Climate of the Past Discussions

Clim. Past Discuss., referee comment RC2
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Comment on cp-2021-62

Anonymous Referee #2

Referee comment on "Revised alkenone $\delta^{13}C$ based CO_2 estimates during the Plio-Pleistocene" by Osamu Seki and James Bendle, Clim. Past Discuss., https://doi.org/10.5194/cp-2021-62-RC2, 2021

The manuscript considers the potential CO2 implications of published determinations of carbon isotopic fraction in phytoplankton biomarkers (ep shorthand for epsilon p throughout) over the last 5 million years. The manuscript does not present any new data nor propose a new framework for calculation of pCO2 from ep. Rather it suggests two minor adjustments in the original calculation of pCO2. First it proposes application of a constant adjustment factor of pCO2 ranging from -36 ppm to +30 ppm to the results of a given site. Secondly it suggests two small adjustments in the "b" coefficient used to convert ep to CO2 at a given site, which in some models have been estimated from PO4 concentrations - the adjustment to use average mixed layer rather than surface ocean PO4, and for two sites the use of a specific regional rather than global correlation.

Overall, I do not find this contribution suitable for further consideration for publication in Climate of the Past. The contribution does not provide a reasonable discussion of the current and recent advances of the framework for interpreting ep and its relationship with CO2, and neglects key references. The contribution is not well organized to clearly set up the rationale for its approach and why this approach is advantageous in light of current understanding. Errors in key equations (eg Eq 2) further give the impression of a hastily prepared contribution. FInally the scope of the contribution - with no new data, no new interpretative framework - is really insufficient for an article in a journal of the standing of Climate of the Past. It jiggles with a few details but does not provide much helpful for improving the big picture or useful to future studies.

- **Missing a meaningful assimilation of previous work and its relevance to the proposed recalculations**

Recent evaluation of available ep data for periods in which CO2 is independently known (water column, core top, and late Quaternary glacial cycles) has highlighted a number of challenges with the original model for pCO2 estimation used by the authors here (assuming a CO2 slope following a diffusive regulation of carbon uptake and the inference of an empirical relationship of the form intended to be presented in equation 2)

ep=ef- (b/CO2aq)

The introduction and discussion of Seki and Bendle give only cursory citation to the state of the art, without addressing the challenges recognized in previous studies and the implications they have for the exercise presented here.

(a) Zhang et al 2019 have documented that the non-CO2 (physicological) factor b is highest during the interglacial and lowest during the glacial, suggesting that present day photic zone correlations between b and PO2 are not broadly representative of the past. They highlight a greater ep sensitivity to glacial interglacial variations in sites of higher CO2 than lower CO2, opposite to predictions of diffusive behavior.

(b) Stoll et al (2019) document that over glacial cycles, the difference between observed ep and that predicted by diffusive models is correlated to CO2 aq, suggesting that diffusive models overestimate the ep sensitivity to CO2 aq, a finding consistent with additional data presented by Badger et al (2019).

Both results a) and b) imply that application of a constant "b" derived from interglacial (core top or water column) regressions to PO4 to ep measurements downcore can lead to errors in estimating the magnitude of past changes in CO2, *regardless of the water depth or regional regression from which this b might be derived.*

(c) Phelps et al (2021) have suggested that integrated irradiance, rather than growth rate, is the main physiological influence on ep

d) Wilkes and Pearson (2019) have highlighted that ef in alkenone producers was observed to be -11 rather than -25 as generally implemented in Eq 2, implicating a significantly different sensitivity of ep to CO2 and a large role for CCM-related processes in producing high ep values

e) Hernandez-Almeida et al (2020) have presented several proxies for estimation of mixed layer PO4 concentrations in the past (should be acknowledged line 104-105); and also document that growth rate is not the key driver of b (contrast with line 176).

These results have additional implications for the processes responsible for the observed covariation of b with PO4 and its potential to generate robust estimates of pCO2 in the past.

This paper therefore needs to acknowledge these previous findings and account for them and justify why it is useful to neglect all of these advances to return to previous paradigms despite the large errors that have been shown to result from application of such paradigms.

In the introduction the paper gives as a motivation improving the estimates of absolute values of CO2 by reducing the "up to 150 ppm errors" from not accounting for "physical oceanography" . (lines 47-48.) yet in lines 185-187 appears to suggest that the neglect of CCM in this approach will at least generate robust trends, implying that the absolute values might not be accurate but this is oK for the goal of the study. This reads as an inconsistency in the goal of the study.

- **The idea to use mixed layer PO4 concentrations to estimate b is not novel here, and the previous papers describing the idea has not been cited nor contrasted with the current approach.**

Andersen et al (1999) were using PO4 concentrations averaged over the 0-50m depth interval to evaluate b vs PO4 relationships in the South Atlantic. Pagani et al (2002) interpreted core top data in the Pacific using consideration of alkenone production depth in each setting (ranging from 0 to 160 m) and considering production seasonality, and estimated PO4 for the relevant production depths, a more sophisticated approach than that taken here.

Even the publication in which much of the ep data recalcuated here were originally presented describes " We use alkenone unsaturation indices (UK'37) to determine SST and assume haptophyte production depths between 0 and 75 m at each site, bounding a range of [PO43−] determined from modern mean-annual-phosphate depth profiles (Supplementary Information) "

Thus line 111 which states " standard approach assumes alkenone production depths at the surface of the mixed layer" is not an accurate representation of the more sophisticated approaches that do exist in previous studies.

Section 3.4 on variations in cell geometry is not well-reasoned

This section cites studies without discussing the fundamental issues. First of all Zhang et al 2020 contrast with previous approaches and suggest that cell size (coccolith size) is a proxy for growth rate, and the net effect of decreasing cell size on pCO2 estimates is opposite to the effect considered in previous treatments evaluating the surface area to volume process or empirical culture data (eg Henderiks et al 2007; Phelps et al 2021, Stoll et al 2019). This fundamental difference should be acknowledged, not lumped into a single statement that all suggest ep is affected by cell geometry. Additionally, the authors claim that an influence of cell geometry based on changes in coccolith size should not be considered, because alkenone accumulation rate in one site does not covary with the accumulation rate of coccoliths inferred to produce the alkenones. This interpretation ignores the important influence that contrasting preservation factors may have on accumulation rate of organic components (sensitive to stabilizing mineral and deep sea O2) and calcium carbonate components (sensitive to bottom water carbonate undersaturation). The authors furthermore present no alternative producer of alkenones other than the lineage responsible for modern alkenone production.

The presentation of the paper:

Error in the key equation 2: the second ep should be ef

In methods section, it is unclear why all of the steps in ep and SST calculation are described. Was ep recalculated from the individual data, and if so why? ONly because the authors have adopted alternate SST equations? Also it is unclear why the authors have adopted these particular Uk'37 calibrations rather than Tierney et al Bayspline; additionally it is misleading to report only analytical error component on SST and not the calibration error which is substantial in the high temperature range. The first few lines of the methods should clarify what was taken "as published" and what was recalculated and why.

Really the introduction should have framed the question clearly and indicated exactly what aspects of "physical circulation" were leading to such gross errors in pCO2 as to justify a new paper.

Why is the post-industrial Takahashi et al (2009) used as the reference for pre-industrial (through Pliocene) air-sea disequilibrium corrections. This is not a coherent approach, the pre-industrial air sea disequilibrium must be used at each site.

Table 1 I would expect to list the source of the input ep data for each site.

References cited:

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