Comment on cp-2021-62
Anonymous Referee #1

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-RC1, 2021

Overview

This manuscript covers precisely as its title suggests, "Revised alkenone $\delta^{13}C$ based CO$_2$ estimates during the Plio-Pleistocene". In the manuscript, the authors apply the traditional method for the alkenone-based CO$_2$ proxy, in which the proxy model assumes passive diffusion of CO$_2$ into the cell. Their revisions to the alkenone-based proxy are based on corrections for regional differences in physical oceanographic factors, including depth, season of production, and air-ocean disequilibrium. Correcting for these physical oceanographic factors can result in offsets of up to 150 ppm and now set the alkenone-based CO$_2$ estimates in the range of other reported CO$_2$ reconstructions.

Overall, the paper addresses a relevant scientific question within the scope of CP: testing the influence of regional differences in physical oceanographic factors on the alkenone-based CO$_2$ proxy. However, I have some questions regarding the aim of the study and some of the assumptions made, and there are unfortunately many presentation issues, which I outline below.

Major Comments

My main comments are related to the aim/perspective and some of the assumptions in the approach.
The authors state in the introduction (Line 44-46) that “the aim is to not provide newly definitive CO2 estimates but to demonstrate the importance of physical oceanography”. However, the authors cite that Pagani et al. (2010; 2011) has already identified that physical oceanography affect values up to 150 ppm (Line 47, Pagani et al., 2010). This calls the question the novelty of this study.

I would also like some clarifications on the assumptions used to make these revised calculations and whether these revisions could be replicated in future studies, e.g. at different sites or during different time periods.

For example, there needs to be a bit more care around [PO43-]. It seems like mixed messages to state on one hand that this must be corrected for, and then on the other, state (Line 103-105) that modern values can be used under the assumption that it has not differed in these open marine settings. In other words, the study emphasizes the importance of changes in region but entirely neglects time. Have the authors considered estimating [PO43-] from δ15N values?

Another example of needed clarification: in some sections, the authors refer to these sites at open marine settings, while in other sections, the authors discuss upwelling and sea-air disequilibrium. Are these open or upwelling sites?

The authors state that they control for active upwelling (Line 154). However, the studies that the authors cited for this upwelling data (Takahashi et al., 2007) demonstrate that there are large changes within the year, large changes from year-to-year, and that these dynamics have been influenced by anthropogenic CO2 rise. Based on this, these upwelling intensities would presumably change over these million year timescales. Again, this appears to be correcting everything to modern day conditions. I think this section needs more explanation.

Another example is with the regional b-term regressions. Three of the six sites use global regressions and three use regional regressions. I think the lack of consistent treatment among sites needs more care.

All raw data needs to be included, either in the manuscript or as a supplement, and all related calculations. This is crucial for replicability and transparency. In addition to those reasons, I would also like to see the raw Uk’37 abundances and ratios, given that some tropical Uk’37 ratios have been known to approach saturation during this time.

Along with the raw data, all estimates of uncertainty should be included. For example, the authors only include the analytical error on the Uk’37-based proxy, but do not include the error on the proxy itself which is much greater (closer to 4 degrees). These uncertainties should be included in the CO2 estimates shown throughout the manuscript.
In the Introduction, the authors should include a couple sentences to explain what alkenones are (producer, organic compound, etc.) and how the alkenone-based proxy works (e.g. isotopic fractionation), given that this entire manuscript revolves the improvement of this proxy.

Specific Comments

Is Site 1000 used? It is occasionally mentioned (e.g. Fig 2, Line 168) but then is not included in other places (e.g. Fig. 1 map of the sites or discussions).

There are numerous mistakes in equations, grammar, spelling, and formatting throughout the manuscript, which have made this manuscript difficult to read and understand. This is not an exhaustive list, but some examples include:

Eq. 2: Fix the equation to read: $\epsilon_p = \epsilon_f - \frac{b}{[CO2]}$. In its current form, there is no $\epsilon_f$ and there is a missing bracket on the CO2(aq).

Line 16-21: Multiple grammatical issues (“though”, “understating”)

Line 48: Fix year, current cited as Pagani et al., 1010

Line 57: Delete “an”

Line 85-88: Why are these, for example, $\delta$CaCO3 instead of $\delta^{13}$C of CaCO3

There are two sections labeled 3.7.

Fig. 2: Add a title to explain what this figure is, add consistency in the panel labeling, and correct the numerous reference formatting issues.
Fig. 6: Change the scale to show all data and uncertainty (the error bars appear to extend beyond the figure). Change the y-axis label to “Reconstructed CO2” or similar (currently, the y-axis is labeled as boron-based CO2, but the figure shows both boron-based and alkenone-based CO2).

Define terms the first time they appear (e.g. $\delta^{13}C_{37}$, $\delta^{13}C_{CaCO3}$).

Please also note the supplement to this comment: