**Climate
of the Past**

Discussions

Interactive comment on "Insensitivity of alkenone carbon isotopes to atmospheric CO_2 at low to moderate CO_2 levels" *by* Marcus P. S. Badger et al.

Anonymous Referee #1

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Badger et al. present an examination of the CO2 proxy derived from the stable carbon isotope composition of alkenones in marine sediments, assessing the potential factors driving apparent differences in the sensitivity of this proxy to CO2 under different climate conditions. The accurate and precise reconstruction of atmospheric CO2 is of critical importance for climate studies, because it allows us to consider in detail the overall radiative forcing of the atmosphere, the global scale response in terms of climate sensitivity, and in turn to identify regions or systems of sensitivity in terms of their response to CO2 and/or possible feedbacks driving CO2 variations. Previous investigations have proved valuable for providing information on global climate sensitivity to CO2 forcing beyond that which can be determined from the instrumental record or model experiments. It is therefore important that the highest quality CO2 data can be

generated, and this manuscript is a very valuable contribution.

As outlined clearly by Badger et al., there is a history of two different proxy systems being applied. One based on boron isotopes in foraminifer calcite, and the second utilising the known isotopic fractionation which occurs in alkenones during coccolithophore production, and which has been shown to be related (in part) to aqueous CO2 concentrations. A long standing challenge for these two proxies has been the observed discrepancy in the absolute values of atmospheric CO2 which are recorded, especially during the Pliocene and Pleistocene. As outlined here, the close alignment of recent boron-derived CO2 measurements with ice core CO2 data now prompts detailed examination of the alkenone proxy, to understand why this seems insensitive to the large fluctuations in late Pleistocene glacial-interglacial cycles. Badger et al. undertake this testing here, and also for the late Pliocene ($\sim$2.8 Ma). Their approach is well designed: they avoid issues around comparing samples from different locations/times by specifically applying both proxy approaches to the same sediment samples. They also push the data further than simply making descriptive, visual comparisons: by using the ice core CO2 data as their target, they use Bayesian analysis to explore whether the parameters used in their calculations can account for some of the discrepancies. This is a really valuable part of the manuscript. The boron isotope data has already been published, and whilst some of the alkenone data has previously been published (>3.0 Ma), both a larger detailed data set and interesting statistical analyses are presented for the first time here to allow the authors to thoroughly tackle the stated problem.

The authors identify two main issues: (1) CO2 reconstructions from alkenones record interglacial values but not glacial values for the late Pleistocene; (2) CO2 reconstructions from alkenones in the late Pliocene show little difference to those of the late Pleistocene (despite boron estimates suggesting higher Pliocene CO2). There is therefore some insensitivity of the alkenone CO2 proxy to known variations in CO2, which requires a re-examination of this proxy. Their Bayesian analysis highlights a potential influence from the SST calculations (for the Pliocene data) as well as potential flaws in

the way that physiological factors in the alkenone producers are accounted for. These are critical findings, and suggest that with our knowledge as it stands, alkenone stable carbon isotopes should not be applied as a proxy for CO2.

Overall the manuscript is generally well written (some minor typos), with high quality figures. It is clear that further and intensive work is required to address the concerns here, but the authors make some logical suggestions about areas to be targetted, drawing on a range of literature in support.

My main concerns rest with a need for some increased detail in the Introduction (to strengthen the need to tackle the question they pose) and Methods (at times it feels that the details are rather swiftly handled). I also have some questions around the discussion of differences in the signals recorded on glacial-interglacial timescales and longer term (Pleistocene-Pliocene). My suggestions are provided in more detail below, alongside some minor corrections (typos etc.):

(1) The Introduction (page 2) makes many statements about 'low' and 'high' CO2 worlds, but no numbers are given. It would be useful to give this context, considering that an expected audience might span Quaternary scientists (for whom an interglacial CO2 might be 'high') and those interested in Cenozoic climate evolution. Either state the known ranges where descriptive terms are used, or consider tabulating some of the studies you cite. Likewise, on page 2 lines 20-21 there is a note to different earth system sensitivity studies and their 'differences', but it isn't clear whether these are (in)significant, within error etc. Adding some of these details would really help the reader to get a quick sense of whether the problem posed here (different CO2 from different proxies) is something of major importance, or more nuanced and perhaps less critical.

(2) Methods detail. The methods section is well written, but on several occasions some details are missing which would help the reader to follow the flow and/or to understand the rationale for why certain approaches were taken. Specifically:

a. page 4 line 11: which alkenone-SST calibration was used? what was the value of modern salinity? The same as stated later for boron isotopes?

b. page 4 line 14-15: what were the instrument conditions for the d13C analysis? (GC method, IRMS conditions, reference gases or standards used for d13C ...). Or, less ideally, make reference to the Badger et al. (2013) study but only if the full instrument conditions are clearly stated there.

c. page 4 line 14-15: You state where the boron measurements were taken - for consistency can you also say where the d13C was measured?

d. page 5 line 5: this range and uncertainty for UK37 and calcite d13C are not explained. Given known non-linearity in the SST calibration at the upper end, and the notes of analytical variation in generating SSTs in this study (line 7 on this page), can the authors state whether this range of uncertainty is more than required, or is it instead a realistic estimate when different calibrations and replicates are considered? Later in the manuscript there is a suggestion that 'realistic' values are the focus here, but that is not obvious from this paragraph.

e. page 5 line 10: state how was the disequilibrium was accounted for, even if it is just a simple step.

f. page 6 line 1: confirm whether these are the same salinity values used for the alkenones (see comment (a) above).

g. Page 6 line 5: clarify whether these 'Values from Foster' are the reconstructed CO2, or something else (the inorganic chemical constants from the previous sentence?).

(3) Discussion of different timescales. On page 7 (line 17) the authors state that the pCO2 record is "largely stable and invariant ... through both the Pliocene and PLeistocene...". But in Figures 3 and 4 I would argue that there is still variability on orbital (glacial-interglacial timescales) which can be identified in the original alkenone d13C data as well as in the reconstructed pCO2. The apparent stability and lack of variance

is instead reflected in the comparison of the longer term data sets i.e. between the Pliocene and Pleistocene, but only for pCO_2 (all other measurements do seem to show an offset). This statement on page 7 (line 17) requires some expansion to account for the differences in temporal response i.e. whether there is "a lack of variability". What now becomes intriguing is that not only does pCO_2 fail to record Pleistocene glacials, but apparently also Pliocene interglacials, despite offsets being determined in the original alkenone d13C and epsilon-p values.

a. page 10 line 24: notes to the possible influence of an incorrect SST calculation on the CO_2 calculation. Here, it would be useful to reflect on the uncertainty range used in the original calculations. Would using a different SST calibration yield a better result, especially given the known non-linearities in UK37-SST calibrations at high SSTs?

b. page 11 paragraph 2: parameterisation of physiological factors. The authors note that the dominant alkenone-producing species today is Emiliania huxleyi. But, given the importance of physiological factors suggested here, is it known that E hux has always been present/dominant at this site through the Pleistocene glacial-interglacial cycles? (the cited paper by Winter et al., 2002 is for modern seawater) Is it known which other species might contribute, and if they are closely related? For the Pliocene, this becomes perhaps more crucial: the manuscript does not highlight that in the absence of E hux, there must be a different set of producers in the Pliocene (which could perhaps account for a different relationship between epsilon-p and CO2?). Is there any information from this site about which coccolithophore species are present in the Pliocene and through the Pleistocene? If there isn't, then it would still be useful to state this as an uncertainty. Have the authors looked at alkenone accumulation rates as a possible indicator of export flux (and potentially productivity) to see if there are any glacial-interglacial or Pliocene-Pleistocene differences?

Minor corrections

- Format UK37' with the correct sub/superscript throughout

- page 7 line 16 – comment about glacial temperatures: no comment made about the unusually cold SST which isn't in the glacial

- page 6 line 11 – explain how "using alkenones limits the variation of cell geometry"... aren't alkenones synthesised by multiple species of haptophyte, which could have different cell geometries? Any citation for support?

- page 7 lines 18-20 – this information about estimating 'b' seems out of place here, and interrupts the flow. Better in the methods section, or in the paragraph which follows where the differences to Seki can be outlined?

- page 10 line 15 – "and test which variables maybe responsible" ?

- page 10 line 16 – "largely invariant for the Pleistocene ..."?

- add analytical uncertainty bars to Figure Panels 3a and 3e (or state if these are too small to be seen)

- why are figures 3 and 4 showing different width of time for pliocene? Please can figure 3 show the pliocene data as well (which is shown in figures 2 and 4?)

- caption figure 4 – isnt lith size panels a and d? Clarify that the drop in lith size (page 9 lines 12-15) is reflected in mean/median (figure 4?), since there doesn't seem to be any shift in the ranges between the two time intervals.