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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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Raitzsch et al present a new planktic boron isotope record across the mid Miocene Climate Transition, and interpret this in terms of changing CO2 and carbon cycle changes. The record enables deeper interrogation of potential climate and carbon cycle feedbacks during this important interval of global cooling. This interval also spans the end of the Monterey Excursion, which contains the well-known "carbon maxima" events. Having more CO2 data across this interval is very exciting, and thus the submission represents a substantial contribution worthy of publication in CP.

However, the narrative of the manuscript could be much improved – e.g. the conclu-

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Discussion paper

sions are that a particular carbon cycle model is supported by the new records, but this model (or the mechanisms within it) are not referred to in the introduction. Much of the discussion hinges on assumptions of processes that have not been observed but are presented here as fact (e.g., that middle Miocene CO2 variations are caused by changes in shallow water carbonate production). The manuscript also fails to cite some key recent studies. However, I believe that if the narrative of the paper is improved and a few specific scientific questions are addressed then the robust interpretations of this fantastic dataset will be clearer and this will become a really exciting and useful contribution. Below I list the specific scientific questions I would like to see addressed, followed by more minor comments.

AC: We thank the referee for his constructive and thorough review of our manuscript. We will address all questions and comments in the following. The narrative of the manuscript will be changed during the revision.

1. Is high eccentricity definitely associated with decreasing CO2? Would it be more robust to focus on the clear relationship between the d13C and CO2? The key finding presented in the abstract of the paper is that “long-term pCO2 variations between ∼14.3 and 13.2 Ma were paced by 400 k.y. eccentricity cycles, with decreasing pCO2 at high eccentricity and vice versa.” I struggle to see this relationship in Figure 4 or Figure 5 – i.e. an inverse correlation between the pCO2 record and the thin grey line. I’m not saying the pCO2 record doesn’t contain a long eccentricity signal, but the temporal relationship with the eccentricity curve could perhaps be demonstrated more robustly. While I struggle to discern a negative correlation between the authors’ pCO2 record and the long eccentricity cycle, the relationship that does seem convincing is the positive relationship between d13C and CO2 across CM6 (Figure 4 and described in section 3.1). Perhaps therefore a clearer and simpler approach would be to set out different mechanisms in the introduction with their respective d13C-CO2 relationships. E.g., Holbourn et al 2007 ascribes the eccentricity signal in the longer d13C record to EITHER increased productivity and burial of Corg (the classic Monterey hypothesis)

which would result in a negative correlation between d13C and CO2, OR a monsoon-driven increase in shallow water carbonate deposition, removing alkalinity from the oceans and releasing CO2, producing a positive correlation between d13C and CO2, as observed here. This explanation would be particularly useful because the increase in monsoon intensity variability has different impacts on the carbon cycle, but these are not discussed in the introduction. For example, an increase in nutrient delivery to the oceans and increasing Corg burial tends to increase d13C and decrease CO2. But in the Ma et al 2011 model this is outweighed by the concomitant increase in carbonate burial and associated CO2 release. It would be useful if this current manuscript could comment on the robustness of the relative importance of these processes in the model. However, see also my comment below about the uniqueness of CM6 - what might be expected to happen if for example the climate transition led to a general increase in marine productivity superimposed on these orbital variations? Should we expect the d13C-CO2 relationship for CM6 to hold true for all CM events? This complication should be clearly addressed in the introduction also.

AC: The long response time of the carbon cycle appears to be consistent, when comparing other major d13C excursions (for instance, Cretaceous OAEs). However, it is difficult to determine phase relationships, when dealing with relatively short low-resolution records such as at Site 1092. In the highly resolved d13C U1338 record, there is a rebound during the onset of CM6, which corresponds to a precessional warming peak reflected in a transient d18O decrease. This feature is not captured at Site 1092. The age correlation between Sites U1338 and 1092 is in fact quite loose over the onset of CM6, making it difficult to evaluate the timing of the pCO2 increase in relation to the detailed evolution of d13C during the CM6 onset. Another issue is that the 400 kyr filtered curves that are often used to evaluate phase relationships between data sets can be strongly biased by the selected bandwidth. An important consideration here are asymmetries of the 405 kyr cycle in d13C that are not apparent in the filtered curves. Estimated phase relationships are based on the assumption that the corresponding signals are periodic. However, in case of the onset of the positive d13C excursions is fast and would lead to artificial phase relationships when decomposed into sinusoidal base functions. This is especially the case for CM6. In contrast, the rates of change during the peak or plateau and recovery of the d13C excursion are much slower.

2. What is the evidence for the increased shallow water carbonate deposition? As far as I know there is no direct evidence for eccentricity paced changes in shallower water carbonate burial. There are dissolution cycles in deep sea carbonates, but I am not aware of any study that rules out the influence of bottom water mass ventilation on these? I believe Holbourn et al 2007 favoured the monsoon hypothesis due to the 50 kyr lag between eccentricity and d13C. But this lag is not discussed in this manuscript, and no supporting evidence is given for the statements that shallow water carbonate burial changed at this time.

AC: Estimates of Miocene shallow water carbonate burial and shelf-basin fractionation of carbonate accumulation are only available in rather low temporal resolution and do not capture orbital variability that would allow assessment of global trends. Some recent references for global trends include: âĂć Boudreau & Luo, 2017, Earth and Planetary Science Letters, v. 474, p. 1–12, https://doi.org/10.1016/ j.epsl.2017.06.005. âĂć Boudreau et al., 2019 Earth and Planetary Science Letters 512, 194–206. âĂć Levitan, 2018 Fractionation of Carbonate Carbon (Đącarb) Accumulation between Continents and Oceans in the Late Mesozoic–Cenozoic. ISSN 0016-7029, Geochemistry International, 2018, Vol. 56, No. 7, pp. 702–710, Pleiades Publishing. Original Russian Text © M.A. Levitan, 2018, published in Geokhimiya, 2018, No. 7. âĂć van der Ploeg, R. et al., 2019, Cenozoic carbonate burial along continental margins: Geology, v. 47, p. 1025–1028, https://doi.org/10.1130/G46418.1).

Another limitation is that attempts to estimate shallow water carbonate burial on orbital timescale are limited to regional studies in very different environments that cannot be easily synthesized to provide global estimates. The following regional studies have focused on: âĂć Italy (Auer et al. (2015), https://doi.org/10.1002/2014PA002716), âĂć Iberia (Abdul Aziz et al., 2003, Sedimentology, 50. pp. 211-236.

https://doi.org/10.1046/j.1365-3091.2003.00544.x.), âĂć Bahamas (Kroon et al 2000, in Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 166; Reuning et al 2002 Marine Geology 185 (2002) 121-142; Williams et al 2002, Marine Geology 185 (2002) 75-93), âĂć Maldives (Betzler et al 2018 Prog Earth Planet Sci. 5.; Reolid et al 2019 Marine Geology 412 (2019) 199–216), âĂć New Zealand (Ohneiser & Wilson 2018 Eccentricity-paced Southern Hemisphere glacial-interglacial cyclicity preceding the middle Miocene climatic transition. Paleoceanography and Paleoclimatology, 33, 795–806. https://doi.org/10.1029/2017PA003278).

We will add this information to the revised manuscript.

3. Does the Site 1092 planktic d11B record global pCO2? This relationship between d13C and CO2 is key, and is independent of age model issues because the d13C has been recorded at each site and is a global signal. So it is interesting therefore that the Malta record shows a decrease in d11B-derived pCO2 associated with the onset of CM6 (increasing d13C) whereas the 1092 d11B-derived pCO2 shown here shows an increase. This raises the important question – is Site 1092 recording global atmospheric pCO2, or a more localised signal? A more local signal showing C storage in the high latitudes of the south Atlantic over the MMCT would also be very interesting of course. The change in the frontal positions is acknowledged in the text (Kuhnert et al 2009) but the change in stratification at this time is not mentioned. Paulsen (2005) (Bremen thesis) shows an increase in stratification at Site 1092 starting at 13.85 Ma (using the divergence of surface:deep planktonic foraminiferal d18O). Could this stratification have been associated with an increase in surface water [CO2]? This possibility should be addressed in the manuscript.

AC: There is broad agreement that G. bulloides is a planktic foraminiferal species associated with upwelling of cold water at low latitudes. Accordingly, it is consistently used in the monsoonal upwelling zones of the Arabian Sea and equatorial Indian Ocean as an indicator of upwelling intensity. See classic papers of Kroon & Darling (1995) Journal of Foraminiferal Research, v. 25, no. 1, p. 39-52 and Peeters et al. (2002)

Global and Planetary Change 34 (2002) 269–291 and discussion of its utility as pCO2 indicator in upwelling regions by Palmer et al. (2010) Earth and Planetary Science Letters 295 (2010) 49–57. However, this is not the case at high latitudes, and we argue that the majority of G. bulloides lives in the upper 100 m within the mixed layer (Line 66). We will add in the revised text that the plankton-tow data we refer to are from the Atlantic sector of the Southern Ocean (Mortyn and Charles, 2003). Further, we will add the result by Diekmann et al. (2003) that the sedimentological record of this site hints at oligotrophic conditions throughout the Miocene interval. In addition, we think that if the boron isotope signal was mainly driven by a regional change in stratification after 13.85 Ma (Paulsen's data), as envisaged by the reviewer, this would not explain the low pH earlier during CM5, as shown in our record. We will briefly discuss the global/local origin of the signal in the revised version of the manuscript to address this criticism from both reviewers.

4. Is it appropriate to compare the records across CM6 with those of a model that does not consider the impacts of the MMCT itself? CM6 immediately follows the ice growth of the MMCT and is the largest by far of the CM events, making its interpretation more complex than the other CM events. It follows a major sea level fall, which would have affected the shelf:basin burial of carbonate, d13C and CO2 (e.g., Mckay et al 2016, Ma et al 2018). Further, the ice advance was likely associated with changes in ocean circulation and ventilation of bottom water masses (with implications for both d13C and CO2). Is it therefore appropriate to make a straightforward comparison of the d13C and CO2 records to the Ma et al 2011 model without any consideration of these other processes? The Ma et al 2011 model was constructed to explain the long eccentricity signal in the d13C record throughout the Miocene Climatic Optimum, rather than examine CM6 specifically. It is solely forced by ETP, and does not include processes triggered by cryospheric thresholds in the climate system and resulting impacts. On the other hand, the Ma et al (2018) model suggests that a significant cause of the d13C increase at CM6 was the increased weathering resulting from the sea level fall. By saying the results here support the Ma et al 2011 model for CM6, where does that leave our

understanding of the importance of shelf-basin carbonate deposition on global d13C signals?

AC: CM6 does exhibit major differences to the other 405 kyr cycles within the Monterey Excursion, as stated by the reviewer. This is a very interesting point and we will include a brief discussion of possible explanations for the difference in amplitude between CM6 and other Monterey CM events. Changes in shelf-basin partitioning of carbonate burial and enhanced global deep-water ventilation as well as increased weathering resulting from a major sea level fall at 13.8 Ma (Ma et al., 2018), as mentioned by the reviewer, are possible mechanisms to explain the higher amplitude of CM6. In addition, the following mechanisms may have contributed to the amplification of CM6: 1) Increased organic carbon burial by enhanced carbon sequestration through the biological pump linked to intensified upwelling in low latitude areas. 2) Substantial outgassing of CO2 from the deep ocean (d13C of approx. -1 to -2 ‰ into the atmosphere (d13C of approx. -6 to -6.5 ‰ would not only result in increased atmospheric pCO2 but also in a positive excursion in atmospheric d13C. The size of the relevant reservoirs (38000 Gt deep ocean vs. 750 Gt atmosphere, if the proportions were similar to today) would suggest that this process can be sustained over considerable time intervals. 3) The amplitude of 405 kyr cycle paced carbon isotope excursions depends on the size of the global marine DIC pool (e.g. Paillard & Donnadieu, 2014, Paleoceanography, A 100 Myr history of the carbon cycle based on the 400 kyr cycle in marine δ13C benthic records https://doi.org/10.1002/2014PA002693). This size may have decreased following the loss of shelf seas caused by the major regression associated with the onset of CM6 – resulting in a higher amplitude d13C response to eccentricity forcing.

5. How does the pCO2 record compare with the high-resolution B/Ca record of Sosdian et al 2020? It is odd that the manuscript does not compare the d11B-CO2 record with the high resolution B/Ca records published by Sosdian et al 2020. Those authors suggest that the increasing d13C of the CM events is associated with decreasing surface water DIC at Site 761. This is consistent with an increase in Corgburial:Carbonate

burial which would predict a negative relationship between d13C and global CO2 across CM events, rather than the positive relationship observed across CM6 at Site 1092 here. Although, before a direct comparison can be made the origin of the d11B signal at Site 1092 needs to be thoroughly addressed.

AC: Although the new study by Sosdian et al. is an interesting and important study, we are not convinced that B/Ca in planktic foraminifera is a reliable proxy for borate/DIC or borate/bicarbonate ratios. While culture studies seem to clearly reveal such a relationship, our own experience showed that coretop and downcore samples are not that straightforward, and in some cases reveal opposite trends to what is expected from theoretical and culture studies. In contrast to benthic B/Ca and d11B, which evolved into reliable tools for reconstructing calcite saturation state and pH, respectively, planktic B/Ca is still far from being established. However, in the revised manuscript, we will mention the paper of Sosdian et al.

6. What is the significance of the change in the Malta age model for the GSSP? The GSSP for the Langhian-Serravallian boundary is placed in the Malta section. There should be some comment about this in the age model section as the authors have changed the Malta age model.

AC: The Langhian-Serravallian boundary at 13.82 Ma is still coincident with the revised age model, even if it was not used as a tie point, confirming the general agreement between the different age models. This will be mentioned in the revised text.

More minor comments:

Line 45: “However, most proxy records for the history of pCO2 across the MMCT are incomplete or at low resolution, thus prohibiting resolution of the CM events (Pagani et al., 1999; Kürschner et al., 2008; Foster et al., 2012; Ji et al., 2018; Sosdian et al., 2018; Super et al., 2018) and making it difficult to identify the mechanism responsible for the major step into the “icehouse” world.” This statement is a bit disingenuous, these published records clearly show a significant pCO2 decrease just prior to the MMCT (see also Sosdian et al 2020). What is interesting of course is the higher resolution CO_2 changes, and questions such as: what caused the CM events? how do the CM events depend on background climate state? Why is CM6 (immediately following the major ice growth) the largest of the CM events?

AC: It is correct that existing records show that pCO_2 was higher before EAIS expansion than afterwards, but our statement that none of them is sufficient to fully resolve the CM events is not incorrect. It was certainly not our intention to belittle these very important studies, which mostly aimed at reconstructing long-term changes, while our record just focusses on CM5b and CM6. This will be attenuated in the revised manuscript.

Line 35: “In a recent study, it was proposed that a more sluggish meridional Pacific Ocean overturning circulation, due to reduced deep-water formation in the Southern Ocean, enhanced the weathering of 13C-enriched shelf carbonates”. This is incorrect, the enhanced weathering in this model was ascribed to the sea level fall. This model (Ma et al 2018) is very different to the Ma et al 2011 model. The Ma et al 2018 model treats the MMCT as an “event” whereas the Ma et al 2011 uses continually evolving orbital parameters as forcing. This important point is not explained in the current manuscript.

AC: Correct, this will be changed and discussed in more detail in the revised version.

I find it odd that pH and pCO_2 are plotted as the same curve with the same uncertainty envelope in Figure 4. pCO_2 clearly has additional uncertainties (e.g. estimate of TA, d11Bsw), and I think these should be better represented in Figures 4 and 5.

AC: The uncertainties in the pCO_2 record are propagated uncertainties from boron isotope measurements (i.e. translated to pH uncertainty), TA, S and T, using the ’seacarb’ package. What is missing, and here the reviewer is right, are the uncertainties from T, S and the d11B_borate/d11B_foram calibration propagated into the pH uncertainty itself. This will be done using a MonteCarlo approach. As pH has the largest influence on pCO_2 estimation, the resulting pCO_2 uncertainty will be considerably greater as shown here. The uncertainty in d11Bsw is a systematic error, 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 2 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. In addition, we will also account for the effects of seawater [Ca] and [Mg] on the dissociation constants of carbonic and boric acid, following Hain et al. (2015). Further, in the revised manuscript, we will also 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 of this species (Greenop et al., 2019).

Line 31: Need to also cite Foster et al 2012 as demonstrating climate-CO2 relationship across MMCT.

AC: OK, will be corrected.

Careful with all references – e.g. Fig 3 caption “Badger et al 2015” should be “Badger et al 2013”.

AC: Thanks for spotting this, will be corrected.

Line 168 – Fig 5 should be Fig 4.

AC: Thanks, will be corrected.

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