Climate of the Past Discussions

Clim. Past Discuss., referee comment RC2
https://doi.org/10.5194/cp-2020-158-RC2, 2021

Comment on cp-2020-158

Anonymous Referee #2

Referee comment on "Atmospheric CO_2 estimates for the Miocene to Pleistocene based on foraminiferal δ^{11}B at Ocean Drilling Program Sites 806 and 807 in the Western Equatorial Pacific" by Maxence Guillermic et al., Clim. Past Discuss., https://doi.org/10.5194/cp-2020-158-RC2, 2021

The manuscript by Guillermic et al presents new Mg/Ca and d11B measurements of planktonic foraminifera spanning the last 17 million years from the Western Pacific Warm Pool at ODP 806 and 807 with the aim of estimating past evolution of Sea Surface temperatures and atmospheric pCO2. . The most significant new contribution of this study is the addition of measurements between 5 and 17 Ma, as the majority of previous d11B measurements since the mid-Miocene are concentrated in the last 4 Ma whereas low resolution data illustrating long term trends in the 4 to 17 Ma time window are to date more limited. The estimation of pCO2 from d11B of foraminifera in this time period is sensitive to a number of uncertainties, including the assumptions of the evolution of d11B of seawater and alkalinity over time. This contribution employs the current best estimates for these parameters and illustrates the sensitivity of the pCO2 estimate to uncertainties in these parameter choices.

While the processing of the new data is clear and uses up to date alkalinity and d11B seawater estimates, the comparison with previous pCO2 estimates is not presented as clearly as it could be, and the discussion of phytoplankton (alkenone) pCO2 estimates for the Miocene is not up to date. I summarize the main content issues which I believe need to be addressed for this manuscript to provide a coherent step forward in understanding of pCO2 in this time interval. Subsequently, I have some suggestions on the organization and structure which I propose could improve transparency and clarity in the manuscript, as well as some more detailed comments.

Content and interpretation:

- While the authors present for their own data an updated estimation of the CO2 considering recent proposals for d11B seawater (eg Greenop et al 2017) and alkalinity history derived from Caves 2016 or Zeebe 2005, they do not include in figures (and therefore not thoroughly consider) the published d11B-CO2 estimates which have been recalculated with these same alkalinity and Greenop et al 2017 d11B seawater parameters, namely those compiled and homogenized in Sosdian et al 2018. This is an essential update to make so that the new data from ODP 806 and 807 can be considered in context, and so that the new data contribute to an integrated better picture of the trends and absolute values. In particular, the latest Pliocene CO2 trend is quite clear in the Sosdian et al compilation. Additionally the early Pliocene and Miocene values in the Sosdian et al compilation are higher than in the original publications, and therefore are more consistent with the results as plotted here. Otherwise there is a disconnect between the figures (not homogenized parameters) and the textual mention of pCO2 values recalculated by Sosdian et al 2018. Once this is updated in figures, the discussion should also be updated and clarified.

- The estimation of tropical SST over this time interval is not trivial given the uncertainty in seawater Mg/Ca, and I think this warrants further clarification and transparency. An inferred seawater Mg/Ca history is sketched in Figure 2 but the Figure caption does not specify the origin of this curve. The calculation equations are provided in supplement but the input data on seawater Mg/Ca should be illustrated along with the data forming the basis for its estimation (eg the basis from which it is derived). Figure 7 illustrates some uncertainty around the SST, but the Figure legend does not indicate what is represented by this uncertainty. To what extent does the uncertainty in calculated SST (e.g choice of Mg/Ca seawater correction, and regression) affects the estimated pCO2 due to solubility? Also, have the authors considered the influence of a pH correction to the Mg/Ca SST, as conducted in recent study (Sosdian and Lear, 2020) and shown to be significant across the MCT (Leutert et al 2020)?

- The references on the alkenone pCO2 reconstruction are not up to date. Lines 308-310 refer only to older publications based on a theoretical diffusive model of CO2. Recent metanalysis of culture carbon isotopic fractionation (epsilon p or ep) data suggested that due to the operation of carbon concentrating mechanisms, ep exhibits a much lower sensitivity to CO2 than originally inferred; application of the sensitivity observed in cultures to sedimentary ep measurements yields a significant pCO2 decline since the mid-Miocene (Stoll et al., 2019). This low ep sensitivity is supported by recent determinations over glaial cycles (eg Badger et al 2019) and further suggests significant pCO2 decline in the late Miocene (Tanner et al., 2020) which would be a relevant reference for comparison in section 3.4. A detailed updated discussion is provided in Rae et al, 2021.

- The discussion of previously published d11B records is in many places overly superficial. For example in lines 314-316, previously published d11B records of the MCO (Sosdian et al 2018, Greenop et al 2014) are diminished in importance by suggesting " it is unclear if these values accurately reflect the atmosphere given the sites may or may not have been in equilibrium with the atmosphere.." The cited studies reflect multiple sites (ODP 926, 999, 668, 761..), all in comparably reasonable locations to be close to equilibrium with the atmosphere. Unless the authors would like to present clear new evidence that some of all of these sites are less likely to have remained in equilibrium with the atmosphere than ODP 806 or 807, the original interpretation that these sites (of preindustrial pCO2 disequilibrium <25 ppmv) remained close to equilibrium should be respected, and other potential explanations for the differences should be explored.

- Site 806 and 807 are sites estimated to have fast rates of diagenetic recrystallization (Mitnik et al 2018). For example, averaged over the upper 80 m of sediment (appx 3 million years given sedimentation rates), authigenic carbonate is estimated to comprise 19% of total carbonate at 806 and 36% at 807; in comparison other sites like ODP 999, the authigenic carbonate is <1% of total carbonate in the same depth and time interval. It might be helpful for the authors to acknowledge this and comment on evidence for how this may or may not affect the 11B and Mg/Ca results of the planktic foraminifera.

- The coherency of the d11B-pCO2 estimates with ice core pCO2 is always a useful comparison, but its effectiveness relies on the precision of the age model used for this portion of the sediment core (as well as the precision of the ice core age model, which cannot be investigated here). Particularly relevant to the last 800 ka, section 2.2. should detail on what the age models are based not just the publication source. From the reference cited for the last 1.35 Ma, it appears the age model is based on d18O of planktic G. ruber - is it still tuned to SPECMAP chronology as in Lea et al 2000, or is it retuned to LR05? In Figure 5, I think it would be better to show the site 806 d18O G. ruber in the upper panel, eg the metric from the same site and age model as the d11B estimates, rather than the LR05. Then, I would suggest in addition to the time series, a scatterplot of the d18Oplanktic vs d11B-based pCO2 from 806 (assuming that d18O is available for the same core intervals - this gives an estimation of the coherency of pCO2 and glacial cycles in the same core without age uncertainties; were any d18O made on 807?), and also importantly a scatterplot of the d11B-based pCO2 vs ice core pCO2 .

Suggestions on organization:

I recognize the challenge of illustrating the effects of possible assumptions of d11B and alkalinity on the final CO2 calculation, but I am not convinced the current organization is the most effective and it leads to an unusual ordering of figures. The Methods heading "2.7 " effectively starts presenting results and sensitivity analysis.

The authors might consider if a more direct presentation of results and discussion could:

a) begin with section 3.1, and start with the current Figure 5 - the last 800 ka uses modern d11B sw and alkalinity so is not subject to the uncertainties/sensitivity analysis on both parameters .

b) continue with a section on the measured indices and summarizes the findings in of the current Figure 2 which presents the measured results

c) comment on the inferred trends in SST and uncertainties in their calculations , and comparison with other SST histories both from Mg/Ca (Sosdian and Lear 2020) as well as TEX86 (Zhang et al. 2014,) Lines 286-288 needs to clarify if the measured Mg/Ca is consistent with the other published Mg/Ca, or if the calculated temperatures are consistent with the published Mg/Ca calculated temperatures; and in the latter case, have the temperatures for all these studies been recalculated using the same assumptions of Mg/Ca seawater and temperature regression as used for the new data here?

d) discuss sensitivity of Neogene pCO2 estimations to assumptions of d11B seawater and alkalinity, which could introduce the current Figures 3 and 4 as the sensitivity of the results to d11Bseawater and alkalinity (and is there sensitivity to SST) and incorporate the introduction to this currently in the methods section

-continue with the discussion of temporal trends in calculated pCO2

As the manuscript begins to go through the main pCO2 results, I am not fully convinced that the current organization of the discussion is the most straightforward and concise. In the current organization the authors new data seems like it gets buried within the discussion. If the current time interval based structure is used, I believe it would be useful if in each heading of the results/discussion section, the authors presented first the summary of their own new results, and followed it with comparison to other proxy pCO2 results and finally to climate. Also, if organization based on time periods is used then clearer section headings are needed For example 3.3 is "Miocene" but 3.4 is "Late Miocene" which is a period nominally included included within the Miocene heading. I am not sure if division of the Pliocene into the warmth then glacial intensification then Pleistocene (3 sections) is really needed to discuss the author's new data, as these are time periods with substantial previously published data and interpretations and the authors new data are largely consistent with and reproduce these earlier results. Overall, I believe the discussion section can be streamlined and made more concise. Some sections such as 3.9 seem very extraneous, as there is really limited new SST data and it is not coherently presented to evaluate east west gradients; I suggest this section be eliminated from the discussion. Section 3.8 is not really clear in advancing a mechanism for the CO2 variation, and I suggest the key points might be effectively commented within the context of the Miocene and Pliocene sections of the text.

Detailed comments:

ALL of the figures should more accurately show the true data density, including Figures 3 and 4 - continuous fill patterns and no symbols is not a clear way to represent the data. At minimum, symbols are bars are needed to show where there are datapoints (alternatively rather than complete shading, points with error bars could be illustrated to show the sensitivity).

And in FIgures 6-8 and 10, the broken shading at least alerts to the data gap, but I think it would be ideal to show no shading over the long intervals without datapoints.

Please clarify the basis of the age model (eg benthic d18O, biostratigraphy, etc), Section 2.2 is not sufficiently clear.

Could a more direct heading for Methods section 2.6 be developed?

References cited (not cited in the manuscript):

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Rae, James WB, Yi Ge Zhang, Xiaoqing Liu, Gavin L. Foster, Heather M. Stoll, and Ross DM Whiteford. "Atmospheric CO2 over the Past 66 Million Years from Marine Archives." Annual Review of Earth and Planetary Sciences 49 (2021).

Sosdian, S. M., and C. H. Lear. "Initiation of the Western Pacific Warm Pool at the Middle Miocene Climate Transition?." Paleoceanography and Paleoclimatology 35, no. 12 (2020): e2020PA003920.

Stoll, Heather M., Jose Guitian, Ivan Hernandez-Almeida, Luz Maria Mejia, Samuel Phelps, Pratigya Polissar, Yair Rosenthal, Hongrui Zhang, and Patrizia Ziveri. "Upregulation of phytoplankton carbon concentrating mechanisms during low CO2 glacial periods and implications for the phytoplankton pCO2 proxy." Quaternary Science Reviews 208 (2019): 1-20.

Tanner, Thomas, Iván Hernándezâ□□Almeida, Anna Joy Drury, José Guitián, and Heather Stoll. "Decreasing atmospheric CO2 during the late Miocene Cooling." Paleoceanography and Paleoclimatology (2020): e2020PA003925.