "...ice on land, leaving seawater more enriched in heavier deuterium isotopes."

- **Authors:** *We will correct it.*

RC2: Line 30: Awkward wording choice to describe 'leading the formation of ...'. Perhaps something along the lines of: "...the decrease in global ice volume releases low density fresh water with relatively low..." Also, consider throughout the manuscript when discussing isotopic values whether you are being consistent in your description of 'low vs high' or 'heavier vs light' or 'enriched' etc. isotopic signatures. Choosing one way to describe the directionality of the isotopes is much clearer.

- **Authors:** *Agree, we will use low and high values and highlight that low means more negative.*

RC2: Line 31: seawater

- **Authors:** *We will change it.*

RC2: Line 32: "... have a close relationship..." is perhaps not the most technical way to describe this, perhaps something more like "... are correlated with..." or "...are tightly coupled with..."

- **Authors:** *We will change it.*

RC2: Line 33/35: seawater (please check this throughout, I won't call it out in my further comments)

- **Authors:** *Thank you for pointing this out, we will check its consistent use.*

RC2: Line 36: I was always taught to refer to the "isotopic" composition of something... so perhaps "... is a function of the oxygen isotopic composition of ambient seawater..."

- **Authors:** *We agree and will check the text.*

RC2: Line 41: "... or clumped carbon isotopes (Δ_{47})..." for those unfamiliar with Δ_{47} .

- **Authors:** *Thank you, we will change it.*

RC2: Line 41: "In some cases, independent temperature proxies based on organic..." The authors might consider including the word 'independent' here to indicate they are proxies not coming from forams themselves but other sources.

- **Authors:** *OK.*

RC2: Line 43: "...records and modelling..." is a bit awkward wording. Please consider re-evaluating this sentence structure.

- **Authors:** *We will try to improve the wording.*

RC2: Line 46/47: "... relationship between $\delta^{18}\text{O}_{\text{sw}}$ and salinity." The 'salt content' is strange wording.

- **Authors:** *We will change this.*

RC2: Line 47: Perhaps the last sentence would be clearer if written something like: "However, it is uncertain whether this relationship holds through time."

- **Authors:** *Thank you for the suggestion and we will address this in the updated manuscript.*

RC2: Line 50: Again, please be clear on the direction of the isotopic change.

- **Authors:** *We will indicate the direction of the shift clearer.*

RC2: Line 51: Perhaps define $C_{37:2}$ and $C_{37:3}$ here because you do not define this 'shorthand' earlier. Since you are opting to combine the signals, it is important to describe to the reader what these two parameters are.

- **Authors:** *We will indicate that $C_{37:2}$ and $C_{37:3}$ mean the long chain alkenone with 37 carbon atoms and two and three double bonds, respectively.*

RC2: Line 57: What δ^2H signature are you referring to here? The algal δ^2H response to changes in salinity? I believe here is where the authors describe the range in salinity reconstructions possible when using culture vs SPOM vs core top δ^2HC37 – salinity calibration models. I do think it would be a powerful discussion to include a small discussion on what the data in this new core would show if a δ^2H_{C37} -salinity calibration model was used to reconstruct salinity directly from δ^2H_{C37} . Especially given the authors argue that the dominant species of alkenone producers in this region are likely to be *E. hux*

- **Authors:** *We refer to the alkenone δ^2H , we may state this clearer. We agree with the reviewer's idea, however, we believe this was already extensively discussed by Weiss et al. (2019b). We will therefore refer the reader to that study and only briefly summarize it in the current manuscript (see response to the earlier comment on this topic)*

RC2: Line 60/61: This sentence is difficult to follow, larger than expected based on what?

- **Authors:** *We will rephrase this. We mean to say that the salinity changes Weiss et al. (2019b) reconstructed based on the different δ^2H_{C37} -salinity calibrations are larger than salinity estimations which have been made based on δ^8O and ice volume modelling.*

RC2: Line 72: The authors mention that the $\delta^{18}O$ – salinity relationship may not hold through time (line 47), to use δ^2H_{sw} to reconstruct salinity, do the authors bot also have to assume this relationship holds through time? Or at least indicate here that we also do not know if this holds through time?

- **Authors:** *Yes, as described in line 47 the δ^8O – salinity of the open-ocean could have changed and the reviewer is right with this the δ^2H_{sw} – δ^8O and δ^2H_{sw} – salinity relationship would change as well. We discuss this possibility in section 3.4, line 269-270.*

RC2: Line 73: Again, I would suggest the authors reconsider whether this truly speaks to regional versus local variability.

- **Authors:** *Please see our reply above.*

RC2: Line 81/82: This sentence is difficult to follow in the figure legend. Please consider re-phrasing.

- **Authors:** *We will rephrase it.*

RC2: Line 86: "... from a previously collected deeper neighboring ODP..." Be sure to give credit/indicate this was a previously collected core.

- **Authors:** *We will indicate this more clearly.*

RC2: Line 90: Transports cold saline waters where? Isotopically depleted water can potentially be added where?

- **Authors:** *What we mean to say is that the cold and saline water transported from the ACC into the Peru-Chile Countercurrent could be mixed with fresher and ^{2}H -depleted fjord water along the southern margin.*

RC2: Line 91: The average salinity in the area was defined how? Based on a quarter grid perhaps?

- **Authors:** *Yes, it was based on the World Ocean Atlas quarter grid (WOA18_0.25deg_All_Years_Annual.Data). This will be indicated in the revised version.*

RC2: Line 97: I think you are missing a word in this sentence. This should maybe read: "... of <2 ka, and a total of 27 samples were..." Also, you might consider noting how ODP 1234 was sampled (the same way?).

- **Authors:** *We will change the sentence. We did not sample ODP 1234, the sampling is described by de Bar et al., (2018) and Weiss et al., (2019b).*

RC2: Line 101: I think you meant to use a comma not a period to indicate 41,000 years.

- **Authors:** *Yes, thank you.*

RC2: Line 103: Perhaps the word 'with' should be replaced with 'at' here.

- **Authors:** *Yes, thank you.*

RC2: Line 113: Please define the average differences here – is this a standard error or standard deviation etc.?

- **Authors:** *This needs to be corrected to standard deviation of replicate analysis of the same sample.*

RC2: Line 114: The standard deviation of what is within 0.1 per mil?

- **Authors:** *Both isotope calibration standards, NBS 19 and NFHS-1, are within 0.1‰ standard deviation of accepted values.*

RC2: Line 119: Indicate the model number or instrument name for the ASE.

- **Authors:** *OK. It is a Dionex 350 ASE.*

RC2: Line 143: RSME should be RMSE

- **Authors:** *Yes, thank you.*

RC2: Line 146: Are you referring to the measured salinity in the modern surface open-ocean?

- **Authors:** *The hydrogen isotope values are mostly from surface waters, however for the oxygen isotope data, we included values between 0–600 m. We will include the sampling depth information in the supplementary information.*

RC2: Line 149: Again, are you referring to surface ocean data?

- **Authors:** *The data points from the surface ocean dataset are from sampling depths between 0–600 m.*

RC2: Line 154: Is there a good citation to include here for detailing that the oxygen isotopic composition of forams depends mainly on temperature and the isotopic composition of seawater?

- **Authors:** *In the lines following line 154 we do discuss publications regarding this matter, e.g. McCrea et al. (1950) being the first laboratory study showing the relationship of oxygen isotope signal of the foraminifera with that of growth water and temperature.*

RC2: Line 155: "...calcite sources..." is likely not the best/most correct term. Perhaps, calcite species or polymorphs?

- **Authors:** *Yes, we will correct it to polymorphs.*

RC2: Line 159: "... temperature proxies and **then** obtain salinity..."

- **Authors:** *We will correct it.*

RC2: Line 161: "... (2011), **where** the $\delta^{18}\text{O}$ - paleotemperature..."

- **Authors:** *We will correct it.*

RC2: Line 162: in-situ should be italicized.

- **Authors:** *We will change it.*

RC2: Line 166: "...at the time of Eq. (4)..." is awkward wording, please consider clarifying.

- **Authors:** *We will clarify it.*

RC2: Line 167: Please define this equation, where is it from? As it stands it is not well introduced/prefaced.

- **Authors:** *Thank you. Line 166 needs to be corrected, it is referring to Eq. (5).*

RC2: Line 169 (Equation 6): perhaps the authors might define earlier how temperature is solved for in this equation typically? Which proxy(ies) is/are used to resolve temperature.

- **Authors:** *We explained in the Introduction how the temperature is usually resolved, see line 39-43. We made an assumption for the temperature change, since we were not able to determine bottom water temperatures, as described in the Results and Discussion at lines 195-202.*

RC2: Line 190: "The oxygen **isotopic signatures** of benthic *Uvigernia* in ODP core 1235 range between 4.15..."

- **Authors:** *Thank you, we will change it.*

RC2: Line 192: $\delta^{18}\text{O}_{\text{foram}}$

- **Authors:** *We will check the abbreviations for consistency.*

RC2: Line 192: Perhaps change the word "till" to "to".

- **Authors:** *We will change it.*

RC2: Line 193: This sentence structure needs work. "...showing an LGM to 1 ka shift of..." is difficult for a reader to follow. Again, indicate the direction of the shift.

- **Authors:** *We will change it.*

RC2: Line 195: This sentence structure could be improved.

- **Authors:** *We will improve it.*

RC2: Line 201: What is the temperature change reported in ODP 1234 – if it is consistent, please report the value(s).

- **Authors:** *We will report it clearer.*

RC2: Line 204: It is a little bit difficult to follow when the authors are referring to surface and benthic water isotope values – is there a clearer way to indicate benthic vs surface throughout?

- **Authors:** *We will try to make this clearer. However, we want to point out that chapter 3.1 only describes bottom seawater isotopes as stated by the title and chapter 3.2 only surface seawater isotopes. We chose this structure to make the discussion clearer and help the reader. Chapter 3.3 is comparing the seawater isotopes, oxygen and hydrogen isotope proxies, and surface versus bottom water signals – here we should make clear when we speak of bottom and when of surface water. Chapter 3.4 discusses only the global surface water signal.*

RC2: Line 206: Please indicate the directionality of the isotopic shift.

- **Authors:** *We will make the direction of the isotope shift clearer.*

RC2: Line 218: "...globally surprisingly similar in magnitude," is not very clear wording.

- **Authors:** *We will change the wording.*

RC2: Figure 2: General introductory statement first. "**Alkenone** hydrogen isotopic ratios measured in ODP 1235....". What does 5pt average refer to? Where are the black circles on the figure indicating $\delta^{18}\text{O}$ of the benthic foram from ODP 1234? What are the seawater temperature data reconstructed from? TEX UK37?

- **Authors:** *We noticed that it needs to be: "The green line shows the 5pt average $\delta^{18}\text{O}$ values of benthic Foraminifera from ODP 1234 (from de Bar et al., 2019)". We will edit the figure description accordingly.*

RC2: Line 246: Where was de Bar et al.'s work? Indicate this to the reader.

- **Authors:** *At core site 1234, Chilean Margin, this will be indicated in the updated manuscript.*

RC2: Line 262: I am not sure if it is commonplace to capitalize 'Recent'?

- **Authors:** *Yes, it is a noun in Geology; singular proper noun: Recent*

RC2: Line 269: salinity – ^2H should be salinity- $\delta^2\text{H}_{\text{sw}}$?

- **Authors:** *We will change it to $\delta^2\text{H}$ to avoid confusion.*

RC2: Line 271: "... of a dominating **evaporative regime** on the slope of the isotope..." and on which isotope are the authors referring? Both?

- **Authors:** *We are referring to both seawater isotopes.*

RC2: Line 273: "Surface waters may be more sensitive **to** changes in this..."

- **Authors:** *We will change this.*

RC2: Line 274: salinity – ^2H should be salinity- $\delta^2\text{H}_{\text{sw}}$?

- **Authors:** *We will change it to $\delta^2\text{H}$ to avoid confusion.*

RC2: Line 274: "... for surface waters, due to, **for example...**"

- **Authors:** *We will change this.*

RC2: Line 275-276: This sentence is very confusing to follow, please consider elaborating on the message here.

- **Authors:** *We will write it clearer.*

RC2: Table 1: Please consider adding a general statement to describe what this table is detailing. I would also consider being explicit about why the Kasper data are not included in your discussion.

- **Authors:** *We will add this.*

RC2: Line 297-298: Please consider adjusting the "Globally distributed..." sentence as it is difficult to follow. Subscript C37 (C₃₇).

- **Authors:** *We will change this.*