

# ***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.***

## **Anonymous Referee #1**

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General comments: This paper evaluates the effects of seawater carbonate chemistry (pH) on the partitioning of Mg/Ca from seawater into foraminifer shells, and implications for adjusting T estimates based on Mg/Ca ratios of fossil shells. The study utilizes results from a recent laboratory culturing study of *G. ruber* along with data from previous culturing and field based studies to quantify the sensitivity of partitioning to pH, and devise a correction for fossil shell Mg/Ca. The results support previous findings that with declining pH, particularly in the range of 7.6 to 8.4, the Mg/Ca ratios rise. *G. ruber*

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is highly sensitive in this range, and insensitive above and below, a logistic relationship. Based on the combined calibration data, adjustments are computed and applied to previously published Mg/Ca based SST records spanning the two major climatic events of the Cenozoic, the EOT and PETM. The study utilizes recently published Boron-based paleo pH data generated for these two critical transitions. The authors argue that the effects of pH change during those events could potentially account for discrepancies in T estimates based on Mg/Ca as well as oxygen isotopes, which in the past were attributed to possible changes in salinity. In the case of the PETM, a 0.3 drop in pH would amplify Mg/Ca T estimates by  $\sim 1.5^{\circ}\text{C}$ , which along with pH effects on O, could account for much the difference that was previously attributed to  $\Delta\delta^{18}\text{O}_{\text{sw}}$ . Overall Quality: While the general concepts regarding pH on carbonate geochemical proxies are not novel, this study represents the first attempt to provide a more quantitative assessment of the potential effects of pH on Mg/Ca based records of T. The approach to quantifying sensitivity is fairly rigorous, utilizing data from a collection of culturing studies involving several species of planktonic foraminifera, thus providing a good sense of the range of sensitivities, which is critical for applying adjustments to extinct species. It is clear that a pH effect must be accounted for in converting Mg/Ca to T, as it must with  $\delta^{18}\text{O}$ . As a primary case study, the application of the adjustments to ODP Site 1209, which has B based pH record for the PETM, is a relatively solid and clear demonstration of how the pH influences the estimations of  $\Delta\text{SST}$  and  $\Delta\text{SSS}$ . As such, this case study will serve as a useful guide for future studies intent on establishing  $\Delta\text{T}/\Delta\text{SSS}$ , if not for pH adjusting estimates of T, at least propagating potential error. The laser ablation work on early Oligocene foram shells is interesting, the first robust data for shells of this age, though it seems out of place given the primary focus of the manuscript. At the very least it demonstrates the benefits of using LA-ICPMS to distinguish the potential effects of contaminants on shell chemistry. Despite all that is good with this paper, there are a few issues that need to be addressed. 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

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changes in salinity (as inferred from  $\Delta\delta^{18}\text{Osw}$ ). This comparison is problematic as it involves several sites (at low latitudes) that are condensed or truncated to varying extent (e.g., Sites 527, 865, 401), and thus do not even record the peak T anomalies. All of the pelagic sites cited in this paper experienced dissolution at the onset of the PETM, and are condensed. Some sites show evidence of depositional hiatuses (erosion?), Sites 865 and 401 for example. Not surprisingly these sites have the smallest T anomalies. In fact, a simple comparison of the carbon isotope anomalies for this collection of sites would demonstrate this. In short, the graph depicting the PETM  $\Delta T$  and  $\Delta\delta^{18}\text{Osw}$  as a function of latitude with the same pH correction applied uniformly is misleading as it implies time equivalence of the T data/corrections. All this weakens the final conclusions regarding the likely direction of change in  $\delta^{18}\text{Osw}$  as a function of latitude, as climate was not stable during the PETM, but in a transient state from onset to recovery. To be sure, observations from fluvial sections (Wing et al 2005; Schmitz and Pujalte 2007; Sluijs et al. 2007; 2009) suggest that as the PETM progressed, the general state of the hydrologic cycle evolved, with a much more extreme state during the initial phase of warming, which many of the pelagic sites might not capture. In the end, this exercise, to truly reconcile time dependent changes in local and global E-P, requires a much more rigorous treatment, including careful consideration of the sources of data on site by site basis, as well as placing data within a proper stratigraphic context (more on this in the specific comments). In contrast, the application of the pH adjustment to the Mg/Ca and  $\delta^{18}\text{O}$  record at Site 1209 is robust simply because the B isotope based pH data are from the same core, and the sampling density is high, so no issues concerning correlation and/or signal to noise ratio. 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/pCO<sub>2</sub> is low resolution and the signal is small, and not necessarily consistent with other observations or theory. 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  $\pm 100$  ky or more. . . not that this matters much as the pH adjustment has little impact on the relative trends

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in T, though is very important for computing absolute T. 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. Despite these issues, the paper addresses a critical issue on proxy records and merits publication. My recommendation is for minor/moderate revision. Recommendations for revision are provided within the specific comments below. Specific comments: 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” is extremely low. I would recommend using the term “(pH) adjusted”. 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. 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. 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? 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. 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. 3160, 12-15; “We now apply these findings to the PETM and the EOT in detail, in order to better constrain SST and hydrological

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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 overstatement. I recommend the first fully pH adjusted. . . 3160, 26; Wilson Lake core was drilled in New Jersey. 3161, 7; Minor point, but I believe the original reconstructed Mg/Ca temperature anomaly at 1209 was closer to 5°C. 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. 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  $\Delta T$  recorded in the  $\delta^{18}\text{O}_{\text{calcite}}$ . If so, the  $\Delta\delta^{18}\text{O}_{\text{sw}}$  would have to be larger, not smaller to offset this. The pH (or  $[\text{CO}_3]$ ) anomaly increases the foraminifer  $\delta^{18}\text{O}$  independent of other factors, and therefore should result in an underestimate of  $\Delta T$  from  $\delta^{18}\text{O}$ , and an overestimate of  $\Delta\delta^{18}\text{O}_{\text{sw}}$ . . . correct? Rewrite for clarity. 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 the pH effects on Mg/Ca and  $\delta^{18}\text{O}$ , the possibility of a positive  $\Delta\delta^{18}\text{O}_{\text{sw}}$  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. 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

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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. 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. 3164, 25; Should be clear that the "Global" reversal in pH at 33.4 ma is based on 2 data points from a single shelf sequence. This is in conflict with alkenone based pCO<sub>2</sub> reconstructions from pelagic sites which show the opposite pattern. 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. 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? 3167, 17-18; Actually. . .it would appear that the LA data does highlight a potential issue with standardizing Mg in carbonates using NIST glasses. 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.

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