

Glacial-interglacial sea water isotope change near the Chilean Margin as reflected by $\delta^2\text{H}$ of C_{37} alkenones.

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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 1:

General Comments

RC1: In this paper, Hättig et al. generate a paired surface-benthic ocean temperature / hydrogen / oxygen isotope record from the Chilean Margin spanning the last 40 kyr. Their new data are similar to those from a neighboring site and they also show that the mismatch in planktic-benthic seawater isotope change is consistent to that observed in the handful of other extant LGM-modern alkenone hydrogen isotope records. This multi-proxy approach is creative and demonstrates the potential of the alkenone $\delta^2\text{H}$ proxy. This manuscript also shows a good awareness of prior work and current technical and analytical limitations. I believe it is well within the purview of *Climate of the Past* and therefore recommend it for publication following extensive but relatively minor revisions.

My first suggestion is a careful grammatical overhaul; I am sure I did not identify every single instance where the language and logical flow could be improved and I would encourage the authors to actively seek out opportunities to do so rather than merely addressing those listed below.

- **Authors:** *We thank the reviewer for the technical corrections pointed out and we will take the opportunity to go through the text carefully.*

My other main recommendation would be a more extensive treatment of the uncertainties. This work involves several transfer functions (i.e., $\delta^{18}\text{O}$ to $\delta^2\text{H}$, $\delta^{18}\text{O}$ to salinity, foraminiferal $\delta^{18}\text{O}$ to seawater $\delta^{18}\text{O}$, alkenone $\delta^2\text{H}$ to seawater $\delta^2\text{H}$), calibration error, and general unknowns (benthic paleotemperatures); the authors do a good job of bringing these to our attention, but I believe a slightly more quantitative assessment of how these compounded uncertainties (roughly calculated) affect their final conclusions would be beneficial. (E.g., does this mean that the last deglaciation is the smallest change we can reasonably do this type of analysis for? Is the surface-depth isotope offset within error?)

- **Authors:** *We will try to draw and include statements on how these uncertainties affect the final conclusions. There are three main components one needs to consider: 1) The reproducibility and accuracy error of compound-specific hydrogen isotope analysis which is ca. 5‰ based on replicate analysis for the standards (for MIX B the source is A. Schimmelmann, Indiana University). 2) The calibration error between δ^2H_{SW} and δ^2H_{C37} reflected by the root-mean-square error of 5.8‰ for the calibration from Gould et al. (2019) and 7‰ for Mitsunaga et al. (2022). 3) The variability of the modern open-ocean waterline with an RMSE of 3‰. All three components result in a propagated error of ca. 9‰ for the absolute δ^2H_{SW} estimations. However, the error of the relative change in δ^2H_{SW} is likely smaller. For example, when we use the error of the calibration slopes (Gould et al., 2019; Mitsunaga et al., 2022, which is ca. 3‰, and of the water line, which is ca. 1‰), then the propagated error of $\Delta\delta^2H_{SW}$ is approximately 6‰.*

Specific Comments

RC1: Lines 52-56: My understanding was that the alkenone-seawater hydrogen isotope fractionation's salinity-dependence was observable in culture (Schouten 2006 and your other references) but not always in sediment (Weiss et al., 2019; Mitsunaga et al., 2022). I think you can say this and acknowledge that effect of salinity on alkenone-water fractionation is not settled.

- **Authors:** *Yes, the impact of salinity is unclear, we will rephrase these lines.*

RC1: Line 73: I think you should put a sentence around here on why you are using Site 1235; explicitly call out the benefits of having the nearby Site 1234 δ^2H_{C37} and temperature records, then get into why your site and approach are different (which you do: different depths, etc.). Also, in general, especially in your abstract and introduction, you can do a better job saying why your study is so important and why you needed to make these measurements so close to an existing δ^2H_{C37} . A sentence or two here or there could make a big difference.

- **Authors:** *We will add text at the different parts of the revised manuscript making it clearer why we chose site 1235 and how it is beneficial.*

RC1: Lines 94-97: Were planktic foraminifera unavailable? That could be another means of reconstructing surface water $\delta^{18}O$. And then you could avoid the $\delta^{18}O$ - δ^2H transfer function, which is an additional source of error...

- **Authors:** *Planktic foraminifera were picked when abundant in core slides and their $\delta^{18}O$ was analysed. However, this record did not cover the whole 20 ka shift sufficiently enough to calculate the surface oxygen isotope water shift during the last deglaciation.*

RC1: Lines 128-130: How different were the $\delta^2\text{HC}_{37:3}$ and $\delta^2\text{HC}_{37:2}$ values? I.e., was there any $\text{C}_{37:3}$ - $\text{C}_{37:2}$ (inter-alkenone) fractionation? I think you should mention it in your results; I know it is not the main thrust of this paper, but some people (Sachs, D'Andrea) have observed an offset while others (Weiss, Mitsunaga) have not, and this could be of interest to the biochemists studying coccolithophore cell water dynamics. At the very least, if there is no (statistically significant) offset, mentioning that legitimizes your choice to report combined $\delta^2\text{HC}_{37}$.

- **Authors:** *Yes, to account for inter-alkenone fractionation we integrated $\delta^2\text{H}_{\text{C}_{37:3}}$, $\delta^2\text{H}_{\text{C}_{37:2}}$ separately as well as combined peaks of $\text{C}_{37:2}+\text{C}_{37:3}$ alkenones, $\delta^2\text{H}_{\text{C}_{37}}$. Our analyses allowed us to do so in one measurement. All values are reported in the data file on Pangaea (<https://doi.org/10.1594/PANGAEA.958880>). The submitted supplement file reports only the integrated $\delta^2\text{H}_{\text{C}_{37}}$ and $\delta^2\text{H}_{\text{C}_{38}}$ values, we will add the individual C_{37} alkenone values to the supplement. The $\text{C}_{37:3}$ alkenone suggests a $\delta^2\text{H}$ shift of 24‰ and the $\text{C}_{37:2}$ alkenone a shift of 16‰. However, van der Meer et al. (2013) have shown that a weighted average or combined integration of C_{37} peaks might be more appropriate than individual values when using alkenone hydrogen isotopes for reconstructing paleo sea surface salinity changes. An additional reason for using the combined C_{37} alkenone values is that older datasets are all based on the integrated C_{37} alkenones and we compare our results to these datasets (e.g. Pahnke et al., 2007; Kasper et al., 2014). Lastly, the published $\delta^2\text{H}_{\text{C}_{37}} - \delta^2\text{H}_{\text{SW}}$ calibrations (Mitsunaga et al., 2022; Gould et al., 2019) are also based on the combined C_{37} peak, we therefore prefer to stick to this.*

RC1: Lines 137-150: I think an obvious question is why bother with converting $\delta^2\text{HC}_{37}$ to $\delta^2\text{HSW}$ to salinity if there are existing $\delta^2\text{HC}_{37}$ -salinity calibrations, and I think you need to address this, at least briefly. What could be said is that the direct salinity calibrations are worse than the $\delta^2\text{HC}_{37}$ to $\delta^2\text{HSW}$ ones in core-tops (Mitsunaga, Weiss). Of course, then you have to explain why $\delta^2\text{HC}_{37}$ -salinity is worse than $\delta^2\text{HC}_{37}$ - $\delta^2\text{HSW}$ if the $\delta^2\text{HSW}$ -salinity relationship is so tight...

- **Authors:** *As we mentioned in the Introduction at line 55-69, culture $\delta^2\text{H}_{\text{C}_{37}}$ -salinity calibrations are based on single species and fixed conditions, which could be problematic when translating to environmental calibrations. The core-top calibration should be the most suitable since it includes multiple species and environmental variability including sedimentation and to some degree preservation. However, salinity changes become very large when applying these $\delta^2\text{H}$ -salinity relationships, suggesting that we are missing a piece of the puzzle (discussed in Weiss et al., 2019b). The SPM calibration of $\delta^2\text{H}_{\text{C}_{37}}$ to $\delta^2\text{H}_{\text{SW}}$ also includes contributions from different species and the effects of other environmental parameters and fits very well with the updated core-top calibration of Mitsunaga et al. (2022). With the reconstructed $\delta^2\text{H}_{\text{SW}}$ information, salinity interpretations can carefully be made with a global (as demonstrated) and local waterline.*

RC1: Lines 195-208: I get that you were unable to measure benthic paleotemperatures, but that does introduce some holes in your argument. It is good that you have the Schrag et al. bottom-water temperatures, because otherwise I would be skeptical that planktic and benthic warming would be the same. Is there any way you could show how much the uncertainty in your calculations matters? I.e., if you are off by X °C, how much does it matter to your calculations of benthic $\delta^{18}\text{OSW}$ change? And then how does that error propagate to $\delta^2\text{HSW}$ calculations?

- **Authors:** *We agree with both reviewers that the bottom water isotope reconstruction with respect to the temperature uncertainty needs more attention. We therefore performed a sensitivity analysis (see below) which showed that one degree of temperature change affects the $\delta^{18}\text{OSW}$ shift by 0.2‰ and the $\delta^2\text{HSW}$ by 1.4‰. In fact, the sensitivity analysis shows that even with negligible bottom water temperature change, the magnitude of $\delta^2\text{HSW}$ change of bottom waters will still be lower than that of surface waters ($\delta^2\text{HSW} = 14‰$).*

The following table shows the impact of different bottom water temperature changes (ΔT) on the bottom water oxygen and hydrogen isotope change at ODP Site 1234 and 1235. $\Delta\delta^{18}\text{O}_{\text{foram}}$ estimate is based on the average observed at sites 1234 and 1235 (see Table 1 in preprint).

$\Delta\delta^{18}\text{O}_{\text{foram}}$	ΔT	$\Delta\delta^{18}\text{O}_{\text{SW}}$	$\Delta\delta^2\text{H}_{\text{SW}}$
$1.6 \pm 0.2‰$	0 °C	$1.6 \pm 0.2‰$	$10.6 \pm 3‰$
$1.6 \pm 0.2‰$	1 °C	$1.4 \pm 0.2‰$	$9.3 \pm 3‰$
$1.6 \pm 0.2‰$	2 °C	$1.2 \pm 0.2‰$	$7.9 \pm 3‰$
$1.6 \pm 0.2‰$	3 °C	$1 \pm 0.2‰$	$6.5 \pm 3‰$
$1.6 \pm 0.2‰$	4 °C	$0.8 \pm 0.2‰$	$5.1 \pm 3‰$

RC1: Lines 249-259: Makes sense – if you assume the same LGM-modern temperature change, you get similar changes in benthic $\delta^{18}\text{O}$ as global. If you talk about temperature uncertainties earlier, this might be a good time to discuss what you discovered. What if deglacial benthic temperature change (and therefore $\delta^2\text{HSW}$ change) was more / less than expected based on Schrag et al. numbers? Does it come close to affecting your argument that planktic $\delta^2\text{HSW}$ change was much greater than benthic?

- **Authors:** *If the bottom water temperature change was higher than the assumed 4 °C, this would result in a smaller seawater isotope change and therefore smaller bottom water salinity change. Even if the bottom water temperature change is close to 0, then the seawater isotope change of the bottom waters is still smaller than that of surface waters.*

RC1: Line 261-281: I think you need to qualify this a bit. It is a very interesting trend if true, but since there are only seven records—including the anomalous Mozambique channel Kasper et al. one—from mostly low to mid-latitudes, as you acknowledge, I am not sure the data is there to do so quite yet. Presumably, there are other Mozambique channel-type sites out there, we just have not discovered them yet. I think you need a sentence or two at the start of this section acknowledging the small number of extant records. But as long as the trend is real...

- **Authors:** *We agree that the published records do not cover the entire globe and definitely not equally, though we note that it will be some effort to generate substantially more records. We will take this into account in our discussions.*

RC1: Lines 268-269: I think it is believable that the surface ocean would have freshened first, but I think it is intriguing that these changes would not have propagated to the deep ocean within several thousand years given the mean mixing time of seawater. Do you have any other sources that could support this?

- **Authors:** *We are not aware of any other studies which could support this. We agree to the reviewer that due to mixing over thousands of years we would expect a propagation of the surface changes eventually towards the bottom. However, modern hydrogen isotope data of the ocean is limited and therefore the distribution and underlying processes in the surface water versus the bottom water are not well known yet.*

RC1: Lines 274-275. I think you could come right out and say that the LGM was drier than the modern. A source or three here could really strengthen your argument and / or I think you need to flesh out the mechanisms by which a drier atmosphere could change the salinity- $\delta^2\text{H}$ relationship, which then more directly affects the surface than the depths. (That last part makes perfect sense to me.)

- **Authors:** *We thank the reviewer for this suggestion and we will look for sources to strengthen the argumentation.*

RC1: Table 1: I think you need to explain in the text or table caption somewhere why the Mozambique channel Kasper record is excluded from your calculations (i.e., changing riverine inputs rather than seawater $\delta^2\text{H}$ change). I would also use “source” instead of “paper” for the leftmost column.

- **Authors:** *Thank you for the suggestion, we will make it clearer why the Mozambique channel data is excluded (e.g., high BIT index, changing distance to the river mouth). We will change “paper” to “source”.*

Technical Corrections

RC1: Line 2: [Here, and subsequently] I do not have strong feelings about this, but I have been told that delta notation—i.e., “ $\delta^2\text{H}$ ” or “ $\delta^{18}\text{O}$ ”—is an adjective and therefore that it always needs to be followed by a noun, i.e., “ $\delta^2\text{HC37}$ values,” “this $\delta^2\text{HC37}$ record,” “our new $\delta^2\text{HC37}$ data,” etc.

- **Authors:** *We will check and fix this.*

RC1: Line 2: [Here, and subsequently] I believe that the number of carbons should be subscripted, i.e., “C37.”

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

RC1: Line 12: “Shift” is overused throughout the abstract, try to find synonyms.

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

RC1: Line 12: The last / most recent deglaciation?

- **Authors:** *Yes, we will adapt this.*

RC1: Line 16: Separate “waterline” into two words.

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

RC1: Line 21: “Physiochemical”

- **Authors:** *We do mean to say physicochemical, as it refers to both physical and chemical attributes e.g., temperature, salinity, pressure, density.*

RC1: Line 26: “Local climate regime” is vague; do you mean temperature?

- **Authors:** *We mean different climate parameters such as precipitation, temperature, humidity.*

RC1: Line 28: “Low oxygen and hydrogen isotopic values” is vague, could be referring to D/H ratios, etc. If you mean “ $\delta^2\text{H}$ or $\delta^{18}\text{O}$ values,” just say so. (You do this in lines 30-31 anyway.)

- **Authors:** *Yes, we mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values.*

RC1: Line 36: The “P” in “ $\delta^{18}\text{O}$ foram” is sometimes capitalized, sometimes not. I would go with lowercase, but just be consistent. You also re-abbreviate this (Line 95) elsewhere; you only need to once.

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

RC1: Line 36: [Here, and elsewhere?] You already introduced an abbreviation for the oxygen isotopic composition of seawater ($\delta^{18}\text{O}_{\text{sw}}$), might as well use it.

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

RC1: Lines 43-45: Also LGM porewater $\delta^{18}\text{O}_{\text{sw}}$ measurements; see Adkins & Schrag 2001.

- **Authors:** *We will add it here.*

RC1: Line 45: "To derive" should be "deriving."

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

RC1: Line 61: What is the expected deglacial salinity change?

- **Authors:** *In line 43-44 we describe the oxygen isotope change; we should add that based on this data and modelling attempts the expected salinity change is 1-2 psu.*

RC1: Line 70: "Alkenone" should be "alkenones."

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

RC1: Figure 1: The location of the word "Chile" is misplaced. I get not wanting to put it near where Chile actually is, because it's a bit crowded there, but maybe that means it is unnecessary. There are also several typos in the caption.

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

RC1: Line 85: [Here, and elsewhere] I would mostly use "site" instead of "core" in this section since you are referring to the physical locations of the cores rather than the cores themselves. I would use "core" if you were discussing the characteristics of the core (i.e., length, lithology, etc.).

- **Authors:** *We thank the reviewer for this suggestion and will change it accordingly.*

RC1: Line 86: Remove "located."

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

RC1: Line 88: Add a comma between "upwelling" and "stimulating."

- **Authors:** *We will add a comma.*

RC1: Line 96: [Here, and elsewhere] be consistent with using a comma after "i.e." or "e.g." I believe the difference is British versus American English; see which the journal follows.

- **Authors:** *Indeed, the difference is American English and British English. We follow in the text British English and will therefore remove the commas.*

RC1: Lines 96-97: This is a run-on sentence.

- **Authors:** *We will try to improve this.*

RC1: Line 106: Misplaced parenthesis.

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

RC1: Lines 107-108: “Ka” should be “kyr.” (Ka [or Ma] specifically means years ago, where here I think you just mean x cm per x thousand years.) Also, you do not need the periods between “cm” and “kyr.”

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

RC1: Line 111: Check if you need the hyphens here. I am not sure that you do.

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

RC1: Line 114: Is the standard deviation referring to NBS-19 or the internal standard or both?

- **Authors:** *It is referring to both. We always try to have both standards within 0.1%. NBS19 is the official IAEA reference standard and is very homogeneous. The NFHS1 in house standard is also foraminifera material, but less homogeneous.*

RC1: Line 115: Both might be acceptable, but I have more commonly seen “per mille.” Also, I do not think you need to define the ‰ symbol, but if you do, you should do so the first time you use it, not here.

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

RC1: Line 133: [Here, and elsewhere] to clarify, “online” refers to the value measured in the lab that day and “offline” refers to the published / “correct” values (via Schimmelmänn or others)?

- **Authors:** *The reviewer is right. Alternatively, we will replace this with predetermined values for in house standards and certified values for certified standards (in this case MIX B from A. Schimmelmänn, Indiana University).*

RC1: Lines 134-135: [Here, and elsewhere] be consistent with spacing between mathematical symbols (\pm , $<$, ‰, etc.). Check journal-specific conventions.

- **Authors:** *OK. Between symbol and number no space e.g. -173, ± 5 , between number and ‰ no space as it is not a Unit. Between number and unit space.*

RC1: Line 144: “RSME” should be “RMSE.”

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

RC1: Line 145: “Waterline” should be two words.

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

RC1: Line 162: Italicize “in situ,” but I cannot tell what it adds here. (Do you mean from sediment versus from the water column or culture?) Try “estimated using the benthic genera Cibicidoides and Planulina.”

- **Authors:** *The equation by Lynch-Stieglitz et al. (1999) as rearranged by Cramer et al. (2011) is calculated from core-top samples, i.e. a field calibration. Pearson et al. (2012) described this calibration as “in situ”.*

RC1: Line 163: Not sure these are recent. “Subsequent,” maybe? Also, phrased a little awkwardly (“other species’ values are projected onto the Cibicidoidies and Planulina function?”).

- **Authors:** *We will change it to: “Uvigerina genera $\delta^{18}\text{O}$ values are corrected to Cibicidoidies and Planulina $\delta^{18}\text{O}$ values. ”*

RC1: Lines 251-252: I am wondering if you could use separate abbreviations for surface and deep water $\delta^2\text{HSW}$ values and change – $\delta^2\text{HSWp}$ and $\delta^2\text{HSWb}$? I am sure you can think of something better and / or do not be afraid to use synonyms for “surface” and “deep” (“planktic” and “benthic,” etc.) too.

- **Authors:** *We think it is good to stick to surface and bottom water, this is how the article from Results to Discussion is structured and we think this will be clear to the proxy and modelling community. We hesitate to use planktic and benthic as it could lead to more confusion, and we like the reader to focus on the water masses, rather than the proxies. We thank the reviewer for the suggestion, and we will use the abbreviation $\delta^2\text{H}_{\text{SSW}}$ for surface seawater and $\delta^2\text{H}_{\text{BSW}}$ for bottom seawater. This would be similar to the abbreviations used for sea surface and bottom temperature i.e. SST and BWT.*

RC1: Line 262: “Remarkable” should be “remarkably,” although I would probably just take it out.

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

RC1: Line 265: “Waters” typo.

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

RC1: Line 269: “Salinity- $\delta^2\text{H}$ ” instead of “salinity-2H?”

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

RC1: Line 285: “Std” = standard deviation?

- **Authors:** *Yes, with Std we mean the standard deviation and will expand the abbreviation.*