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Interactive comment on "Eccentricity-paced atmospheric carbon-dioxide variations across the middle Miocene climate transition" *by* Markus Raitzsch et al.

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GENERAL COMMENTS Obtaining more B isotope-pH and CO2 estimates for the middle Miocene climate transition is a long overdue goal, making this study very timely and of great importance. The authors provide a comprehensive view of CO2 evolution for this period and potential mechanisms overlying potential eccentricity driven variations. The paper would benefit from some re-organization and focus on clarity, incorporation of recent studies in the discussion and the data, and a more comprehensive propagation of uncertainties, beyond the sensitivity analyses performed for alkalinity and salinity.

AC: We thank the referee for his constructive and thorough review of our manuscript. We will address all questions and comments in the following.

SPECIFIC COMMENTS Uncertainties: a) The analytical uncertainty reported is quite small compared to the uncertainty of replicate analyses. There may be differences between the use of IC vs. Faraday detectors in different studies and here. Nevertheless, the authors should provide more details here as well on how they calculate analytical uncertainty. For example, the consistency standard used to calculate long term precision should have been run at similar concentrations to those of samples, and the uncertainty of this should be larger at low B-levels. Additionally, the authors should provide more details on the B blank contribution (if any).

AC: The reviewer is right, the long-term reproducibility is taken from runs with different [B], but not that much as the referee thinks, as most analyses were performed using ion counters or Daly detectors. We will check the "Daily performance" file to extract the values derived from measurements at $\sim$2-3 ppb. However, the average uncertainty from the sample replicate analyses is not so far from the long-term reproducibility of a consistency standard, given that all uncertainties for replicates <0.3 permil are replaced with the long-term value of 0.3 permil. If the actual numbers are taken into account, the average uncertainty of replicate measurements is $\sim$0.35 permil, which is very close to the long-term reproducibility. This small difference of 0.05 permil may be due to the fact that we run our sample rotationally, i.e. like ABC-ABC-ABC, while the consistency standards are run consecutively at the beginning and the end of a session, such as AAA-sample sequence-AAA. This could result in a slightly higher replicate uncertainty for the samples, as the measurements are temporally distinct, which might reflect slightly changing plasma conditions over the course of a day. The change in sample sequencing is certainly something worth looking at in the future. The information on lab blanks is in detail described in our 2018 EPSL paper, but we will briefly echo it in the revised manuscript.

b) Why is d11Bsw error systematic? If weathering is extremely pronounced, couldn't this cause variations in d11Bsw across this time window, even if the average residence time for B may be longer? Even if so, because of the non-linearity of the d11B-pH proxy, at different d11Bsw the dpH and thus dCO2 could differ. Some could, thus, argue the uncertainty in d11Bsw encompasses both uncertainty in absolute value across the MMCT but also potential variations across the window. The authors should provide at minimum two scenarios based on minimum and maximum d11Bsw estimates for this period.

AC: The uncertainty in d11Bsw is systematic, due to the long residence time of boron in seawater, and we think it will thus give a wrong impression of uncertainty in terms of relative pH (and pCO2) changes. However, since also referee 1 asked to account for it, we will either also propagate the d11Bsw uncertainty into the pH uncertainty, or will put our record into an envelope of extreme d11Bsw scenarios, as suggested by the referee. In addition, in the revised manuscript, we will account for the effect of d11Bsw on the d11B_borate/d11B_calcite calibration, but which will not yield much different results, due to the ~1:1 slope of the calibration for G. bulloides (Greenop et al., 2019).

c) The level of details in Fig. 7 with all sensitivity analyses is very much appreciated. However, could the authors provide more explanation on how they estimate the Alk and Temp uncertainties? If they compare to literature or proxy estimates, shouldn't they use the maximum uncertainty reported (i.e. $\pm$ 2C, and $\pm$ 130 umol/kg Alk)? Comparing to other studies: The authors should discuss their results in light of two recent publications for the middle Miocene, Leutert et al. 2020 (Nat. Geo) for both their SST and dpH estimates, and Sosdian et al. 2020 (Nat. Comm.) for C cycle in relationship to climate.

AC: Correct, we will provide more details on the estimated uncertainties used for error propagation, and will discuss the results in context of the new publications. Concerning Sosdian et al. (2020), the same comment came from referee 1 and we will include this contribution in the discussion.

Comparing CO2 records: e.g. Fig. 5: what drives the differences between different

d11B records for the target age-window? Section 4.1 needs some more discussion, with focus on how this new record could differ from previous d11B records. Could there be an upwelling signal at the study site driving those high CO2 estimates when they deviate from the other records? It could also be differences in the calibration used for d11B, or the assumptions for calculating carbonate system parameters. It may be wise to process the d11B records in the same manner, exclude the potential of any regional and variable CO2 disequilibrium, and then merge reliable d11B records into a single record with full propagation of uncertainties. If uncertainties are not propagated, and instead sensitivity runs are provided (i.e. d11Bsw), then better to display relative changes in pH/CO2 instead of absolute values. (Here it may be wise to remove the alkenone CO2 as they are not discussed enough beyond what is already available in the literature and thus do not contribute to the story).

AC: What the referee suggests here is what we applied for the boron-based reconstructions: We re-calculated pCO2 of the Foster et al. (2012) and Badger et al. (2013) data, using a TA of 2000 μmol/kg and a d11Bsw of 37.8 permil, as for our data. This was only mentioned in the Fig. 5 caption, so it was not adequately described in the main text, but will be done so in the revised manuscript. However, we will improve the data compilation and comparison by using exactly the same calibrations (although the differences between the ones used in the different studies are very small), as well as to account for the effect of d11Bsw on the calibrations (which might shift some reconstructions a bit). In addition, the effect of [Ca] and [Mg] of seawater on the dissociation constants will be included. Thanks for the suggestion to create a pCO2 "stack" from all reliable reconstructions. We will definitely try this, but at this point we expect it might not be too helpful since only few data exist with a too-low resolution. Concerning the possibility of a regional signal, the same question came from referee 1, and will be addressed in the revised manuscript.

Focusing on the d11B records available and this new one, it would be also beneficial to display not only CO2 but also pH evolution across the MMCT, and how different records compare.

AC: As we re-calculated the boron-based pCO2 records, using identical boundary conditions (TA and d11BSw), we assume that also the pH curves will mimic the pCO2 curves, but we will certainly test this further.

Site setting: It is argued that the site is not affected by upwelling being north of the frontal systems in the Southern Ocean. However, can this be said with certainty for the middle Miocene? Is there any evidence for that?

AC: As mentioned earlier, we will address this question in the revised manuscript, which was also requested by reviewer 1.

Carbonate system calculations: The authors should consider the effect of Mg and Ca concentrations in seawater on carbonate system calculations (i.e. K1, K2, Ksp), such as in Hain et al. 2015; 2018 or Zeebe and Tyrrell 2019.

AC: Yes, good point. As mentioned earlier, this will be done for the revised manuscript.

Benthic-planktic pH records: Although the uncertainties are very large to make discernible conclusions about pH gradient values during the middle Miocene, it is interesting to further explore the dpH evolution and the surface-to-deep gradient evolution during the Miocene, and what drives this. If the benthic foraminiferal pH record is included, it should be discussed further.

AC: In our opinion, the resolution of the planktic and benthic pH isotope records in Figure S1 is too low to derive a meaningful interpretation concerning the temporal evolution of the surface to deep gradient. We would keep the figure in the supplement, but mention that the interpretation of the surface to deep gradient is limited by the low resolution of the data, especially the benthic curve is of lower resolution than the planktic curve.

Discussion on role of eccentricity and deep water ventilation: Here the section leaves us wanting more! It could benefit from some reorganization for clarity and flow, includ-

ing recent studies such as those mentioned above.

AC: As this point is also raised by reviewer 1, the discussion will be re-organized and extended in the revised manuscript.

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