

Interactive comment on “Revisiting carbonate chemistry controls on planktic foraminifera Mg/Ca: implications for sea surface temperature and hydrology shifts over the Paleocene–Eocene Thermal Maximum and Eocene–Oligocene Transition” by D. Evans et al.

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General comments:

Remark: The most serious issue concerns the attempt to apply pH corrections to both Mg/Ca and $\delta^{18}\text{O}$ records of the PETM to establish the true temperature anomalies as a function of latitude (figure 7), and then estimate local changes in salinity (as inferred

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from $\delta^{18}\text{O}_{\text{sw}}$). [continues]

Response: We answer this in relation to the specific point regarding figure 7 and associated text below.

Remark: Along these lines, the adjustment for pH across the EOT also has a few minor issues, not the least of which is that the B based reconstruction of pH/pCO₂ is low resolution and the signal is small, and not necessarily consistent with other observations or theory.

Response: Whilst boron isotope pH records from both climatic events require replication, and higher resolution records are always desirable, we use both records as illustrative examples of how these corrections should be applied. Many datasets require revision as new records become available, and this study is no exception, although the fundamental point that a pH correction on Mg/Ca is necessary is robust. As highlighted in the next comment, the fact that the pH signal is relatively small compared to the PETM means that the low resolution of this record is a smaller issue than it would otherwise be.

Remark: Also, the correlations between the Tanzania sections from which the B record was generated, and the Mg/Ca records of St. Stephens Quarry, have uncertainty on the order of ± 100 ky or more: not that this matters much as the pH adjustment has little impact on the relative trends in T, though is very important for computing absolute T.

Response: As stated, this is of minor importance for the point we are addressing here because the pH shift across the transition is relatively small. As a direct result of this, it follows that the uncertainty in the correlation between the sites is also of minor importance for our absolute temperature reconstruction. By far, the largest uncertainties are the error in the boron isotope-derived pH reconstruction and that derived from seawater Mg/Ca at the time. These are clearly shown by the error bars

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on the figure.

Remark: Also, until the Tanzania B record is replicated in a second site and at high resolution, applying pH adjustments to isotope and mg/ca records seems a bit premature.

Response: For this reason we head this section ‘Towards accurate absolute Mg/Ca-derived temperatures. . .’. Again, our intention was not to provide a definitive temperature reconstruction, but to show how Mg/Ca data are more appropriately corrected for secular shifts in seawater carbonate chemistry and alkali earth element concentration. However, we propagate the full uncertainty in Mg/Ca-derived absolute temperatures for the first time (including calibration errors) and it is unlikely that a higher resolution pH record would cause a large shift in the absolute numbers, although a minor revision in the degree and timing of the precursor cooling is possible. We propose to rephrase the text where appropriate to more clearly highlight these issues, and to state that these are best estimates based on the currently available data.

Remark: Despite these issues, the paper addresses a critical issue on proxy records and merits publication.

Response: Thank you.

Specific comments:

Remark: 3145, line 16; I would recommend against using the phrase “properly corrected” datasets, since you cannot prove that these are truly “correct”. These are extinct species with different sensitivities to pH. Furthermore, there are the other unknowns regarding seawater chemistry that complicate any “corrections”, not to mention diagenesis. The probability that these SST estimates are precisely “correct”

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is extremely low. I would recommend using the term “(pH) adjusted”.

Response: We agree and will make this change.

Remark: 3145; When adjustments were being proposed to account for the effects of meridional salinity gradients on planktonic foram $\delta^{18}\text{O}$ based SST estimates, someone thought it might be a good idea to first apply the adjustments to core top data: to see if the adjustments improved the fit with observed SST. Can you provide a similar evaluation figure for Mg/Ca (& $\delta^{18}\text{O}$) in Holocene core tops? Modern seawater pH ranges from 7.9 to 8.1 in the open ocean, so there might be a detectable offset in unadjusted T estimates.

Response: We fully concur that this is an interesting line of inquiry, however, this is a large undertaking and beyond the scope of this study. Many papers have been published on Mg/Ca core top data, and something along these lines could constitute a paper on its own. Furthermore, a difficulty in doing so is that the dissolution signal on many core tops dominates the correction which may (partially) mask the pH effect, which is the reason that the earlier studies investigating the effect of salinity significantly over-estimated that effect [see Hönisch et al., 2013].

Remark: 3148, 24; I suppose its all relative, but the one pH record available for the EOT (Pearson et al., 2009) would not be considered high resolution with a data point every several hundred thousand years.

Response: We will rephrase this.

Remark: 3149, 10; Given that Mg concentration (Mg/Ca ratio) of seawater is an important variable on the sensitivity of partitioning to both T and pH, and the limited range of Mg/Casw applied in culturing studies, can the effects of 50% lower Mg/Ca in the Eocene be adequately accounted for?

Response: We actually show data that indicate that seawater Mg/Ca may not affect

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the relative partitioning of Mg due to pH. Figure 1 shows two *G. ruber* cultures at a seawater Mg/Ca ratio ~60% of modern, which fall on the same Mg-pH regression as those in modern seawater. We show data in figure 5 for the sensitivity of Mg/Ca to temperature in both modern seawater and at a ratio of 3.4 mol/mol. Whilst this is not as low as the Eocene, we propagate the full uncertainty associated with extrapolating this, defined by the model lines in figure 5. Whether this is adequate depends on the question one is addressing; figures 6-8 show that there is considerable uncertainty in relative temperature shifts as a result. We think that this uncertainty is clearly displayed (indeed it is one of the main messages of our manuscript); whether it is adequately known with the current culture data depends on the required precision of a relative temperature reconstruction.

Remark: 3156; The discussion of a mechanistic model(s) for the Mg/Ca partitioning is interesting, but it should be noted that these models are based primarily on culturing of larger benthic foraminifera, and might not directly apply to planktonic foraminifera.

Response: We will add a statement that includes this caveat.

Remark: 3159, 26-28; Exactly the point made above, that the lower Mg/Ca sw should influence the T related partitioning, potentially to the point of offsetting much of the pH effect.

Response: This is the point we intend to make with this statement. However, pH is likely to be more spatially and temporally variable than seawater Mg/Ca, by simple virtue of the fact that the residence times of these elements is substantially longer than the atmosphere-ocean equilibration time. For this reason, it should never be assumed that the two effects cancel each other, and until further culture data become available, the error in the sensitivity of the Mg/Ca-temperature relationship with seawater Mg/Ca should be given.

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Remark: 3160, 12-15; “We now apply these findings to the PETM and the EOT in detail, in order to better constrain SST and hydrological shifts over the former, and to produce the first fully-corrected (for Mg/Casw and pH) absolute Mg/Ca-derived temperatures across the EOT.” Again, fully-corrected might be considered an over-statement. I recommend the first fully pH adjusted. . .

Response: We will make this change.

Remark: 3160, 26; Wilson Lake core was drilled in New Jersey.

Response: This mistake will be corrected.

Remark: 3161, 7; Minor point, but I believe the original reconstructed Mg/Ca temperature anomaly at 1209 was closer to 5°C.

Response: The data shown in our figure 6 is based on *Morozovella*, whereas the ~5°C anomaly originally reported is only the case for *Acarinina*.

Remark: 3161, 20. I wonder if the Eocene planktonic taxa, *Morozovella*, might have been more similar to that of *G. orbulina* which has a less sensitive Mg/Ca/pH relationship than *G. ruber*. Rather than applying an average for all species, why not apply the relationships of the *Orbulina* and *Ruber* separately, as representing the low and high end adjustments.

Response: We are not sure if you mean *G. bulloides* or *O. universa*? In fact it makes little difference which species is chosen if one were to go down the route of using the species-specific Mg-pH calibrations. This is because whilst *G. ruber* is indeed characterised by a steeper slope between pH 7.8-8.0 than the other species, the best fit logistic curve flattens off at around pH = 7.7, which is not the case for *O. universa* or *G. bulloides*. As a result, using the *G. bulloides* calibration would result in a minor change in the pH sensitivity on Mg/Ca (12% change resulting from the PETM pH shift) compared to the overall calibration curve (13%). However, it is indeed the case that *O.*

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universa is characterised by a steeper slope over this range (18%). In order that figure 6 does not become unreadably complicated (there is a limited range of scenarios we can show here), we propose that we show the full range of possible sensitivities in a new supplementary figure, and add a statement to the text highlighting that this is a further uncertainty that should be considered.

Remark: 3161, 21-23. The way this statement is written is a bit confusing (at least to me); "...a 0.3 shift in pH over the PETM would result in overestimating the combined T and $\delta^{18}\text{O}_{\text{sw}}$ component of the foraminifera $\delta^{18}\text{O}$ " by 0.27 to 0.75", so correcting for this would yield an even smaller ΔT recorded in the $\delta^{18}\text{O}_{\text{calcite}}$. If so, the $\delta^{18}\text{O}_{\text{sw}}$ would have to be larger, not smaller to offset this. The pH (or [CO₃]) anomaly increases the foraminifer $\delta^{18}\text{O}$ independent of other factors, and therefore should result in an underestimate of ΔT from $\delta^{18}\text{O}$, and an overestimate of $\delta^{18}\text{O}_{\text{sw}}$...correct? Rewrite for clarity.

Response: We intended to make the point that the reconstructed pH shift means that the negative $\delta^{18}\text{O}$ excursion has been underestimated by 0.3-0.8 ($\delta^{18}\text{O}$ increases/becomes less negative with decreasing pH), a general point which was made by Uchikawa & Zeebe [2010] but which can now be phrased more specifically following the publication of the 1209 pH record by Penman et al. [2014]. Because of this, uncorrected $\delta^{18}\text{O}$ records show a reduced amplitude as a result of pH which would result in an apparent or over-estimated salinity increase. We agree that this could be worded more clearly, and words such as larger/smaller/increases etc. which are ambiguous in this context will be changed to state whether the $\delta^{18}\text{O}$ excursion is more or less negative. Furthermore, there is a mistake on line 22 of page 3161: 'overestimating' should read 'underestimating'.

Remark: 3162, 3. Yes, the pH effects would tend to diminish the magnitude of the offsets, but considering the propagation of error from B based pH estimates, and in

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the pH effects on Mg/Ca and $\delta^{18}\text{O}$, the possibility of a positive $\delta^{18}\text{O}_{\text{sw}}$ anomaly at Site 1209 is still within reason, especially if the sensitivity to pH is lower than modern. And just from a vapor transport perspective, raising the salinity of the sub-tropical Pacific by the equivalent of 0.20‰ in $\delta^{18}\text{O}$ is not trivial.

Response: It is indeed possible that the salinity shift at 1209 was positive, as is clearly shown on figure 7. This is the case even if the pH effect on $\delta^{18}\text{O}$ is within the range observed in cultures. We will rephrase this sentence which may be misleading as this error is the standard deviation of the specific record that we show in figure 6C rather than the full range of possible errors accounting for all of the effects discussed. However, the point that this site lies within error of no salinity change is not inaccurate.

Remark: 3162, 5-20 (& figure 7); The manner in which these data are presented is misleading, and would give anyone who is unfamiliar with the event an inaccurate picture of the climatic changes associated with the PETM. To start, the low latitude sites in this figure, 527, 865, 401, and 1209, are all pelagic and all compromised/truncated to varying degrees because of carbonate dissolution, reworking and other processes, and as a consequence the base of the PETM is either missing or condensed. This would be obvious if you looked at the bulk/planktonic carbon isotope data from those same sections; the magnitudes of the $\delta^{13}\text{C}$ excursions are significantly reduced compared to the shallow marine siliciclastic and pelagic sites with high accumulation rates (Sites 689/ 690). This undermines the implications, that the corrections for pH demonstrate that there was polar amplification, and the salinity anomalies were all negative. I recommend deleting part of this section and figure 7. To show how the adjustments would effect each individual SST and SSS records, just plot the adjusted data in the depth domain, as in figure 6. This would be more appropriate as continuity of deposition is not implied, though transferring the pH data from 1209 does imply time equivalence.

Response: We agree that the potential complications with these data should have been more carefully noted. We propose that we add a third panel to figure 7 showing

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the magnitude of the CIE at each site, giving an obvious indication of those for which the record may have been truncated or partially lost through dissolution. We will also add a statement along these lines to the main text. However, it is unlikely that our conclusions will be altered even if all sites were complete for two reasons. (1) 1209 (from which the pH record is derived) is one of the sites this reviewer lists as being potentially problematic. It is therefore more likely that it is applicable to the other deep pelagic sites, and would actually underestimate the degree to which the salinity anomaly has previously been overestimated at the shallower sites. (2) Alternatively, assuming the 1209 record captures the full PETM pH excursion: For the hypothetical case that another site was missing the peak Mg/Ca and $\delta^{18}\text{O}$ data, we would see an underestimated negative $\delta^{18}\text{O}$ excursion which would bias the salinity shift we show towards more positive values.

Remark: 3163, 0-10. The estimated T anomalies from foram $\delta^{18}\text{O}$ and GDGT's are not very different (within error?), and pH/ salinity/calibration issues (GDGT) could easily account for much of the discrepancy. However, there is probably a shift in the degree of seasonality at these sites in terms of E-P and runoff, and it's likely that the GDGT's and foram $\delta^{18}\text{O}$ are not representing the same seasons. For this reason, comparing shell $\delta^{18}\text{O}$ and Mg/Ca would more appropriate.

Response: They are within error once corrected for pH on $\delta^{18}\text{O}$, which is our main point here. We agree that seasonality should be considered when comparing proxies derived from different material, and we will add this caveat to the main text. We would appreciate any specific comments or references regarding the differential seasonality of the proxies at these sites, if available? Comparing $\delta^{18}\text{O}$ and Mg/Ca of the same material would always be preferable, however to our knowledge there are no published Mg/Ca data for these sites.

Remark: 3164, 25; Should be clear that the “Global” reversal in pH at 33.4 ma is

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based on 2 data points from a single shelf sequence. This is in conflict with alkenone based $p\text{CO}_2$ reconstructions from pelagic sites which show the opposite pattern.

Response: We agree that this should be clearly stated, and we will add a sentence along these lines to the text. A $p\text{CO}_2$ shift of the magnitude of the reversal seen in the boron isotope-derived record is unresolvable in the alkenone record if the full range of uncertainties are considered. We do not use the word global in relation to this pH record.

Remark: 3165, 3-20; this discussion of the *G. ruber* culturing pH/Mg/Ca calibration and application seems partially repetitive from earlier in the manuscript, which is where it belongs.

Response: This is (purposeful) partial repetition in case those focusing on only the PETM or EOT do not miss this if only part of the manuscript were to be read. We would prefer to keep it for this reason, but would be happy to follow the editor's advice.

Remark: 3166, 14-15; This is an unusual preamble..." Because it was not known otherwise at the time,...". Isn't this the case with most previous work in science?

Response: Yes, true. We add this statement because we do not want to be perceived as critical of previous authors. Whilst we update their records, some of the complications we highlight were not previously known and we want to make this clear.

Remark: 3167, 17-18; Actually...it would appear that the LA data does highlight a potential issue with standardizing Mg in carbonates using NIST glasses.

Response: We do not see the basis for this comment. Our figure 3B clearly shows that the laser-ablation and solution ICPMS data are within error of each other, no artefact of either technique is resolvable based on our analyses.

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Remark: 3168, 1; "...this correction is on the order of 10%/0.1 pH unit", which is true for *G. ruber* in modern seawater, but could be much lower depending on species sensitivity and seawater chemistry.

Response: It is true that this correction is characterised by a range of slopes depending on the species and the pH range of interest. We will rephrase to give the full range of slopes.

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