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Discussions

Interactive comment on "Alkenone isotopes show evidence of active carbon concentrating mechanisms in coccolithophores as aqueous carbon dioxide concentrations fall below 7 $\mu\mathrm{mol\,L}^{-1}$" *by* Marcus P. S. Badger

Anonymous Referee #1

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—Summary and Recommendation —

The manuscript entitled "Alkenone isotopes show evidence of active carbon concentrating mechanisms in coccolithophores as aqueous carbon dioxide concentrations fall below 7 μmolL$-$1" explores the lower limitations of the alkenone-based pCO2 proxy. The proxy relies on the assumption that the isotopic composition of alkenone compounds reflect the abundance of aqueous CO2 in its growth water which is passively diffused in the cell. However, there has always been an underlying concern of this assumption, as alkenone-producing algae have been shown to have carbon concen-

trating mechanisms, a concern given that there are different mechanisms involved and the significant difference in the isotopic composition of bicarbonate versus aqueous CO2. To explore the potential influence of carbon concentrating mechanisms on the alkenone-based proxy, the author compiled 6-7 studies using the exact same calculation methods, and then compared these indirect proxy-based estimations with direct ice core measurements from the same time period (with consideration to age uncertainties). The author found that the relationship between the alkenone-based proxy and the ice core data breaks down with decreasing aqueous CO2, with an r2 dropping below 0.5 when aqueous CO2 is below 0.7 μmolL$-$1.

This manuscript represents a substantial contribution to scientific progress in the field of biogeochemistry, as well as paleoclimate, by addressing the physiological limitations of this widely used CO2 proxy. Overall, the scientific quality is high: the methods are robust, the logic is very clear, and there is consideration to the body of literature on this topic. Finally, the presentation quality is also excellent. The manuscript is clear, concise, and well-structured; in fact, this is one of the most easy-to-follow explanations of the alkenone-based proxy that I have read. Furthermore, the figures are well-made and well-suited to the text. I highly recommend this manuscript for publication with minor revisions. Below are some questions and criticisms to be addressed before this manuscript is accepted.

—General Comments—

The fact that these many studies have now all been calculated using the exact same methods should be included in the Abstract and Introduction (re: Line 100-101), as this alone is important for the community. Consider moving (or repeating) Line 173-175 in the Abstract and/or Introduction, as this is also an important point of this study.

The Introduction needs to establish some key topics. Most importantly, there is almost no introduction of carbon concentrating mechanisms, which is the entire crux of the study. In particular, it is important to establish how they work, the different kinds of mechanisms (e.g. external or intracellular carbonic anhydrase, $HCO3-$ transport), and why CCMs are concerning for the proxy (e.g. isotopic difference between bicarbonate and CO2, different fractionation pathways). It might also be useful to further discuss alkenone-producers, including which have CCMs and possible differences among alkenone-producers. In the studies compiled here, is there an idea of which producers are present (i.e. coccoliths preserved in the sediment)? Any size-corrections?

Throughout the manuscript, there is almost no mention of the other possible causes for the breakdown relationship between epsilon p and dissolved CO2. Although CCMs are certainly a strong possibility, the author should also consider changes to the "b" factor or environmental conditions. These need to be addressed in the Introduction and later on in the Discussion. Has the author considered looking for indicators of e.g. upwelling (which would increase the availability of aqueous CO2) or the BIT index (indicating increased terrestrial input, effecting nutrient availability or species composition change)? If possible, include site information such as estimated depth and distance from coast, as this is important to interpreting the results.

Following up on this point, Lines 187-188, the author states that areas of warm water (i.e. tropical or shallow shelf regions) should be avoided. However, essentially all of the sites used in this study are tropical low latitude (30° N to 30° S) and all look quite close to the continents, likely to be shallow. Is there a possibility that the sites are the issue (e.g. warm waters, upwelling, growth factors), not necessarily the proxy mechanisms? This Lines 187-188 statement also seems at odds with Lines 50-51, where the author states that low latitude, gyre sites are likely more oceanographically stable. In the Methods, the author discusses the use of phosphate to determine b. Could the author briefly include why they are not considering the findings of Zhang et al. (2019; 2020)? Any possibility of comparing with δ15N values? (see Andersen et al. 1999 in Use of Proxies in Paleoceanography, Ch. 19, 469–488). The author uses an uncertainty of 11% on b, though the actual possible range is extremely large, ranging from about 50 to 200, as seen in Pagani (2014).

In the Results, Line 102-107, the author suggests that CCMs only come actively start pumping under a certain low-CO2 threshold. This needs further support/references, given that the literature has shown that CCMs are quite complex in their function and varied among species (e.g. Reinfelder, 2011, Annual Review of Marine Science). Line 105-107: rephrase as it is currently misleading. If we assume that carbon concentrating mechanisms are prevalent, then the proxy would perform least well under low CO2 concentrations. However, as currently phrased, if the alkenone-based proxy "relies on the assumption of a purely diffusive uptake of carbon", then actually, we would expect the proxy to perform the same as it does at any level.

—Figures and Tables—

Overall, these are very impressive figures. There is a lot of repetition throughout (e.g. Fig. 3 and Fig. 10 are nearly identical) but is effective for telling this story.

Table 1: I suggest adding a column with the approximate age ranges for each site. I would also suggest giving this table some kind of structured order (maybe by latitude?)

Fig. 2: NIOP 464 should be a star but is expressed as a square (there are two square symbols). It is difficult to distinguish these shapes, as they are very small (e.g. the circle and hexagon look identical unless I zoom in). Please add the site numbers next to the locations or at the very least, make the symbols more distinct with an accompanying legend on the figure.

Fig. 3: Consider including the site symbols.

Fig. 6: Consider indicating the breakdown point of proxy vs ice core (e.g. using a dashed line)

Fig. 7: Between ~400-500 [CO2(ep-alk)/uatm], why are there two separate estimates for [emulated uncertainty/uatm]?

Fig. 8: Because Fig 6 and 8 are so similar and are constantly discussed together, it might be worth combining these into one figure with 4-quadrants (instead of two figures

with 2-quadrants).

Fig. 10: Gorgeous!

—Minor comments—

There are numerous spelling and grammatical issues throughout the manuscript, for example: Line 20 (isotopic), Line 26 (Noelaerhabdaceae), Line 106 (diffusive), Line 145 (calculated), Fig. 4 (estimate). Some of the references also have incorrect the incorrect doi or link. Please revise.

Line 20 (and throughout): Add “stable” before carbon isotopic composition

Line 28 (and throughout): Add “concentrations” when regarding atmospheric CO2

Line 29: Consider including other CO2 proxies, e.g. paleosols, leaf gas exchange models, liverworts, C3 plants

Line 33: I would not consider less than 400 uatm “moderate to low”. The author may avoid the subjective term altogether by rephrasing to “. . . at atmospheric CO2 concentrations below 400 uatm of the Pleistocene”.

Line 36: Although the Super et al. (2018) SST reconstruction is incredibly useful, I would not consider the Miocene a “resolved” issue. The Miocene CO2 is a highly debated topic at the moment.

Line 46 (and throughout): Add “values” after all δ13C

Line 118-121: Remove “such as” throughout. Here, the author includes every single site, so there’s no need to express them as examples.

Line 143-150: Please break down into several sentences, quite difficult to read.

Line 167: Repetitive sentence

Line 175: Remove “even”

Line 196: “Recent” what?

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