

Response to Referees and Revised Manuscript

Herein we provide a detailed point-by-point response to all referee comments and specify all changes in the revised manuscript. The response to the Referees is structured as: (1) comments from Referees, (2) author's response, (3) author's changes in manuscript. We also include a marked-up manuscript version showing the changes made (using track changes in Word). This version should be combined with your response file so that the Editor can clearly identify what changes have been made.

Response to Referees

Referee 1

Comment 1: A new multi-proxy record of the PETM from a deep sea core in high southern paleolatitudes is very welcome and adds to our understanding of this very large and still enigmatic climate perturbation. The authors should be congratulated for finding the PETM in such an old drill-core. There can be little doubt that the data should be published and the study is suitable for Climate of the Past. However the data set is moderately complex and (I think) difficult to interpret unambiguously, hence the challenge is to distil the salient points as clearly as possible for the wider community interested in this event, and for comparing records. Hopefully the review process can help with that. Some of my comments are relatively minor and can probably be dealt with quite easily but I have two more substantive issues to deal with first.

Response 1: Agreed, thank-you.

Comment 2: The relation between the bulk d13C record and the so-called 'onset' of the PETM, and what happens near the base of the event. The PETM is by definition a warming event hence its onset (for me) is, perforce, the bit where it gets hotter, i.e. where the d18O goes negative (and is also seen in the Mg:Ca excursion in this study). This is the interval 457.25-457.29 m which corresponds to a 4cm chunk of core. However even the 'intermediate' bulk d18O and whole foram values from within this chunk may be affected by differential diagenesis, as the paper rightly points out, and some bioturbation mixing is also likely given the burrows, so it is not clear that the real 'onset' of the thermal maximum is sampled at all in this drill core. The paper mentions almost in passing that the portion directly below the PE boundary (457.3-457.58) has sparse and poorly preserved foraminifera (p. 256 line 3-4) but offers no explanation. This suggests the possibility, even likelihood, of dissolution burn-down caused by a transient rise in the carbonate compensation depth during the real onset, also the time of the benthic extinction, and what the core records would therefore be renewed sedimentation onto a dissolution surface / semi-hiatus.

Most previous records of the PETM have the onset of warming coincident with a large and abrupt negative carbon isotope excursion (CIE), so that the onset of the CIE is pretty much coincident with the onset of the PETM - the coupled excursions mentioned in the introduction. But this record is quite different, basically un-coupled, and I have to admit to being puzzled by the run of intermediate bulk d13C values through most of what appears to be the body of the PETM, even while bulk d18O is becoming slightly more positive. This, for me, is the enigmatic aspect of the record and the discussion (Section 3.3) does not wrestle it down sufficiently.

Part of the problem (I contend) is that the authors refer to the gradually decreasing bulk d13C values as the 'onset of the PETM' (in title, abstract line 8; discussion in Section 3.3) which only confuses matters. The d18O and Mg:Ca show that this interval is in fact the 'body' of the thermal maximum. It may be the onset of the CIE at this location, I grant, but I doubt whether it correlates with the onset of the CIE everywhere else. Why the bulk d13C values are a run of intermediates is difficult to explain, especially given the foram d13C values around 457.22 m appear to be more or less 'fully negative' and similar to those above from around 467.03 m.

I do not offer an explanation for this conundrum, all I can think of is some far-fetched ideas, but the authors need to tackle it head on, and perhaps take the opportunity of clarifying what they mean by onset of the PETM / CIE / event and making sure the text is clear throughout. Incidentally, the claim that the 'onset' lasts 50-100 kyr in other sites (p. 258, line 4) contrasts with what I think most people would think of as around 10-20 kyr or less, with the 'body' being about 150-200 kyr (the Mead Stream section is also peculiar).

Also incidentally, if the lower carbonate content is because of reduced carbonate flux then the PETM here would also represent more time than an interpolated or extrapolated age model, possible equivalent to much of the body of the PETM (see also my comment on cycles below).

Response 2: We admit that we have used the term "onset" too loosely in this article. Strictly speaking we argue that the recovery interval is missing, and so what is preserved is the onset plus at least part of the core of the PETM. We will revise use of "onset" throughout the text. However, we still contend that the bulk d13C record is consistent with a relatively complete PETM. There is certainly an interval below the PETM where carbonate content is lower than background for the Paleocene, but the d13C is very stable through the upper 50 cm of Paleocene sediment, with no evidence for "burn down" affecting the d13C record and hence no basis to infer a hiatus at the base of the PETM.

The stepped decrease in d13C that occurs between the true onset at 457.27 mbsf and the core of the PETM at 457.1 mbsf is not that unusual. As well as Mead Stream, it has been widely discussed for ODP Site 690 (Bains et al., 1999; Stoll, 2005; Zachos et al. 2005; Sluijs et al. 2007), and has led to speculation that the PETM carbon release may have occurred in pulses (Sluijs et al., 2007). A point that we emphasise in the revised MS is that the three steps in the CIE at DSDP 277 correspond reasonably well with the three maxima in Mg/Sus and Fe. Therefore, we can be reasonably confident that we have CIE steps A-C of Zachos et al. (2005) that span cycles 1-3 of Röhl et al. (2007), and therefore our PETM interval probably spans the interval from the base of cycle 1 to the base of cycle 4 or the first ~66 kyr of the PETM (Röhl et al. 2007). Stoll (2005) has shown that the bulk carbonate d13C is a good representation of the coccolith record at ODP 690, which also has a 3-stepped CIE very comparable to Site 277 and Mead Stream. We note that Site 690 is considered to be one of the most expanded records of the PETM and was used to calibrate deeper water records in the South Atlantic where burn-down effects are greater (Zachos et al., 2005).

Differences between the bulk carbonate and single foram signals for the PETM are also well known at ODP 690. As at DSDP 277, Acarinina records a strong CIE at the onset of the PETM. Stoll (2005) has an extensive discussion on this topic but no definitive answer. All we need to say here is that Site 277 is not unusual in having a stepped bulk carbonate CIE. This is why we focus more on the much more pronounced bulk carbonate oxygen isotope excursion (OIE).

We tend to agree with the referee's comment that the fact the PETM is a warming event is often overlooked. Nevertheless, since first identified, the PETM has consistently been defined by the carbon isotope excursion (CIE) that provides a less ambiguous way of correlating the event between geographic regions and of subdividing components of the event than the variable oxygen isotope excursion or other climate proxies (e.g. Bains et al., 1999; Zachos et al., 2005; Sluijs et al., 2007; McInerney and Wing, 2011; Dunkley Jones et al, 2013). The P/E boundary is defined by the CIE (Aubry et al. 2007), not the associated temperature shift or other climate-related phenomena. There are many locations world-wide where the location of the PETM is fixed only by the CIE, with very little known about the accompanying changes in temperature. It is also worth making the point that in the case of modern global warming, associated climate change exhibits considerable geographic variation whereas the steady increase in atmospheric CO₂ is uniform across regions. This is nicely demonstrated by the compilation undertaken by Dunkley Jones et al. (2013).

*Changes to MS (with reference to underlined comments): We reduce reference to "onset" in the MS and clarify where appropriate that we are referring to the onset and body of the CIE (up to the CIE minimum, **Fig. 7; Lines 392-393**) but note that the PETM is defined by the CIE, not by warming (**Line 107**). We argue that neither bioturbation nor burndown can explain the "uncoupled" isotope record or the pre-PETM interval (**Lines 465-472**). We show that the isotope records for Site 277 and Mead are not that unusual but very similar to Site 690 (**Lines 473-499**). We reassess the age based on correlation with precession cycles (**Lines 432-435**).*

Comment 3: Foram preservation and diagenesis: The authors indulge in quite an extended discussion about possible diagenetic effects on foram tests and $\delta^{18}O$ and Mg:Ca. They assert, reasonably I suspect, that the preservation is better in the PETM than below and above because of inhibited recrystallization related to the higher clay content. I have often wondered whether such an effect might be at play in some PETM records which go from chalk to clay (if not cheese) - and indeed other such events such as the Mediterranean sapropels. To demonstrate this effect would be very neat. However the reader cannot evaluate the likelihood of this because no SEM evidence is presented. This paper would benefit hugely from a comparative textural study of the foram walls in internal section under high powered SEM so that the extent of recrystallization can be visually assessed relative to published criteria (which we have produced for just this kind of material - Pearson, P.N., and Burgess, C.E. 2008. Foraminifer shell preservation and diagenesis: comparison of high latitude Eocene sites. Pp. 59-72 in Austin, W.E.N. and James, R. H. (eds.), Biogeochemical Controls on Palaeoceanographic Proxies. Geological Society Special Publication 303: 59-72. Doi: 10.1144/SP303.5). This work has been done ('stringent [SEM] screening criteria were applied to exclude zones within test walls that show evidence of diagenetic alteration' - p.252, l. 5-6) so it really should be shown. Actually I will challenge the authors: given that the carbonate content is fairly high even within the PETM, I predict that all forams at this site will show clear evidence of diagenetic alteration on a micron scale throughout their entire walls (although the effect maybe variable) - I do not believe you can exclude recrystallization at this site - so go prove me wrong by illustrating the typical biogenic microgranular texture of a well-preserved foram!

It would also be nice to see what is causing the reputed poorer preservation of the forams immediately below the PETM - are they dissolved? In short, I think we should be moving away from near-meaningless phrases like 'carbonate microfossils are moderately well preserved' (p. 256, line 3)

and 'relatively well preserved tests' (p. 258, line 23) to something much better documented, but for that we need the SEM images.

Response 3: We are forced to admit that upon review of our SEMs, all the forams in this record are affected by diagenesis, with clear evidence of overgrowths and recrystallisation. We cannot confidently use visual examination as a basis for stating that the forams in the PETM are any better preserved than below or above the PETM. The "stringent" criteria referred to in the text relates to geochemical criteria. Specifically in relation to diagenesis, this means we have not used specimens or parts of LA-ablation profiles with Sr/Ca values lower than 0.8 or higher than 1.6 in the determination of paleotemperatures from Mg/Ca ratios. Following the recommendation of Referee 2, we have constructed cross-plots to show how these criteria are applied (new Fig. 3).

These cross-plots explore the relationship between Mg/Ca ratios, silicate contamination and diagenesis. The full dataset consists of average elemental ratios across selected integrated laser ablation profiles (visually screened for the effects of silicate contamination and diagenesis). This dataset has been first plotted as cross-plots of Al/Ca and Mg/Ca for Cibicides and Acarinina (the only two genera that have records spanning the entire studied interval). The data have been colour coded to differentiate samples from within the PETM and the pre-PETM interval extending down to 462.2 m. A significant linear correlation is observed for both genera, confirming that silicate contamination results in anomalously high Mg/Ca values where Al/Ca >4 (3.4 and 3.7 being the calculated screening limits with method explained in the MS). For Cibicides, silicate contamination is seen to be more common within the PETM than in the pre-PETM interval or elsewhere in the record. This is consistent with other evidence for an increase in clay within the PETM. This pattern is also evident for Acarinina but Al/Ca values are generally higher and more pre-PETM samples show evidence of silicate contamination. This may reflect differences in morphology, with the smoother surface of Cibicides providing fewer opportunities for clay particles to become fixed to the test wall.

The second set of cross plots consists of data that has first been screened for silicate contamination using the screening limit of Al/Ca > 3.4 or 3.7. The Sr/Ca ratio is used as a proxy for diagenesis, with the typical ratio in Eocene foraminifera being 1 to 1.4 (Creech et al., 2010) and the values < 0.8 or > 1.6 are considered to reflect dissolution or recrystallization (Eggins et al., 2003; see also Kozdon et al., 2013). Linear regression lines are shown for the three groups and the correlation co-efficient is added where it is significant. For Cibicides, most values lie within the screening limits but there are some significant differences in the clusters of PETM and pre-PETM samples. First, we note that the overall trend for all the samples is roughly horizontal, suggesting that the Sr/Ca ratio is generally stable around ~1 for varying Mg/Ca. However, we observe that there is a weak negative trend and stronger and steeper negative trend for PETM and pre-PETM samples, respectively. This suggests that diagenesis has a significant effect on pre-PETM Mg/Ca values for Cibicides, and may also have a small effect on PETM values. The net effect would be to introduce a warm bias to pre-PETM temperatures, and possibly also to some PETM temperatures.

For Acarinina, a clearer relationship is observed between Sr/Ca and Mg/Ca. The effects of diagenesis appear more evident, overall, probably reflecting the thinner test and greater surface area relative to the smooth walled Cibicides. The overall trend is consistent with predictions and observation from other studies: a negative correlation indicates that as diagenesis progresses Sr/Ca decreases and

Mg/Ca increases (Eggins et al. 2003; Kozdon et al. 2013). The slope of the trend lines indicate that the pre-PETM interval is most affected by diagenesis, and the PETM is the least affected. As for *Cibicides*, this implies that temperatures based on the Mg/Ca are significantly overestimated in the pre-PETM interval and also, but to a lesser extent, overestimated in the PETM.

In summary, we have shown how screening has been applied to exclude samples with significant levels of silicate contamination and diagenesis. We have shown that diagenesis tends to be higher in the pre-PETM interval than in the PETM. We have shown that *Acarinina* is more affected by both silicate contamination and diagenesis than *Cibicides*. And we have shown how diagenetic effects may affect temperature estimates (even for samples within the screening limits), probably overestimating pre-PETM temperatures relative to the PETM.

Therefore, although we lack visual evidence to support our hypothesis that the extreme OIE at the “onset” of the PETM in this record is an artefact of preservation changes across the P/E boundary, we do have geochemical evidence in the form of Sr/Ca ratios. In addition we observe and increase in the $\delta^{18}O$ gradient between bulk carbonate and benthic foraminifera: from <0.6 in all but one sample below the PETM to >1.1 in 2 of 3 samples within the PETM. A low gradient is also observed above the PETM (0.23 – 0.42).

We have added a supplementary figure to show the general distinctions between moderate and poor preservation, based on SEM images and LA-ICPMS profiles, but acknowledge that others may term these preservation states, poor and very poor.

Changes to MS: it is beyond the scope of the current study to include detailed study of wall texture (“stringent criteria” referred to geochemical screening), but we have included SEM images of whole tests (**Fig. S1**) and accept that preservation is generally poor to moderate (**Lines 353, 449-454**).

Comment 4: p. 246, line 3. Reword? These references are compilations, not original studies, but in any case all early Paleogene pCO₂ reconstructions are very uncertain - and yet the statement seems to take it as fact.

Response 4: Insert “is inferred to have” (**Line 45**).

Comment 5: p. 250, line 9. *Acarinina* is spelt wrong. Were species combined in these analyses? We know *Acarinina* species can differ quite a bit in habitat, so it would be better to stick to species where possible as in the trace elements.

Response 5: Move the text from Mg/Ca methods to this location (**Lines 151-166**), and revise to say: “Individual specimens from five foraminiferal genera were used for stable isotope analysis and elemental geochemistry. Specimens were selected for analysis based on visual assessment of their preservation under a stereo microscope. Wherever possible, analyses were performed on *Morozovella aequa*, *Acarinina coalingensis*, *Subbotina patagonica*, *S. roenasensis*, and *Cibicides proprius/praemundus*. The following species were substituted when these species were not available: *Morozovella subbotinae*, *M. acuta*, *M. apantesma*, *Acarinina soldadoensis*, *A. subsphaerica*, *A. esnaensis*, *A. nitida* and *Cibicidides tholus*. The stable isotope signature of *Acarinina soldadoensis*, *A. subsphaerica*, *A. nitida* and all species of *Morozovella* indicates they were mixed layer dwellers (Olsson et al., 1999; Quillévéré and Norris, 2003), and therefore are appropriate indicators of near

surface conditions. *Subbotina patagonica* is inferred to have had a deep planktonic habitat (Pearson et al., 2006), within the thermocline. There is no data on the habitat of *S. roesnasensis*."

Comment 6: p. 256, line 12. The missing NP7 and NP8 are not shown on the log on Figure 2, where the zones are combined. Hence the text says something important that is absent from the fig.

Response 6: The zones are missing, so they are not shown on Fig. 2. An unconformity is shown to lie between NP6 and NP9, which is consistent with the text.

Comment 7: p. 256. Can you say something about planktonic forams in the PETM? Did you find any excursion taxa or influx of warm forms?

Response 7: Yes, this important text to be added (Lines 338-341). "The genus Morozovella has its lowest occurrence at the base of the PETM and greatest diversity within the PETM. Two species of Morozovella are restricted to the PETM: M. aequa and M. velascoensis. The latter species has rarely been found outside the PETM in the SW Pacific but M. aequa ranges into the middle late Eocene on mainland New Zealand (Hornibrook et al. 1989)."

Comment 8: p. 257, line 9. Can you prove the Fe record is cyclical by power spectra? Are these cycles likely obliquity? If so you have virtually all the PETM here, not the 'onset'!

Response 8: There are two few cycles present for spectral analysis or to conclude that there are four obliquity cycles. However, we have commented earlier on the likelihood that that they correspond to the precession cycles described by Röhl et al. (2007). Reword statement of duration of onset and body based on correlation with Site 690 (Lines 359-361, 396-403).

Comment 9: p. 257, line 18. This positive shift in $d18O$ of 0.4 per mil is not obvious to me on Fig 2. I wonder if this is a burn-down dissolution effect, also the enigmatic peak in Fe and mag. susc. which you say the cause is unknown.

Response 9: The shift is there, but not obvious how this could be due to burn down. Also as discussed there is no equivalent shift in $d13C$. We interpret it as suggesting pre-PETM cooling (also noted at Site 690). The enigmatic shift in FE and mag sus is well below the PETM (Lines 377-385, slightly reworded; Lines 433-440, more commentary)

Comment 10: p. 260. "Benthic foraminifera tests are dense [true] and thus less prone to recrystallization [not true?]" This has been claimed many times, and I blame myself partly for it, as we all hoped it would be true, but whenever we have actually studied the tests they are in fact just as recrystallized as the plankton. Again, you could substantiate this with SEMs or omit the statement / claim.

Response 10: Unnecessary sentence deleted (Line 533)

Comment 11: p. 262. Is there any paleontological evidence for a change in fossil assemblage that perhaps might be related to the subtropical gyre?

Response 11: Incoming of Morozovella and diversity of the genus to be noted here (Line 633-634).

Comment 12: In summary this is a fascinating new record from the high southern latitude but the text needs to be clearer regarding what is meant by the onset of the event; and images from the textural-diagenetic SEM study that has been done would improve the case for understanding what has been observed regarding foram test preservation and quantifying the temperature excursion.

Response 12: Endeavoured to address these issues in further discussion of the effects of diagenesis but have not included detailed SEMs of test walls. Whole test SEMs and Element/Ca profiles serve to (new Fig. 3) illustrate issues with silicate contamination and diagenesis.

Referee 2

Comment 1: A sediment core drilled in 1973 on the western margin of the Campbell Plateau by the Deep Sea Drilling Project (DSDP Site 277) was re-examined by Hollis et al. Within the past 40 years, a large number of studies was published based on material from this core, however, Hollis et al. are the first to discover that the PETM is preserved in a 34 cm-thick interval within these sediments. The authors used an innovative multi-proxy, multi-instrument approach (in situ measurements of trace elements in individual planktic and benthic foraminiferal shells by LA-ICP MS, d18O and d13C analyses in bulk carbonate and foraminiferal shells, XRF scans of core sections, measurements of carbonate content and magnetic susceptibility) to delineate the PETM recorded in these sediments and to compile a robust paleorecord by combining data created by this multi-proxy approach to assess the degree of alteration of foraminiferal shells and exclude Mg/Ca measurements from samples that underwent significant diagenesis.

While this study certainly warrants publication and is suitable for the journal "Climate of the Past", I highly encourage the authors to address the potential impact of diagenesis on the Mg/Ca, d18O, and d13C values in more detail. According to the authors (page 250, lines 6 ff.), "samples were selected based on light microscope assessment of preservation, which was subsequently confirmed by SEM". In my experience, this approach of sample screening is not sufficient. Within the past years, I analyzed hundreds of foraminiferal shells in high magnification by SEM and screened more than one thousand polished chamber wall cross-sections in epoxy mounts using SE, BSE, and CL detectors in order to locate suitable, well preserved domains for SIMS analyses. Thereby, I realized that it is practically impossible to estimate the actual preservational state of 'frosty' foraminiferal shells from their outer appearance. Two shells, that appear to feature the same preservational state, may turn out to be altered to completely different degrees when examining their polished chamber wall cross sections. Thus, my concern is that differential diagenesis within the studied core section may have been overseen. For example, it was shown in previous studies that foraminiferal shells at the PETM onset may be altered to a larger degree due to the effect of 'burn-down' (e.g. Walker and Kasting, 1992; Kozdon et al., 2013). Hollis et al. emphasize a different trend in PETM-warming at DSDP Site 277 compared to other sites, but I am not convinced that the data shown in this study exclude the possibility that part of this observation could also be caused by differential diagenesis within the core. However, the laser ablation data provide a great wealth of information that can be used to assess foraminiferal diagenesis in more detail, and I am surprised that the authors didn't explore all the benefits of this in situ approach. Based on the method description and the data presented in Fig. 3, the Element/Calcium ratios of the three laser ablation analyses (=profiles through chamber wall)

for each shell were simply averaged. If the (averaged) Al/Ca and Sr/Ca ratios exceeded certain threshold values, the shell was considered to be significantly affected by alumina-silicate contamination and/or diagenesis, consequently, the Mg/Ca ratio was not used for climate reconstruction. In my opinion, there is much more to explore. While the laser is 'drilling' through the foraminiferal chamber wall (with an ablation rate of 0.2-0.3 $\mu\text{m/s}$), the Element/Ca ratios are measured in real time (with a few seconds delay, as the ablated material needs to pass through tubes and the spray chamber before being ionized in the plasma). Therefore, it is possible to compute elemental concentration profiles through foraminiferal chamber walls at micrometer resolution. These laser ablation profiles provide detailed insights in the degree of diagenesis and/or recrystallization, as demonstrated in previous studies (e.g. Hathorne et al., 2003; Regenberg et al., 2007; Pena et al., 2008; van Raden et al., 2011). In processing these LA depth-profiles, it should be possible to determine if diagenesis and/or alumina-silicate contamination affects only on the outer and inner surface of the shells, or if these 'unwanted' phases penetrate deeper into the chamber wall. These information can also be used to locate domains that are less affected by diagenesis than the remaining shell (likely the inner part of the chamber wall). Would it be possible to compile – for comparison – an alternative Mg/Ca record using exclusively data from less altered portions of the shell? These are just suggestion, but I think they are worthwhile to explore. There are certainly more information in the data set than shown/discussed by the authors. Is it also possible to show some representative laser ablation profiles in the supplementary material?

Response 1: The referee asks that we give greater consideration to the potential impacts of diagenesis on Mg/Ca, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. We have addressed this in our response to Referee 1, who made a similar general comment. It is important to note that the aim of the foraminiferal isotope analysis was to provide constraints on the bulk isotope and Mg/Ca data. Based on the relatively poor preservation of the material, we fully expected to find the data somewhat compromised by diagenesis. We recognise that there may well be scope for further detailed work on the isotopic character of the foraminifera in this record of the type that the referee has pioneered, but this is outside the aims of the current study.

For LA-ICPMS analysis, we have improved the description of methods to clarify that we followed exactly the approach the referee recommends (Lines 204-229). After visual examination and cleaning, specimens were ablated. The LA depth profiles were then carefully screened to identify and exclude zones of contamination, diagenesis, or elemental anomalies of uncertain origin (Fig. S1). After this process, average values were determined for the selected segments on the profiles, not the entire profiles (Data plotted in new Fig. 3). Further screening was then performed on these average values to derive the Mg/Ca values used for temperature reconstructions (New Fig. 4 and S2). We agree that further study should be undertaken on the profiles to directly quantify diagenetic variation through this interval. However, this is outside the scope of the current study.

Other comments:

- Hollis et al. analyzed nine element by LA-ICP MS (Mg, Al, Si, Ca, Ti, Mn, Zn, Sr, and Ba), however, only Al/Ca, Sr/Ca and Mg/Ca ratios were used to assess the degree of diagenesis. What about Mn/Ca and Ba/Ca? The authors themselves cite studies using Mn/Ca and Ba/Ca ratios to evaluate contamination or diagenesis of foraminiferal shells. As the mechanisms of diagenesis are very

complex and site-specific, it may be possible that the data are not conclusive, however, results from other Element/Ca ratios should be at least briefly mentioned.

We could add Mn/Ca and Ba/Ca plots to Fig. 3 but they don't add much to the record as they show very similar trends to Al/Ca. We have included them in Fig. S2. Further discussion of other elements is outside the scope of this paper. Note that we also have a full suite of XRF data for the PETM interval that is not discussed here.

Furthermore, the authors emphasize a positive linear correlation between measured Al/Ca and Mg/Ca ratios. This linear correlation is difficult to identify from the data shown in Fig. 3. Therefore, I suggest to include an Al/Ca:Mg/Ca cross plot in the supplementary material - Page 259, lines 23-26:

We found the suggestion of adding cross-plots most helpful. Although they were part of our working files, we have not interrogated them sufficiently and are very pleased to see how well they appear to resolve questions relating to diagenesis (new Fig. 3, Lines 230-241, 503-527)

The observation that the Mg concentration is not being reset during shell recrystallisation is important and confirms in situ measurements of Mg/Ca ratios in diagenetic overgrowth that approach the values of biogenic foraminiferal calcite (Kozdon et al., 2013). However, these findings contradict the results of inorganic precipitation experiments showing about an order of magnitude more Mg in diagenetic than in biogenic calcite (e.g. Mucci and Morse, 1983; Oomori et al., 1987), and I encourage the authors to take this opportunity and emphasize the difference between diagenesis in the sediment column and the results from inorganic precipitation experiment. Some scientists still believe that non-elevated Mg/Ca ratios are an indicator for good preservation.

We agree that our results are in good agreement with Kozdon et al. (2013), with very similar relationships between Sr/Ca and Mg/Ca, and an order of magnitude lower than the changes observed in laboratory experiments (Lines 515-517, compare our new Fig. 3 with Kozdon et al. 2013, Fig. 6)

Page 259, line 22: it shall read "Fig. 4d".

Corrected

Fig. 4d: is it possible to add a horizontal axis for d18O and Mg/Ca?

We think this is unnecessary because Mg/Ca is shown in Fig. 4c and d18O in Fig. 2 but yes, it's possible (at least for d18O).

1 ~~Onset of the~~The Paleocene-Eocene Thermal Maximum at DSDP Site 277, in the southern
2 ~~Pacific Ocean (DSDP Site 277, Campbell Plateau, southern Pacific Ocean)~~

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4 C.J. Hollis¹, B.R. Hines², K. Littler^{3,4}, V. Villasante-Marcos⁵, D.K. Kulhanek⁶, C.P. Strong¹, J. C.
5 Zachos³, S.M. Eggins⁷, L. Northcote⁸, A. Phillips¹

6
7 ¹ GNS Science, PO Box 30-368, Lower Hutt 5040, New Zealand

8 ² School of Geography, Environment & Earth Sciences, Victoria University of Wellington,
9 New Zealand

10 ³ Earth & Planetary Sciences, University of California – Santa Cruz, California 95060, USA

11 ⁴ Camborne School of Mines, University of Exeter, Penryn Campus, Cornwall, TR10 9FE, UK

12 ⁵ Observatorio Geofísico Central, Instituto Geográfico Nacional, 28014 Madrid, Spain

13 ⁶ International Ocean Discovery Program, Texas A&M University, College Station, TX 77845-
14 9547, USA

15 ⁷ Research School of Earth Sciences, The Australian National University, Canberra 0200, ACT,
16 Australia

17 ⁸ National Institute of Water and Atmosphere, PO Box 14901, Wellington, New Zealand

18
19 **ABSTRACT**

20 Re-examination of ~~a~~sediment cores collected by thefrom Deep Sea Drilling Project (DSDP) Site 277)
21 on the western margin of the Campbell Plateau,~~Southwest Pacific Ocean~~ (paleolatitude of ~65°S),
22 has identified an intact Paleocene-Eocene (P-E) boundary overlain by a 34 cm-thick record of the
23 ~~initial phase of the~~Paleocene-Eocene Thermal Maximum (PETM) within nanofossil chalk. The upper
24 part of the PETM is truncated, either due to drilling disturbance or a sedimentary hiatus. An intact
25 record of the onset of the PETM is indicated by a gradual decrease in $\delta^{13}\text{C}$ values over 20 cm,
26 followed by a 14 cm interval in which $\delta^{13}\text{C}$ is 2‰ lighter than uppermost Paleocene values. After
27 accounting for effects of diagenetic alteration, we use $\delta^{18}\text{O}$ and Mg/Ca values from foraminiferal
28 tests to determine that intermediate and surface waters warmed by ~~~5-6°~~ at the onset of the PETM
29 prior to the full development of the negative $\delta^{13}\text{C}$ excursion. After this initial warming, sea
30 temperatures were relatively stable through the PETM, but declined abruptly across the
31 ~~unconformity horizon~~ that truncates the event at this site. Mg/Ca analysis of foraminiferal tests
32 indicate peak intermediate and surface water temperatures of ~19°C and ~32°C, respectively. These

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33 | temperatures may be influenced by residual diagenetic factors, changes in ocean circulation,
34 | ~~enhanced poleward ocean heat transport during the PETM~~ and surface water values may also be
35 | biased towards warm season temperatures.

36 |
37 | **1. Introduction**

38 | Stable isotope analysis of foraminiferal tests from sediments cored at DSDP Site 277 (Shackleton and
39 | Kennett, 1975) provided the first paleotemperature record for the Paleogene of the Southern Ocean
40 | and laid the foundation for many subsequent studies of the regional paleoclimate and
41 | paleoceanography (e.g., Kennett 1977, 1980; Kennett and Shackleton, 1976; Hornibrook, 1992;
42 | Nelson and Cook, 2001). Over the last decade, there has been renewed interest in the early
43 | Paleogene (66 to 35 Ma) climate history of the Southern Ocean, partly driven by a societal
44 | imperative to understand how the Antarctic ice sheet will respond to anthropogenic global warming
45 | (e.g., Joughin et al., 2014). The early Paleogene was the last time that Earth is inferred to have
46 | experienced greenhouse gas levels in excess of ~600 ppm CO₂ (Zachos et al., 2008; Beerling and
47 | Royer, 2011), and therefore provides insight into a climate state that civilization may experience in
48 | coming centuries. One event in particular has been touted as a geological analogue for greenhouse
49 | gas-driven global warming: the Paleocene-Eocene Thermal Maximum (PETM, ~56 Ma). This event
50 | was a short-lived (~220 kyrs) perturbation to the climate and carbon cycle in which global
51 | temperatures rose by 4–5°C within a few thousand years (Sluijs et al., 2007; McInerney and Wing,
52 | 2011; Dunkley-Jones et al., 2013; Schmidt, 2014), with warming of up to 8°C in higher latitudes and
53 | some coastal settings (Thomas et al., 2002; Sluijs et al., 2006, 2011; Zachos et al., 2006; Hollis et al.,
54 | 2012; Frieling et al., 2014). Multiple lines of evidence suggest that this warming may have been
55 | driven by a rapid injection of greenhouse gases, possibly sourced from submarine gas hydrates, as
56 | evidenced by coupled negative excursions in oxygen and carbon isotopes (Dickens et al., 1995,
57 | 1997). Several other potential sources of the light carbon have also been implicated to account for
58 | all or part of the carbon isotope ($\delta^{13}\text{C}$) excursion (Dickens, 2003, 2011; Kent et al., 2003; Svensen et
59 | al., 2004; Higgins and Schrag, 2006; De Conto et al., 2012).

60 | The PETM has been identified in several sites in the Southwest Pacific, including onshore
61 | records in both siliciclastic and pelagic bathyal sections in eastern New Zealand (Kaiho et al., 1996;
62 | Crouch et al., 2001; Hancock et al., 2003; Hollis et al., 2005a, b, 2012; Nicolo et al., 2010), non-
63 | marine to marginal marine sediments in western New Zealand (Handley et al., 2011) and in shelfal
64 | sediments at Ocean Drilling Program (ODP) Site 1172, offshore eastern Tasmania (Sluijs et al., 2011).
65 | Here we report a new record of the PETM in pelagic bathyal sediments at DSDP Site 277, at a similar

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66 paleolatitude to Site 1172 (~65°S). These two sites represent the southernmost records of the PETM
67 in the Pacific Ocean (Fig. 1).

68 Initial studies of Site 277 suggested that the Paleocene-Eocene (P-E) boundary occurred
69 within a gap between cores 43 and 44 (Kennett et al., 1975). A subsequent biostratigraphic review of
70 the site (Hollis et al., 1997) revealed that the boundary was lower in the drillhole, potentially within
71 a relatively continuous interval preserved in core 45. Detailed re-sampling confirmed the location of
72 the P-E boundary (Fig. 2), based on the highest occurrence (HO) of benthic foraminifer *Stensionina*
73 *beccariformis* at 457.3 mbsf (277-45-3, 80 cm). High resolution stable isotope analysis of bulk
74 carbonate confirms that this horizon marks the base of a 34 cm-thick negative excursion in $\delta^{13}\text{C}$ (CIE)
75 that defines the PETM (Fig. 2 Aubry et al., 2007).

76 DSDP Site 277 was drilled on the western margin of the Campbell Plateau in a water depth
77 of 1214 m as part of DSDP Leg 29 (Kennett et al., 1975). Paleogene sedimentation occurred in fully
78 oceanic conditions well above the lysocline (Kennett et al., 1975), with benthic foraminiferal
79 assemblages indicating lower to middle bathyal water depths since the Paleocene (Hollis et al.,
80 1997). In order to characterise sedimentary and identify the paleoceanographic changes associated
81 with the PETM at this site we have undertaken a multidisciplinary study that includes foraminiferal
82 and calcareous nannofossil biostratigraphy, magnetic susceptibility, CaCO_3 content, elemental
83 abundance using X-ray fluorescence (XRF), $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analysis of bulk carbonate and
84 foraminifera, and single test analysis of foraminifera for Mg/Ca ratios by Laser Ablation Inductively
85 Coupled Plasma Mass Spectrometry (LA-ICPMS).

86 87 **2. Material and Methods**

88 **2.1. Material**

89 We analysed samples over a 45-m interval spanning the upper Paleocene to lower Eocene at
90 DSDP Site 277 (470–425 mbsf). Average sample spacing was 20 cm over much of the interval, with a
91 higher resolution of 2–3 cm sampling across the PETM within core-section 45-3 (~457.30–456.95
92 mbsf). In addition, this core-section was scanned for elemental abundance. Although the PETM
93 interval is preserved, the overall record is discontinuous, with significant gaps between cores from
94 core 42 to 45 (Fig. 2).

95 96 **2.2. Methods**

97 **2.2.1. X-Ray fluorescence (XRF) core scanning**

98 XRF data were acquired using an Avaatech XRF scanner with a Canberra X-PIPS silicon drift
99 detector, model SXD 15C-150-500 150 eV resolution X-ray detector, which is housed at the

100 International Ocean Discovery Program (IODP) Gulf Coast Repository at Texas A&M University in
101 College Station, Texas (Table S1). This scanner is configured for analysis of split core section halves,
102 with the X-ray tube and detector mounted on a moving track (Richter et al., 2006). Section 277-45-3
103 was removed from the core refrigerator and allowed to equilibrate to room temperature prior to
104 analysis. We ~~leveled~~levelled all rock pieces within the section, as the detector requires a flush
105 surface with no gaps between pieces, and then covered the section with 4 µm thick Ultralene plastic
106 film (SPEX Centriprep, Inc.) to protect the detector. The section was scanned at 2 mm intervals using
107 a voltage of 10 kV for elements Al, Si, P, S, Cl, Ar, K, Ca, Ti, Cr, Mn, Fe, Rh, and Ba. The scan was
108 completed using a 1 mA tube current, no filter, and a detector live time of 30 s, with an ~~X~~-ray
109 detection area of 2 mm in the downcore direction and 15 mm across the core. During measurement,
110 intervals were skipped where gaps of more than ~2 mm existed between pieces. Smaller gaps were
111 noted so that suspect data across these gaps could be removed.

112 113 2.2.2. Rock magnetism

114 Bulk magnetic susceptibility of a subset of discrete samples was measured at the
115 Paleomagnetism Laboratory of the Complutense University of Madrid, Spain (Table S2). A KLY-4
116 (Agico) susceptibility bridge was employed, with an applied magnetic field of 300 A/m. Due to the
117 low ferromagnetic content of most ~~of the~~ samples, each sample was measured ten times and
118 averaged. The error bars of the magnetic susceptibility data correspond to the standard deviation of
119 the mean (1σ) obtained during the averaging procedure.

120 121 2.2.3. Micropaleontology

122 Calcareous nannofossil and foraminifera sample preparation and examination followed standard
123 procedures. Samples for calcareous nannofossils were prepared using standard smear-slide
124 techniques (Bown and Young, 1998). A small amount of sediment was mixed with a drop of water on
125 a coverslip, distributed with a toothpick, and then dried on a hot plate. The coverslip was affixed to a
126 glass microscope slide using Norland Optical Adhesive 61 and cured under an ultraviolet light. Slides
127 were examined on a Leitz Ortholux II POL-BK microscope under cross-polarized and plane-
128 transmitted lights. Nannofossil distribution was determined for 41 samples extending from
129 Paleocene to the upper lower Eocene (Teurian to Mangaorapan New Zealand stages) (Table S3).
130 Counts of 400 specimens were conducted at 1000× for each sample, followed by a scan of at least
131 400 fields of view at 630× to look for rare taxa ~~(Table 3)~~.

132 Foraminiferal distribution was determined for 59 samples extending from the Paleocene to late early
133 Eocene (Teurian to Mangaorapan local stages)spanning the same time interval (Table S4).

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134 | -Foraminiferal biostratigraphy is correlated with New Zealand stages (Cooper, 2004) and
 135 | international biozones (Olsson et al., 1999; Pearson et al., 2006). New Zealand stage and biozone
 136 | boundaries are calibrated to the 2012 geological timescale (Gradstein et al., 2012) using criteria
 137 | described by Hollis-Raine et al. (2015) and Norris et al. (2014). Foraminiferal taxonomy is based on
 138 | Hornibrook et al. (1989). Biostratigraphic results for calcareous nannofossils are correlated to the
 139 | biostratigraphic zonation scheme of Martini (1970, 1971), calibrated to the 2012 geological
 140 | timescale (Gradstein et al., 2012). Taxonomic concepts for species are those given in Perch-Nielsen
 141 | (1985) and Bown (1998).

142 |
 143 | *2.2.4. Stable isotopes and carbonate content*

144 | Analysis for stable isotopes and carbonate content was undertaken at three laboratories.
 145 | Results are tabulated in Table S5. Bulk carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements were undertaken at
 146 | the National Isotope Centre, GNS Science, Lower Hutt. Samples were analysed on the GVI IsoPrime
 147 | Carbonate Preparation System at a reaction temperature of 25°C and run via dual inlet on the
 148 | IsoPrime mass spectrometer. All results are reported with respect to VPDB, normalized to the GNS
 149 | marble internal standard with reported values of 2.04‰ for $\delta^{13}\text{C}$ and -6.40‰ for $\delta^{18}\text{O}$. The external
 150 | precision (1σ) for these measurements is 0.05‰ for $\delta^{13}\text{C}$ and 0.12‰ for $\delta^{18}\text{O}$.

151 | Individual specimens from five foraminiferal genera were used for stable isotope analysis
 152 | and elemental geochemistry. Specimens were selected for analysis based on visual assessment of
 153 | their preservation under a stereo microscope. Wherever possible, analyses were performed on
 154 | *Morozovella aequa*, *Acarinina coalingensis*, *Subbotina patagonica*, *S. roesnasensis*, and *Cibicides*
 155 | *proprius/praemundus*, and *Stensioina beccariformis*. The following species were substituted when
 156 | these species were not available: *Morozovella subbotinae*, *M. acuta*, *M. apantesma*, *Acarinina*
 157 | *soldadoensis*, *A. subsphaerica*, *A. esnaensis*, *A. nitida* and *Cibicides tholus*. The stable isotope
 158 | signature of *Acarinina soldadoensis*, *A. subsphaerica*, *A. nitida* and all species of *Morozovella*
 159 | indicates they were mixed layer dwellers (Olsson et al., 1999; Quillévéré and Norris, 2003), and
 160 | therefore are appropriate indicators of near surface conditions. *Subbotina patagonica* is inferred to
 161 | have had a deeper planktonic habitat (Pearson et al., 2006), within the thermocline. There is no data
 162 | on the habitat of *S. roesnasensis*. Individual specimens from five foraminiferal genera were used for
 163 | $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ and Mg/Ca analysis. Samples were selected based on light microscope assessment of
 164 | preservation, which was subsequently confirmed by scanning electron microscope (SEM)
 165 | examination. The genera used include two near-surface dwelling genera, *Morozovella* and
 166 | *Acarinina*, the thermocline dweller *Subbotina* and two benthic genera, *Cibicides* and *Stensioina*.

167 Stable isotope analysis of foraminifera was carried out in the Stable Isotope Laboratory at the
168 University of California, Santa Cruz. Between 1 and 6 (average of 3) specimens of *Cibicides*, 1 and 5
169 (average of 3) specimens of *Stensioina*, 3–17 (average of 10) specimens of *Acarinina*, 2–10 (average
170 of 4) specimens of *Morozovella*, and 1–8 (average of 5) specimens of *Subbotina* were used in each
171 analysis. Specimens were first sonicated in deionised water to remove clay and detrital calcite.
172 Isotopic measurements were carried out on a Thermo-Finnigan MAT253 mass spectrometer
173 interfaced with a Kiel Device. The analytical precision (1σ) is based on repeat analysis of an in-house
174 standard (Carrara marble), calibrated to the international standards NBS18 and NBS19, and averages
175 $\pm 0.05\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.08\text{‰}$ for $\delta^{18}\text{O}$. All values are reported relative to VPDB. For the $\delta^{18}\text{O}$ values
176 of *Cibicides* (= *Cibicoides*; see Schweizer et al., 2009) and *Stensioina*, we apply an isotopic
177 correction factor of +0.28 (Katz et al., 2003).

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178 Paleotemperatures for both benthic and planktic taxa were calculated from $\delta^{18}\text{O}$ using the
179 equation of Kim and O'Neil (1997):

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$$T (^{\circ}\text{C}) = 16.1 + -4.64(\delta^{18}\text{O}_M - \delta^{18}\text{O}_{\text{SW}}) + 0.09(\delta^{18}\text{O}_M - \delta^{18}\text{O}_{\text{SW}})^2$$

Equation 1

182 Where $\delta^{18}\text{O}_M$ = measured value and $\delta^{18}\text{O}_{\text{SW}} = -1.2346\text{‰}$, which is the inferred value for sea water
183 under ice-free conditions (assuming ice-free ocean values of = -1‰). Planktic values are also
184 corrected for adjusted for paleolatitude (Zachos et al. 1994; correction of -0.23‰) and ice-free
185 conditions (assuming ice-free ocean values of = -1‰).

186 The carbonate content of dried powdered samples was determined at the National Institute
187 of Water and Atmosphere (NIWA, Wellington) via gasometric quantitative analysis after acidification
188 (Jones and Kaiteris, 1983), with a precision of $\pm 2\%$.

190 2.2.5. Elemental geochemistry and Mg/Ca analysis

191 Foraminifera were picked from the 150–300 μm fraction of washed sediment samples and
192 individually washed in ultra-pure ($>18.2\text{ m}\Omega$) water and analytical grade methanol three times
193 before being mounted on double-sided tape adhered to a glass slide. Wherever possible, the species
194 *Morozovella crater*, *Acarinina primitiva* and *Cibicides eocaenus* were selected. Where these species
195 were not available, *M. lensiformis*, *A. collactea* and *C. truncatus* were substituted. *Subbotina* was not
196 subdivided beyond the genus level.

197 Mg/Ca analysis was carried out on samples composed of 4–19 specimens for each of the selected
198 genera in each sample (Table S6). Each foraminifer was analysed at least three times using a pulsed
199 Ar-F excimer laser (Lambda Physik LPFpro 205) with a 193 μm wavelength, 30 μm spot size, laser
200 power of 3 J/cm^2 and a repetition rate of 3 Hz, in conjunction with an ANU HelEx laser ablation cell,

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201 at the Research School of Earth Sciences of the Australian National University. An analysis of the
202 NIST-SRM610 silicate standard was taken between every 9–12 foraminifer analyses to correct for
203 elemental fractionation originating from laser ablation and mass-spectrometry effects.

204 The final three chambers of the final whorl in each specimen were analysed individually by
205 ablating slowly at a rate of 0.2–0.3 $\mu\text{m s}^{-1}$ to produce a separate trace element profile through the
206 wall of each chamber (Fig. S1). A Varian 820 ICPMS was used to measure abundances of the trace
207 metal isotopes ^{24}Mg , ^{27}Al , ^{29}Si , ^{47}Ti , ^{55}Mn , ^{66}Zn , ^{88}Sr and ^{138}Ba relative to ^{43}Ca during ablation.
208 Elemental ratios reported ~~in this study for each sample~~ are ~~the~~ average ~~values derived from~~ the
209 multiple ~~screened chamber profiles~~ ~~profile segments measured in individual~~ ~~for multiple foraminifer~~
210 specimens ~~of a given taxon~~. Laser ablation sites were selected ~~using light microscopy and SEM~~
211 ~~imaging~~ to avoid zones of detrital contamination, recrystallization or test ornamentation ~~which that~~
212 might cause irregular trace element/Ca profiles (Fig. S1).

213 ~~The extraction of a reliable paleotemperature record from variably preserved foraminifera is~~
214 ~~dependent on the preservation of primary foraminiferal calcite, and its inherent geochemical~~
215 ~~signature. In addition to using reflected light microscopy and SEM imaging to qualitatively screen~~
216 ~~tests for preservation, stringent Individual chamber profiles screening criteria were applied~~ ~~screened~~
217 to exclude zones ~~with anomalously high Mg/Ca, Al/Ca, Mn/Ca or Ba/Ca ratios, which indicate~~
218 ~~significant within test wall profiles that show evidence of diagenetic alteration or~~ ~~silicate~~
219 contamination ~~as evident from anomalous Mg/Ca, Al/Ca, Mn/Ca, Ba/Ca and Sr/Ca ratios~~ (Barker et
220 al., 2003; Greaves et al., 2005; Creech et al., 2010). ~~Individual trace element~~ ~~These~~ profiles typically
221 show zones of ~~enriched in substantially~~ ~~Mg, Al, Mn, and Ba~~ ~~elevated Mg/Ca, Al/Ca and Mn/Ca ratios~~
222 on the outside and inside surfaces of the ~~foraminifera test chamber~~ wall, ~~indicating siliciclastic~~
223 ~~sediment contamination consistent with silicate contamination (Fig. S1).~~ ~~whereas~~ ~~The Sr/Ca ratio is~~
224 ~~used as an indicator of diagenetic alteration because the concentration of Sr may decrease or~~
225 ~~increase during alteration or secondary calcification (Eggins et al., 2003; Kozdon et al., 2013). A ratio~~
226 ~~of ~1.4 is typical for well-preserved tests (Creech et al., 2010). Therefore, typically occurs at uniform~~
227 ~~levels throughout the test. Concentration may decrease or increase during alteration or secondary~~
228 ~~calcification (Eggins et al., 2003). Thus,~~ samples with Sr/Ca values outside the range of 0.8–1.6
229 mmol/mol were considered to be affected by diagenesis (Fig. 33).

230 Al/Ca and Mg/Ca data show a positive linear correlation when plotted (Fig. 3), reflecting the
231 influence of ~~alumino-silicate mineral~~ ~~contamination~~. ~~This~~ ~~We have used~~ ~~contamination has been~~
232 ~~screened out using~~ the method of Creech (2010); ~~after~~ ~~Barker et al.~~ ~~(2003)~~ ~~to screen for this~~
233 ~~contamination~~. The Al/Mg composition of the contaminant phase was identified by plotting Mg/Ca
234 against Al/Ca and finding the slope of the linear regression. Once this ~~Mg/Al~~ ~~Al/Mg~~ composition had

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235 been determined for each genus, the screening threshold was set by calculating the Al/Ca ratio at
236 which paleotemperature estimates would be biased by more than 1 °C. This screening removes
237 anomalously high Mg/Ca values and reduces the mean value for most samples (Fig. 4, S2). After the
238 measurements have been screened for silicate contamination, the effects of diagenesis are more
239 easily assessed (Fig. 3). A weak negative correlation between Sr/Ca and Mg/Ca suggests that
240 diagenesis may also cause an increase in Mg/Ca values, especially in the planktic genus *Acarinina*.
241 The reasons for this correlation and implications are discussed below.

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242 ~~This involved determining the corresponding Mg/Ca excess value by multiplying the~~
243 ~~observed mean Mg/Ca ratio for each species by the sensitivity of the paleotemperature calibration~~
244 ~~(i.e. an increase of 9% in Mg/Ca per 1 °C after Anand et al., 2003). Once determined the Mg/Ca~~
245 ~~excess value for each species is multiplied by the Al/Mg contaminant phase to determine the Al/Ca~~
246 ~~ratio at which the screening threshold is set. This methodology circumvents the inclusion of~~
247 ~~artificially inflated paleotemperature estimates arising from silicate contamination (Fig. 3). The~~
248 ~~resulting reduction in average Mg/Ca ratios of the screened compared to the unscreened and data is~~
249 ~~shown in Figure 3.~~

Comment [CH1]: Method is described in Creech et al. (2010).

250 ~~The application of these screening limits to trace element data means that no Mg/Ca marine~~
251 ~~temperatures in this study should be overestimated by more than 1°C (as a result of post-mortem~~
252 ~~diagenetic effects or sedimentary contamination).~~

253 Marine paleotemperatures are calculated using the exponential relationship between Mg/Ca
254 and temperature (*Equation 2*). Because the planktic foraminifera used in this study are extinct, sea
255 surface temperatures (SSTs) were calculated using a general calibration based on the mean
256 calcification temperatures of nine modern planktic species ($A = 0.09$, $B = 0.38$; Anand et al., 2003).
257 Sea floor temperatures (SFTs) were calculated using the calibration of Lear et al. (2002) based on
258 three benthic species of *Cibicidoides/Cibicides* species ($A = 0.109$, $B = 0.867$).

$$Mg/Ca_{test} = \left(\frac{Mg/Ca_{sw}^{t=t}}{Mg/Ca_{sw}^{t=1}} \right) \times B \exp^{AT}$$

Equation 2

259 Marine temperature reconstructions based on early Eocene foraminiferal calcite have shown that a
260 high (>3 mol/mol) Mg/Ca_{sw} value is necessary-required to reconcile Mg/Ca-derived
261 paleotemperatures with those derived from $\delta^{18}O$ (Lear et al., 2002; Sexton et al., 2006). Such high
262 Mg/Ca_{sw} values are in line with modelled values from Wilkinson & Algeo (1989) but are at odds with
263 several proxy studies (e.g., Horita et al., 2004; Coggon et al., 2010) and models more recent
264 modelling (e.g., Stanley & Hardie, 1998) that favour lower values for Mg/Ca_{sw} (<2 mol/mol), but are
265 in line with modelled values from Wilkinson & Algeo (1989), and multi-proxy paleotemperature

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267 reconstructions (Hollis et al., 2012). Lower values of Paleogene Mg/Ca_{sw} (e.g., Stanley & Hardie,
 268 1998; Coggon et al., 2010) result in unrealistically high temperatures using Equation 2. However,
 269 recent studies (Hasuik & Lohmann, 2010, Evans & Müller, 2012) have shown reconciled the empirical
 270 relationship between δ¹⁸O and Mg/Ca paleotemperatures with these lower values for Mg/Ca_{sw} by
 271 showing that a power law relationship distribution, rather than an exponential
 272 relationship distribution, may better describes the relationship between Mg-partitioning and
 273 temperature in foraminiferal calcite. (Equation 3).

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$$Mg/Ca_{test} = \left(\frac{B}{Mg/Ca_{sw}^{t=0H}} \right) \times Mg/Ca_{sw}^{t=H} \exp^{AT}$$

Equation 3

274 In applying this method, it is possible to derive realistic paleotemperatures using a lower Eocene
 275 Mg/Ca_{sw} value that is consistent with Mg/Ca_{sw} proxy evidence. To apply this equation we use
 276 Exponential exponential and pre-exponential calibration constants from modern multispecies
 277 calibrations and paleotemperature values derived from oxygen isotopes can be utilised to estimate
 278 the function H for extinct foraminifera. Using published data from well-preserved Eocene
 279 foraminifera at Hampden Beach (Burgess et al., 2008; Hollis et al., 2012) and Tanzania (Pearson et
 280 al., 2007), for which paired Mg/Ca and δ¹⁸O data is available, it is possible have been used to derive
 281 the calibration correction constants (H) for the extinct species used in this study.

282 In calculating the value of H, we have used an early Eocene Mg/Ca_{sw} value of 1.6 mol/mol
 283 (Stanley & Hardie, 1998; Evans & Müller, 2012) and a modern Mg/Ca_{sw} value of 5.17 mol/mol. This
 284 values of H determined for Paleogene foraminifera in this study are an approximation that do value
 285 does not take into account the likely fine-scale possible variability in Mg/Ca_{sw} values through the
 286 early Paleogene. The Mg/Ca-temperature calibrations of Anand et al. (2003) and Lear et al. (2002)
 287 have been used, although it is likely that the pre-exponential constant of Paleogene planktic
 288 foraminifera differed from that of the modern taxa. We calculate an H values of H calculated of
 289 20 for Paleogene planktic foraminifera, which is significantly are lower (H = 0.20) than that for the H
 290 values for modern taxon planktics, such as *Globigerina sacculifer* (H = 0.42; Hasuik & Lohmann,
 291 2010), possibly due to differences in Mg/Ca-temperature calibration. For benthic foraminifera,
 292 Cramer et al. (2011) suggest that the value of H would be similar between *Cibicides* sp. and
 293 *Oridorsalis umbonatus*. Mg/Ca-derived temperature values are calculated using Equation 4.

Comment [CH2]: What is it??

$$T = \frac{\ln \left(\frac{[Mg/Ca_{test}] \times [Mg/Ca_{sw}^{t=0}]^H}{B \times [Mg/Ca_{sw}^{t=t}]^H} \right)}{A}$$

Equation 4

296 | Temperature values derived from Mg/Ca ratios of surface mixed-layer dwelling taxa used in this
297 | study are normalised to *Morozovella crater* following Creech et al. (2010).

298 | Three types of error are applied to paleotemperatures derived from Mg/Ca ratios; the
299 | analytical error, sample error and a standard calibration error. The analytical error is accounted for
300 | in the data processing step, and typically produces very small uncertainties ($\pm 1\text{--}3\%$ 2se) associated
301 | with counting statistics during ablation and data acquisition. The sample error pertains to the 95%
302 | confidence interval calculated for the mean temperature value obtained from multiple analyses
303 | within a single sample, and is calculated by:

$$\bar{X} \pm t \times \frac{\sigma}{\sqrt{n}}$$

304 | Equation 5

305 | Where \bar{X} is the sample mean, t is the inverse of the Students' t-distribution, σ represents the
306 | standard deviation and n is the number of analyses. The calibration error is the residual error of
307 | $\pm 1.6^\circ\text{C}$ on the regression of the multispecies calibrations established by Lear et al. (2002) and Anand
308 | et al. (2003). The cumulative error calculated from the sum of all three errors is applied to each
309 | temperature value, providing upper and lower uncertainties.

310 | **3. Results and Discussion**

311 | **3.1 Stratigraphy**

312 | The 45 m-thick studied interval (425–470 mbsf) consists of five cores, with significant gaps
313 | due to poor recovery in three of the cores, which extend from middle Paleocene to lower Eocene
314 | (Fig. 2). The sediments are greenish-white to greenish-grey nannofossil chalk, with higher clay
315 | content in the upper Paleocene (core 46; 463–470 mbsf) and lowermost Eocene (core section 45-3;
316 | 456.96–457.3 mbsf) and minor glauconite (cores 43-44) and chert nodules (cores 41-43) in the
317 | overlying Eocene. A record of “incipient chert” in core section 45–3 (Kennett et al., 1975) may have
318 | been a misidentification of the darker-grey clay-rich sediments at the base of the PETM (Fig. 54).

319 | Calcareous microfossils are only moderately well-preserved overall, although and there is an
320 | interval directly below the Paleocene-Eocene boundary (457.3 to 457.58 mbsf) in which foraminifera
321 | are poorly preserved and sparse. Planktic foraminifera are used to correlate the 45 m-thick studied
322 | interval to New Zealand stages (Teurian to Mangaorapan) and to international foraminiferal zones
323 | P4a-b to E7 (Fig. 2). Nannofossil assemblages over the same interval have been correlated with
324 | nannofossil zones NP6 to NP12. Whereas previous studies indicated an undifferentiated upper
325 | Paleocene succession spanning Zone NP6–8 (Edwards and Perch-Nielsen, 1975; Hollis et al., 1997),
326 | we infer a ~ 2 Myr hiatus near the top of Core 46 (463.49–463.16 mbsf), representing all of zones
327 |

328 NP7 and NP8. Immediately above the hiatus, *Discoaster multiradiatus* makes up ~2% of the
329 assemblage, suggesting that ~~the first appearance datum (FAD) of this zonal marker (and thus the~~
330 ~~base of lowermost part of~~ Zone NP9) is missing. This ~~horizon-lowest occurrence (LO) of *D.*~~
331 ~~multiradiatus marks the lowest occurrence (LO) of *Discoaster* at this site, including coincides with~~ the
332 LOs of *D. lenticularis* and *D. salisburgensis* ~~in addition to *D. multiradiatus*.~~

333 The PETM is a 34 cm-thick interval within core 45 (457.3–456.96 mbsf) that is clearly
334 delineated by a 40% decrease in carbonate content and 2–3‰ negative excursions in bulk carbonate
335 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (Fig. 2). ~~The location of the PETM is confirmed by biostratigraphy.~~ The ~~B~~enthic
336 ~~F~~oraminiferal ~~E~~xtinction ~~E~~vent (BFEE) is identified directly below the PETM at 457.3 mbsf based
337 on the highest occurrences of the *Stensioina beccariformis*, *Gyroidinoides globosus* and *G.*

338 *subangulatus*. ~~The planktic foraminiferal genus *Morozovella* has its lowest occurrence at the base of~~
339 ~~the PETM and greatest diversity within the PETM. *Morozovella aequa* and *M. velascoensis* are~~
340 ~~restricted to the PETM. The latter species has rarely been found outside the PETM in the SW Pacific~~
341 ~~but *M. aequa* ranges into the middle late Eocene in New Zealand sections (Hornibrook et al. 1989).~~

342 For nannofossils, taxa typical of the PETM in other regions, such as the *Rhomboaster* lineage,
343 *Discoaster araneus* and *D. anartios* (e.g., Bybell and Self-Trail, 1994; Kahn and Aubry, 2004), ~~do not~~
344 ~~occur at Site 277 are absent here.~~ Instead, the nannofossil assemblage is characterized by deformed
345 *Discoaster* specimens, many similar to *Discoaster nobilis* (e.g., Raffi and De Bernardi, 2008), as well
346 as increased abundance of *Coccolithus* spp. and the presence of *Fasciculithus* spp. and *Bomolithus*
347 *supremus*, which is restricted to the PETM interval at this site. Immediately above the PETM (456.92
348 mbsf), the abundances of *Fasciculithus* spp. and *Coccolithus* spp. decrease significantly, with a
349 concomitant increase in *Zygrhablithus bijugatus*. As discussed below, the stable isotope record
350 through the P-E transition indicates that the PETM is truncated, with only the onset ~~and body~~ of the
351 CIE represented by these 34 cm of sediment.

352 ~~An age-depth plot (Fig. S3) based on calcareous nannofossil and foraminiferal bioevents~~
353 ~~(Table S7) provides a preliminary guide to compacted sedimentation rates. This rate appears to have~~
354 ~~been relatively low in the Paleocene (0.4 to 0.45 cm/kyr) either side of the hiatus at ~463.4 mbsf, but~~
355 ~~approximately four times higher in the early Eocene (1.68 cm/kyr). However, a rather patchy~~
356 ~~distribution of events and uncertainty over the duration of hiatuses means that it is possible to~~
357 ~~construct an alternative age model in which rates were consistent across the Paleocene-Eocene~~
358 ~~transition (dashed line in Fig. S3). Although this implies that the sedimentation rate for the PETM~~
359 ~~interval could lie anywhere between the low Paleocene rate and the high Eocene rate, the lower~~
360 ~~rate is consistent with the duration of the CIE from onset to $\delta^{13}\text{C}$ minimum, i.e., ~45–66 kyrs (Röhl et~~
361 ~~al., 2007).~~

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362 The base of the PETM coincides with a distinct colour change to a darker greenish-grey chalk
363 that grades back into greenish-white chalk over 15 cm (Fig. 54). This dark interval is also highly
364 burrowed. Burrowing is also evident in other parts of the core but it is less obvious in more pale
365 lithologies. XRF core scanning shows an increase in Fe content at the base of this interval, followed
366 by a cyclical decrease to background levels at 456.95 m (Fig. 54A). ~~A lower stratigraphic-resolution~~
367 ~~analysis-record~~ of magnetic susceptibility in discrete samples reveals a similar trend: a peak near the
368 base of the darker interval, followed by a quasi-cyclical decrease to background levels. ~~The peaks~~
369 ~~are inferred to represent intervals of higher clay content based on the parallel trends. An increase in~~
370 ~~clay content is inferred from the coupled increases in Fe and magnetic susceptibility and the~~
371 ~~decrease in carbonate content. Many of the other peaks and troughs in the Fe record below and~~
372 ~~above the PETM are scanning artefacts related to core breaks. However, parallel peaks in magnetic~~
373 ~~susceptibility and Fe content in the lower part of core 45 (~457.7 mbsf) appears to be a robust signal~~
374 ~~although the cause is unknown. There are no accompanying changes in isotopic signature or obvious~~
375 ~~lithological changes at this level.~~

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377 A 10 cm interval directly below the PETM also has a reduced carbonate concentration but
378 there is no change in $\delta^{13}\text{C}$ (Fig. 2, 5B) ~~and only a small positive shift in $\delta^{18}\text{O}$ of ~0.4‰ in both bulk and~~
379 ~~foraminiferal calcite (Fig. 2).~~ As there is no accompanying increase in magnetic susceptibility or Fe
380 content (Fig. 5A), the decrease in carbonate content seems to be due to an increase in silica, perhaps
381 associated with the slight cooling indicated by ~~a small positive shift in $\delta^{18}\text{O}$ of ~0.4‰ in both bulk~~
382 ~~and foraminiferal calcite (Fig. 2, 5D) the positive shift in $\delta^{18}\text{O}$.~~ ~~Although the silica is presumed to be~~
383 ~~biogenic, siliceous microfossils have not been recovered from this interval. The cause of a peak in~~
384 ~~magnetic susceptibility and Fe content in the lower part of core 45 is unknown. There are no~~
385 ~~accompanying changes in isotopic signature and no obvious lithological changes.~~

386 An age-depth plot (Fig. 5) based on calcareous nannofossil and foraminiferal bioevents
387 (Table 7) provides a preliminary guide to compacted sedimentation rates. This rate appears to have
388 been relatively low in the Paleocene (0.4 to 0.45 cm/kyr), either side of the hiatus at ~463.4 mbsf,
389 but approximately four times higher in the early Eocene (1.68 cm/kyr). However, a rather patchy
390 distribution of events and uncertainty over the presence and duration of hiatuses means that it is
391 possible to construct an alternative age model in which rates were consistent across the Paleocene-
392 Eocene transition (dashed line in Fig. 5). Although this implies that the sedimentation rate for the
393 PETM interval could lie anywhere between the low Paleocene rate and the high Eocene rate, the
394 lower rate is consistent with the duration of the onset known from other sites, i.e., 50–100 kyr
395 (Zachos et al., 2008, 2010; Nicolo et al., 2010; McInerney and Wing, 2011).

396 For a sedimentation rate of 0.45 cm/kyr, the 34 cm thick PETM interval represents ~85-76
397 kyrs and the three peaks in Fe content represent a periodicity close to the precession band
398 (19-22~21 kyrs). Indeed, there is good agreement between the Fe cycles and $\delta^{13}\text{C}$ record at Site 277
399 and ODP Site 690 (Röhl et al., 2007), where the negative CIE occurs over three steps and the $\delta^{13}\text{C}$
400 minimum (Horizon C of Zachos et al., 2005) occurs within the third Fe peak. Based on this correlation
401 with Site 690, we infer that the interval from the CIE onset to the base of Cycle 4 is preserved at Site
402 277, or the first 66 kyrs of the PETM (Röhl et al., 2007), implying a slight increase in sedimentation
403 rate through the PETM (52 cm/kyr).

405 3.2. Stable isotopes and paleotemperatures

406 Bulk carbonate stable isotopes display a significant offset between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ minima, with the
407 $\delta^{18}\text{O}$ minimum occurring at the base of the PETM and the $\delta^{13}\text{C}$ minimum occurring at the top
408 following a gradual decline in the upper part of the PETM (Fig. 2, 54B). The negative $\delta^{13}\text{C}$
409 excursion CIE of ~2‰ is slightly smaller than observed in most marine sections the average for marine
410 sections elsewhere (e.g., Nicolo et al., 2010; 2.7‰; McInerney and Wing, 2011) and occurs gradually
411 over the entire recovered lower 20 cm of the PETM record. In contrast, the 3‰ negative $\delta^{18}\text{O}$
412 excursion ($\delta^{18}\text{O}$ excursion OIE) is abrupt at the base of the PETM and is far larger in magnitude than is
413 known elsewhere (e.g., Zachos et al., 2008; McInerney and Wing, 2011; Bains et al. 1999; Dunkley
414 Jones et al., 2013). If this a primary feature and due solely to a change in temperature, this 3‰
415 excursion would equate to ~12°C of warming (Fig. 54D); however, it is most likely an artifact artifact
416 of diagenesis as is discussed below.

417 Examination of foraminiferal $\delta^{18}\text{O}$ values and Mg/Ca ratios within three genera of planktic
418 foraminifera and one benthic genus provide insight into the nature of the diagenetic process help to
419 separate the diagenetic effects from the paleotemperature record. As none of the foraminifera
420 recovered in this study have “glassy” preservation (Sexton et al. 2006; Pearson and Burgess, 2008;
421 Kozdon et al., 2013), all are assumed to have been altered to varying
422 degrees. Based on visual and geochemical criteria, we were able to identify relatively well preserved
423 tests. We selected the best preserved specimens for isotopic analysis of those tests (Fig. 2, 5B, 6).
424 Our results indicate that show that their normal surface to deep $\delta^{13}\text{C}$ gradients are preserved in the
425 foraminiferal tests, with bulk carbonate $\delta^{13}\text{C}$ values lying within the range of, or slightly lighter
426 than, planktic foraminiferal $\delta^{13}\text{C}$ throughout the studied interval, with the exception. An exception is
427 noted in of the base-basal of the CIE PETM where two values are more positive than planktic $\delta^{13}\text{C}$
428 (Fig. 5B, 66B). Benthic $\delta^{13}\text{C}$ values are >0.7‰ lighter than both planktic and bulk carbonate values,
429 apart from the basal PETM sample where a negative gradient of -0.37‰ occurs between *Acarinina*

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430 and *Cibicides* (Fig. 5B, 6B). The implication is that the onset of the CIE is recorded more strongly in
431 planktic foraminifera (i.e. surface water CIE of -1.85‰) than in either benthic foraminifera (deep
432 water CIE of -0.55‰) or bulk carbonate (CIE of -0.34‰ across equivalent sample interval).

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433 If it were not for the large magnitude of the OIE across the same sample interval (-1.42‰,
434 and -2.82‰ for the full OIE), we might argue for mixing across the boundary dampening the bulk
435 carbonate CIE. However, the marked differences in the pattern of onset for the CIE and OIE suggest
436 that there was no mixing of sediment across the boundary. Similarly, there is little evidence for the
437 isotope record being affected by carbonate dissolution or burn-down (Dickens, 2000; Kozdon et al,
438 2013) below the base of the PETM. A weak positive shift in pre-PETM $\delta^{18}\text{O}$ values and reduced
439 carbonate content appears to reflect cooler conditions as the shift is accompanied by a cooling trend
440 in the benthic Mg/Ca ratio (Fig. 5D-E).

441 A similar offset between bulk and planktic $\delta^{13}\text{C}$ in the basal PETM was described for ODP
442 Site 690, where Stoll (2005) showed close agreement between trends in stable isotopes for bulk
443 carbonate, coccolith fractions and *Subbotina* but significant offsets with *Acarinina*, the latter
444 recording an earlier CIE onset and a later OIE minimum. Stoll (2005) considered several possible
445 causes for this offset and favoured differences in habitat and seasonal production. For Site 690, the
446 correspondence between coccoliths and *Subbotina* suggests that coccolith production may have
447 occurred at a lower level within the photic zone than the level preferred by *Acarinina*. For Site 277,
448 the $\delta^{13}\text{C}$ gradient suggests a similar explanation but a different relationship. During the PETM onset,
449 coccolith production appears to have occurred at a shallower level than that preferred by planktic
450 foraminifera at this site. This may also explain why bulk carbonate $\delta^{18}\text{O}$ is more depleted than
451 planktic values in this interval, i.e. coccolith production in shallower and warmer waters. Given that
452 this relationship is only fully expressed at the PETM onset, we suggest that this might have been a
453 time of increased stratification and differentiation between water masses in the upper water column
454 at this site. Nunes and Norris (2006) used ageing gradients in benthic $\delta^{13}\text{C}$ to infer a switch in deep
455 water formation across the P/E boundary from the Southern Ocean to the Northern Hemisphere.
456 Our benthic $\delta^{13}\text{C}$ data from Site 277 support this hypothesis. Site 277 benthic $\delta^{13}\text{C}$ is 0.46‰ higher
457 than values in the equatorial Pacific prior to the PETM but 0.12‰ lower within the PETM. It seems
458 likely that comparable changes occurred in surface water circulation.

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459 With the CIE onset seeming explicable in terms of relationships between coccolith and
460 foraminiferal niches and changes in ocean circulation, we turn our attention to the stepped decline
461 in the bulk carbonate CIE at Site 277. Stoll (2005) argued that a similar series of three steps in the
462 bulk carbonate CIE seen at Site 690 reflect the greater capacity for coccoliths to record changes in
463 ocean conditions at a finer scale than is possible from the less abundant foraminiferal fraction.

464 Although we lack the resolution in the foraminiferal record to compare sites 277 and 690 in detail,
465 we observe the same trend and note a broad correlation with the three Fe peaks. It seems likely that
466 these steps represent precessional modulation of the release of ¹³C-depleted carbon into the ocean
467 over ~60 kyrs (Röhl et al., 2007; Sluijs et al., 2007).

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469 **3.3 Diagenetic modification of $\delta^{18}\text{O}$ values**

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470 ~~In contrast~~As noted above, ~~the the~~ bulk carbonate $\delta^{18}\text{O}$ values at Site 277 lie within the range
471 ~~of~~intergrade between benthic and planktic foraminiferal $\delta^{18}\text{O}$ values in the Paleocene and in the
472 Eocene interval above the PETM (Fig. 66A, 6C). Moreover, several planktic foraminiferal $\delta^{18}\text{O}$ values
473 are is only slightly ~0.3‰ lighter than benthic ~~and bulk $\delta^{18}\text{O}$ values~~ in the Paleocene (Fig. 2, 66C). ~~In~~
474 ~~contrast~~Conversely, all bulk carbonate $\delta^{18}\text{O}$ values lie within the range of planktic foraminiferal $\delta^{18}\text{O}$
475 within the PETM (Fig. 66B) and, indeed, bulk carbonate $\delta^{18}\text{O}$ is lighter than planktic foraminiferal
476 $\delta^{18}\text{O}$ in the basal PETM (Fig. 2, 5D).

477 We ~~believe-contend that~~ diagenetic effects explain these relationships. The bulk carbonate $\delta^{18}\text{O}$ has
478 been shifted toward heavier values during early diagenesis (at seafloor temperature) over much of
479 the section above and below the CIE (Schrag et al., 1995; Sexton et al., 1996; Kozdon et al., 2013),
480 whereas within the PETM interval the bulk and foraminiferal carbonate ~~has appears to have~~
481 undergone little-less diagenetic alteration. We ~~suspect-suggest that~~ the increase in clay content, as
482 ~~inferred from higher iron content (Fig. 4), in the PETM protected coccoliths and foraminifera slowed~~
483 ~~from wholesale carbonate~~ recrystallization, thus preserving more of the original $\delta^{18}\text{O}$ signal ~~in the~~
484 ~~coccoliths and foraminifera within the PETM. The presence of Clay-clay content serves to~~ reduces
485 sediment porosity and retards carbonate recrystallization, ~~almost completely in pure clays (e.g.,~~
486 ~~Pearson et al., 2007; Burgess et al., 2008; Sexton et al., 2006; Hollis et al., 2012)~~. This explains the
487 large magnitude of the bulk carbonate $\delta^{18}\text{O}$ excursion across the P-E boundary, with the $\delta^{18}\text{O}$ values
488 below the excursion having been altered toward heavier values (Fig. 2, 54D-E).

489 Similarly, ~~the planktonic planktic~~ foraminiferal $\delta^{18}\text{O}$ values through the Paleocene-Eocene
490 transition at DSDP Site 277 ~~are appear to be~~ compromised to varying degrees by seafloor diagenesis
491 throughout the interval studies. Although ~~Ththe~~ surface-to-deep temperature gradient may be
492 expected to be reduced in high latitude regions such as the Campbell Plateau. Mean annual
493 Subantarctic Water is ~6° warmer than Antarctic Intermediate Water in the present-day Southern
494 Ocean (Carter et al., 1999). However, ~~the the very extremely small~~ low planktic-benthic $\delta^{18}\text{O}$ offset
495 gradient in the Paleocene and post-PETM Eocene (0.8‰, 3°C) suggests alteration of planktic $\delta^{18}\text{O}$
496 toward benthic values (Fig. 2, 5D, 6C). The gradient is only slightly higher in the PETM (1.1‰, 4°C),
497 suggesting that a cool bias affects all paleotemperatures derived from planktic $\delta^{18}\text{O}$ through the P-E

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498 transition at this site. The degree of this bias is uncertain. The warmer paleot-Moreover,
499 temperature estimates derived from Mg/Ca ratios may be more reliablesupport our inference of a
500 cool bias in planktic $\delta^{46}\text{O}$ due to seafloor diagenesis. but, as is discussed below, diagenesis may
501 result in a warm bias.

503 **3.4. Diagenetic modification of Mg/Ca ratios**

504 As for the impact of on Mg/Ca, there is limited opportunity for the Mg concentrations to be reset
505 during diagenetic test recrystallization, in part because the bulk of Mg of the sediment/pore water
506 system resides in the carbonate, whereas for oxygen isotopes, re-equilibration with ample supply of
507 oxygen (in pore water) is possible. There is evidence that diagenesis also has significant and specific
508 effects on Mg/Ca values (Oomori et al., 1987; Kozdon et al., 2013). As noted earlier, we observe a
509 distinct relationship between the Mg/Ca ratio and the geochemical proxy for diagenesis, the Sr/Ca
510 ratio, once we have screened for silicate contamination (Fig. 3). For *Cibicides*, the full screened
511 dataset shows a roughly horizontal trend, with little change in Sr/Ca as Mg/Ca varies. This suggests
512 that this genus is relatively immune to the effects of diagenesis, perhaps related to its relatively thick
513 and smooth wall. However, if we consider Paleocene and PETM samples separately, we observe that
514 Paleocene analyses tend to have lower Sr/Ca ratios than PETM samples and exhibit a weak trend in
515 which Mg/Ca increases as Sr/Ca decreases. This general relationship has also been identified by
516 Kozdon et al. (2013) as a guide to diagenetic alteration, albeit the impact on Mg/Ca ratios is an order
517 of magnitude smaller than found in laboratory experiments (Oomori et al., 1987). The trend is more
518 obvious in *Acarinina* at Site 277, probably because the thinner-walled and more irregular test
519 provides more surfaces for interaction with pore waters and hence facilitates diagenetic alteration.
520 For the full data set, a significant negative correlation is observed, with Mg/Ca increasing as Sr/Ca
521 decreases. A weaker trend is evident in the PETM data but a much stronger trend is shown by the
522 Paleocene data. From these observations we can draw the following conclusions: (i) *Acarinina* is
523 more prone to diagenesis than *Cibicides*, (ii) diagenesis is greater in the Paleocene than in the PETM,
524 and (iii) diagenesis causes an increase in the Mg/Ca ratio and implies that paleotemperatures may be
525 overestimated for some taxa, such as *Acarinina*, and in some intervals such as the Paleocene at this
526 site. This may explain why the SST estimates for the Paleocene based on *Acarinina* Mg/Ca ratios are
527 higher than expected (Fig. 5D, E).

529 **3.5. Paleotemperature**

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530 ~~Consistent with the expected preservation biases, SST estimates of 26–27°C derived from the Mg/Ca~~
531 ~~ratios of *Acarinina* are markedly warmer than the temperatures of 14–17°C derived from planktic~~
532 ~~$\delta^{18}\text{O}$.~~

533 ~~Benthic foraminifera test are dense and thus less prone to recrystallization. Taking into account~~
534 ~~these numerous complications, we can make some general observations on temperature changes~~
535 ~~through the P-E transition at Site 277. Estimates for SFT from benthic foraminiferal $\delta^{18}\text{O}$ and Mg/Ca~~
536 ~~are remarkably relatively consistent at 12–15°C for the late Paleocene (Fig. 54D), with coolest SFTs~~
537 ~~of 11–12°C occurring in the uppermost 10 cm of Paleocene where carbonate content is also lower~~
538 ~~than background. Benthic $\delta^{18}\text{O}$ and Mg/Ca values indicate SFT warmed by ~5–6°C across the P-E~~
539 ~~boundary, with SFTs of up to ~19°C in the basal PETM. There is little evidence for further warming of~~
540 ~~SFT in the body of the PETM. Following the PETM, SFT drops abruptly by ~5°C and remains stable at~~
541 ~~~13°C in the overlying Eocene interval (Fig. 5D–E). Diagenesis may explain why some Paleocene~~
542 ~~Mg/Ca ratios yield higher SFTs than the benthic $\delta^{18}\text{O}$ values.~~

543 The SST record across the P-E boundary is much more difficult to interpret. The small offset
544 between benthic and planktic $\delta^{18}\text{O}$ (~3°C) combined with the large offset between planktic $\delta^{18}\text{O}$ and
545 Mg/Ca values (~12°C) in the Paleocene, are likely consequences of diagenetic alteration, with the
546 actual SST lying somewhere between 15 and 27°C (Fig. 5D). Similarly, the degree of warming across
547 the PETM may be accentuated for $\delta^{18}\text{O}$ but effectively dampened for Mg/Ca due to the effects
548 discussed above. For this reason, the observation that the relative SST increase is ~5–6°C for both
549 proxies (Fig. 5E) is difficult to explain even though it is consistent with the SFT record. Diagenetic
550 effects appear to decrease across the P-E boundary, based on our analysis of the benthic–planktic
551 $\delta^{18}\text{O}$ gradient and the Sr/Ca ratio. Therefore, we would predict that the relative increase in SST
552 across the boundary would be greater for planktic $\delta^{18}\text{O}$ than for Mg/Ca. It may be that the patchy
553 nature of the record through this interval is masking these relationships. Irrespective of the true
554 magnitude of SST change across the P-E boundary, planktic Mg/Ca ratios indicate warmest SSTs in
555 the lower PETM, stable SSTs through the body of the PETM (albeit ~3°C cooler) and an abrupt ~4°C
556 cooling directly above the PETM.

557 ~~This~~ The 5–6°C increase in SST is similar to other PETM records. At ODP Site 1172, the TEX₈₆
558 record indicates that SST increased by 6°C across the P/E boundary (Sluijs et al., 2011) and SST
559 during the PETM was 3–4°C warmer than average Paleocene values (Fig. 77). Elsewhere,
560 temperature anomalies within the PETM range from +4–5°C in low latitudes (Zachos et al., 2003; Aze
561 et al., 2014) to +8°C in high latitudes (Thomas et al., 2002; Frieling et al., 2014) and some low
562 latitude coastal sites (Zachos et al., 2006).

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563 planktic foraminiferal $\delta^{18}\text{O}$ values in the PETM yield SSTs of 26°C, whereas Mg/Ca ratios
564 within the PETM yield much warmer SST estimates of 28–32°C (Fig. 4D). The peak SSTs of ~32° within
565 the PETM are consistent with TEX_{86} -based SSTs from the PETM at ODP Site 1172 (Sluijs et al., 2011)
566 and in the mid-Waipara section, eastern South Island, New Zealand (Hollis et al., 2012). At these
567 locations, the two calibrations for TEX_{86} introduced by Kim et al. (2010) yield peak SSTs for the PETM
568 of 32–34°C ($\text{TEX}_{86}^{\text{H}}$) or 26–28°C ($\text{TEX}_{86}^{\text{L}}$). Although the $\text{TEX}_{86}^{\text{L}}$ calibration was considered more
569 suitable for this region based on comparisons with other SST proxies (Hollis et al., 2012), a new
570 Bayesian approach to TEX_{86} calibrations (Tierney and Tingley, 2014) yields temperatures for the
571 PETM that are very similar to the $\text{TEX}_{86}^{\text{H}}$ calibration. These PETM SSTs are also consistent with the
572 SST estimates of 26°C that were derived from TEX_{86} and U^{K}_{37} for the late Eocene at Site 277 (Liu et al.,
573 2009), given that deep sea temperatures cooled by ~8°C through the Eocene (Zachos et al., 2008).

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574 There is considerable debate about the veracity of such high temperature estimates in high
575 latitude regions, with concerns raised about calibrations, seasonal bias and archaeol physiology ical
576 processes (e.g. Hollis et al., 2012; Taylor et al. 2013; Inglis et al., submitted under revision.).
577 However, the consistency between SSTs derived from Mg/Ca and TEX_{86} (Burgess et al., 2008; Hollis
578 et al., 2012) suggests that the high temperatures are due to factors that the proxies may have in
579 common, such as a warm-season bias, rather than problems with respective calibrations or
580 physiological factors.

581 582 **3.63. Pattern of PETM initiation Comparison with other PETM records**

583 Complications relating to diagenetic overprinting have been discussed and partly resolved in the
584 previous section. To circumvent additional uncertainties surrounding absolute temperature
585 estimates based on $\delta^{18}\text{O}$ values and Mg/Ca ratios (Cramer et al., 2011; Evans and Müller, 2012;
586 Dunkley-Jones et al., 2013), it is helpful to consider temperature trends relative to mean values for
587 the Paleocene (Fig. 4E). For both proxies, SSTs increase by 5–6°C at the onset of the PETM, remain
588 relatively stable through the PETM and decline abruptly across the unconformity that truncates the
589 top of the event. Because the relative temperature trends shown by planktic $\delta^{18}\text{O}$ are inferred to be
590 compromised by diagenesis, Mg/Ca ratios provide a more reliable guide to changes in local SST. In
591 the basal part of the PETM, there are few planktic records that fall below the screening limit for
592 Al/Ca (Fig. 3). Those specimens of *Acarinina* that are judged to be reliable indicate initial warming of
593 SSTs by ~6°C. For the upper part of the PETM, still likely representing the onset phase, Mg/Ca ratios
594 for both *Acarinina* and *Morozovella* consistently indicate SSTs that are ~2°C above average
595 Paleocene values for *Acarinina* (Fig. 4D). Although this increase is within the error range for these
596 measurements, the consistency between samples gives us reasonable confidence in the overall

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597 ~~increase in temperature. This increase in SST is similar to other PETM records. At ODP Site 1172, the~~
598 ~~TEX₈₆ record indicates that SST increased by 6°C across the P/E boundary and SST during the PETM~~
599 ~~was 3–4°C warmer than average Paleocene values (Fig. 7). Elsewhere, temperature anomalies within~~
600 ~~the PETM range from +4–5°C in low latitudes (Zachos et al., 2003; Aze et al., 2014) to +8°C in high~~
601 ~~latitudes (Thomas et al., 2002; Frieling et al., 2014) and some low latitude coastal sites (Zachos et al.,~~
602 ~~2006).~~

Comment [CH3]: This is now covered in the previous section

603 ~~More detailed~~A comparison of the PETM record at DSDP Site 277 with nearby records at Mead
604 Stream (Hollis et al., 2005a; Nicolo et al., 2010) and ODP Site 1172 (Sluijs et al., 2011) reveals several
605 significant features (Fig. 7). Firstly, there seems little doubt that only the onset of the ~~PETM-CIE~~ is
606 preserved at Site 277. The pattern of decreasing $\delta^{13}\text{C}$ is very similar to the expanded onset at Mead
607 Stream. ~~As noted above, the stepped decrease in $\delta^{13}\text{C}$ is also observed at ODP Site 690 (Röhl et al.,~~
608 ~~2007).~~ However, the pattern of warming at Site 277 is quite different from ~~the other sites~~Site 1172.
609 At Site 277, the most pronounced increase in temperatures occurs at the base of the PETM and is
610 associated with a weak negative $\delta^{13}\text{C}$ excursion. Higher in the PETM, temperatures remain stable or
611 decrease slightly as $\delta^{13}\text{C}$ decreases. At Site 1172, the TEX₈₆ record indicates pronounced warming at
612 the base of the PETM but SST continues to increase and peaks just above the $\delta^{13}\text{C}$ minimum. No
613 direct measurements of temperature have been obtained from the indurated lithologies at Mead
614 Stream. However, changes in radiolarian assemblages identify a definite peak in low-latitude species,
615 also directly above the $\delta^{13}\text{C}$ minimum (red star in Fig. 7) (Hollis, 2006).

616 The implication of these differences between SW Pacific sites is that the primary warming
617 pulse occurred in both intermediate and surface waters at the initiation of the PETM on the
618 Campbell Plateau, whereas this initial event was only the precursor to progressive warming in the
619 continental margin settings to the west and north (Fig. 1). ~~A similar pattern of warming is evident in~~
620 ~~the Atlantic Ocean, where the $\delta^{18}\text{O}$ records for ODP sites 690 and 1051 suggest that peak warming~~
621 ~~occurred at the onset of the PETM in the southern Atlantic (Site 690) but at the same level as the CIE~~
622 ~~minimum in the western North Atlantic (Bains et al., 1999; Stoll, 2005). It is important to note that~~
623 ~~w~~We cannot be sure that there was not a second warming pulse above the onset of the PETM on the
624 Campbell Plateau because the main phase of the PETM does not appear to be preserved at Site 277.
625 However, ~~it is equally important to note that~~ the absolute SST values at Site 277 are similar to the
626 peak SSTs at Site 1172, i.e. 30–32°C. Therefore, we need to explain how the Campbell Plateau
627 warmed at the start of the PETM and stayed warm through the onset, while the East Tasman Plateau
628 warmed to a lesser extent initially but then continued to warm into the main phase of the PETM,
629 with both sites experiencing at least seasonal SST maxima in excess of 30°C. We speculate that the
630 gradual warming that followed Southern Ocean cooling at 59 Ma (Hollis et al., 2014) exceeded a

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631 threshold at the start of the PETM that caused the southward expansion of the subtropical-tropical
632 gyre over the Campbell Plateau. This gyre was sustained through the PETM onset but resulted in no
633 additional warming at this location. It is notable that several warm-water species of *Morozovella* are
634 restricted to the PETM at Site 277. The influence of the gyre may have also reached the East Tasman
635 Plateau but an additional factor continued to warm the region into the main phase of the PETM.
636 This factor may have been a proto-Eastern Australian Current, intensifying its southwestern reach
637 during times of extreme warming (e.g. Cortese et al., 2013).

638
639 **4. Conclusions**

640 Part of the motivation in undertaking this study and presenting these results is that there is interest
641 in re-drilling this site as part of IODP Proposal 567 (Paleogene South Pacific APC Transect) using new
642 technology that will greatly improve the quantity and quality of core recovery. We have shown that
643 even with this improved recovery, extracting a paleoclimate record will still be complicated by
644 diagenesis, recrystallization and hiatuses. In order to recover a more reliable climate proxy records
645 for the Paleogene of this region, we recommend consideration of alternative or additional Campbell
646 Plateau sites where sedimentation rates and clay input is predicted to have been higher than at Site
647 277 (Cook et al., 1999). Nevertheless, we have also illustrated how a multi-proxy approach can be
648 used to extract a climate history from this complicated record with due consideration of the effects
649 of differential diagenesis, both between taxonomic groups and across stratigraphic horizons.

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650 The onset of the PETM is recorded in a 34 cm thick interval within core 45 at DSDP Site 277.
651 A significant and rapid warming of surface and deep waters at the onset of the PETM at Site 277
652 parallels a pronounced decline in carbonate concentration and a modest initial negative $\delta^{13}\text{C}$
653 excursion of ~1‰. The full extent of the 2‰ negative $\delta^{13}\text{C}$ excursion occurred gradually over an
654 interval in which temperatures remained stable or declined slightly. Therefore, it would seem that
655 an initial carbon perturbation had a pronounced effect on southern Pacific Ocean circulation,
656 causing poleward expansion of warm surface and intermediate waters. In contrast, the full
657 expression of the event had ~~no~~ little additional effect, perhaps because a threshold was exceeded at
658 the initial event.

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660 **Supplementary material related to this article is available online at:**

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661
662 *Acknowledgements.* This research relied on archival DSDP samples and data provided by the

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663 International Ocean Discovery Program (IODP) and was funded by the New Zealand Government
664 through the GNS Science Global Change through Time Programme (540GCT12, 540GCT62). We thank

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665 [Paul Pearson and Reinhard Kozdon for very constructive reviews, Appy Sluijs for editorial handling,](#)
666 [and Randall McDonnell \(GNS Science\) for technical support.](#)

667

668 **Figure Captions**

669 **Figure 1.** Location of DSDP Site 277 on a tectonic reconstruction for the southwest Pacific during the
670 early Eocene (~54 Ma) (Cande and Stock, 2004). Other localities mentioned in the text are also
671 shown: ODP Site 1172, Campbell Island (CI), Tawanui (TW), Mid-Waipara River (MW) and Clarence
672 Valley (CV).

673

674 **Figure 2.** Biostratigraphy, lithologies, carbonate content and stable isotopes from bulk carbonate
675 and foraminifera across the Paleocene-Eocene transition at DSDP Site 277. Abbreviations:
676 Mangaorapan local stage (Dm); Paleocene-Eocene Thermal Maximum (PETM), Benthic Foraminiferal
677 Extinction Event (BFEE).

678

679 **Figure 3.** Trace element–depth plot for *Acarinina* and *Cibicides* across the PETM interval, showing all
680 the measured Mg/Ca, Al/Ca and Sr/Ca values measured, and the corresponding decrease of the
681 mean Mg/Ca value when Al/Ca and Sr/Ca screening protocols are imposed on the raw dataset. The
682 pink shaded areas show the data points removed by the application of the screening limits, with the
683 consequent decrease in Mg/Ca ratio (and therefore temperature) shown by the black circles (median
684 of unscreened Mg/Ca) and the orange and blue diamonds (mean screened Mg/Ca ratios for
685 *Acarinina* and *Cibicides* respectively). Note the change in scale on the horizontal axes for Mg/Ca and
686 Al/Ca between the *Acarinina* and *Cibicides* records.

687

688 **Figure 4.** Variation in (A) Fe content and magnetic susceptibility; (B) $\delta^{13}\text{C}$; (C) Mg/Ca ratios; (D)
689 paleotemperatures derived from $\delta^{18}\text{O}$ values and Mg/Ca ratios; and (E) changes in paleotemperature
690 relative to average Paleocene values.

691

692 **Figure 5.** Age/depth plot for the Paleocene–Eocene transition at DSDP Site 277. Abbreviations for
693 species names are explained in Table 7.

694

695 **Figure 6.** Cross plot of stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) values for bulk carbonate, *Cibicides*, *Acarinina* and
696 *Morozovella* within the Paleocene, Paleocene-Eocene Thermal Maximum (PETM), and overlying
697 Eocene.

698

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699 **Figure 7.** Comparison of records of the Paleocene–Eocene thermal maximum (PETM) at DSDP Site
700 277, ODP Site 1172 and Mead Stream. Symbols for DSDP Site 277 as in Fig. 4. Note the bulk
701 carbonate $\delta^{18}\text{O}$ record is not plotted as a guide for relative temperature change at DSDP 277
702 because the record is inferred to be affected by diagenesis. The Red star marks single incursion of
703 low latitude radiolarians at Mead Stream (Hollis, 2006).

704 **Supplementary Tables**

705 [Table 1. X ray fluorescence](#)

706 [Table 2. Rock magnetism](#)

707 [Table 3. Distribution of calcareous nannofossils](#)

708 [Table 4. Distribution of foraminifera](#)

709 [Table 5. Stable isotopes and carbonate concentration](#)

710 [Table 6. Foraminiferal Mg/Ca ratios](#)

711 [Table 7. Microfossil and carbon isotope datums](#)

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1006
1007 **Figure Captions**

1008 **Figure 1.** Location of DSDP Site 277 on a tectonic reconstruction for the southwest Pacific during the
1009 early Eocene (~54 Ma) (after Cande and Stock, 2004). Other localities mentioned in the text are also
1010 shown: ODP Site 1172, Campbell Island (CI), Tawanui (TW), Mid-Waipara River (MW) and Mead
1011 Stream (MS).

1012
1013 **Figure 2.** Biostratigraphy, lithologies, carbonate content (B) and stable isotopes from bulk carbonate
1014 and foraminifera (A, C, D) across the Paleocene-Eocene transition at DSDP Site 277. Abbreviations:
1015 Mangaorapan local stage (Dm); Paleocene Eocene Thermal Maximum (PETM), Benthic Foraminiferal
1016 Extinction Event (BFEE). In (A) the new bulk carbonate $\delta^{18}\text{O}$ record is plotted alongside the
1017 uncorrected, mixed planktic and benthic $\delta^{18}\text{O}$ values of Shackleton and Kennett (1975); in (D) and
1018 subsequent figures, benthic $\delta^{18}\text{O}$ values include a correction factor of 0.28‰ (Katz et al., 2003).

1019
1020 **Figure 3.** Cross-plots of Mg/Ca, Al/Ca and Sr/Ca with areas outside the screening limit shaded pink. Formatted: Line spacing: 1.5 lines
1021 All results are shown for the Al/Ca–Mg/Ca cross plots. For Sr/Ca–Mg/Ca cross plots, we only include
1022 measurements that lies within the screening limit for Al/Ca in order to exclude the effects of silicate
1023 contamination. Only R^2 values significant at the 95% confidence interval are shown for the trend
1024 lines.

1025 **Figure 4.** Trace element–depth plots for *Acarinina* (A–C) and *Cibicides* (D–F) across the PETM
1026 interval, showing all measured Mg/Ca, Al/Ca and Sr/Ca values, and the decrease in mean Mg/Ca
1027 value when Al/Ca and Sr/Ca screening protocols are imposed. Areas outside the screening limits are
1028 shaded pink. Note change in scale on horizontal axes for Mg/Ca and Al/Ca for *Acarinina* and
1029 *Cibicides*.

1030
1031 **Figure 5.** Variation in (A) Fe content and magnetic susceptibility; (B) $\delta^{13}\text{C}$; (C) Mg/Ca ratios; (D)
1032 paleotemperatures derived from $\delta^{18}\text{O}$ values and Mg/Ca ratios; and (E) changes in paleotemperature
1033 relative to average Paleocene values.

1034

1035 Figure 6. Cross plot of stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) values for bulk carbonate, *Cibicides*, *Acarinina* and
1036 *Morozovella* within the Paleocene, Paleocene Eocene Thermal Maximum (PETM), and overlying
1037 Eocene.

1038
1039 Figure 7. Comparison of records of the Paleocene–Eocene thermal maximum (PETM) at DSDP Site
1040 277, ODP Site 1172 and Mead Stream. Symbols for DSDP Site 277 as in Fig. 4. Note the bulk
1041 carbonate $\delta^{18}\text{O}$ record is not plotted as a guide for relative temperature change at DSDP 277
1042 because the record is inferred to be affected by diagenesis. The Red star marks a single occurrence
1043 of low-latitude radiolarians in the P-E transition interval at Mead Stream (Hollis, 2006).

1044
1045 **Supplement of**

1046 **The Paleocene-Eocene Thermal Maximum at DSDP Site 277, Campbell Plateau, southern**
1047 **Pacific Ocean**

1048 **Hollis et al. (c.hollis@gns.cri.nz)**

1049

1050 Figure S1. Scanning electron microscope (SEM) images of moderately and poorly preserved
1051 foraminifera specimens from DSDP Site 277 and corresponding trace element/Ca profiles through
1052 the test wall. For moderately preserved *Morozovella aequa* (A), the profile selected during the
1053 screening process is highlighted by the grey bar. Note the elevated trace element/Ca ratios on the
1054 exterior of the test and the increase in Al/Ca ratio on the interior of the test. Ti/Ca displays a patchy
1055 distribution as it is approaching the resolvable limit. Other trace element/Ca profiles are for
1056 moderately preserved *Acarinina* (B); moderately preserved *Subbotina* (C); moderately preserved
1057 *Cibicides* (D); poorly preserved *Morozovella aequa* (E), showing evidence of sediment infilling and
1058 calcite overgrowths, with trace element/Ca ratios are substantially elevated above those of biogenic
1059 calcite and an unusual Ba/Ca profile; poorly preserved *Acarinina* (F) displaying coarsely crystalline
1060 diagenetic outgrowths; poorly preserved *Subbotina* (G) with a ‘chalky’ outer appearance and an
1061 anomalous Ba/Ca peak; and poorly preserved *Cibicides* (H) with a coarse, granular texture
1062 uncharacteristic of this species and attributed to micron-scale recrystallization.

1063 Figure S2. Trace element–depth plots for *Acarinina* and *Cibicides* across the PETM interval, showing
1064 all measured Mg/Ca, Al/Ca, Mn/Al, Ba/Al and Sr/Ca values, and the decrease in mean Mg/Ca value
1065 when Al/Ca and Sr/Ca screening protocols are imposed. Areas outside the screening limits are

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1066 shaded pink. Note change in scale on horizontal axes for Mg/Ca and Al/Ca for *Acarina* and
1067 *Cibicides*.

1068
1069 Figure 7. Age/depth plot for the Paleocene–Eocene transition at DSDP Site 277. Abbreviations for
1070 species names are explained in Table S7.

1071 ary Tables

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1072 Table S1. X-ray fluorescence

1073 Table S2. Rock magnetism

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1074 Table S3. Distribution of calcareous nannofossils

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1075 Table S4. Distribution of foraminifera

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1076 Table S5. Stable isotopes and carbonate concentration

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1077 Table S6. Foraminiferal Mg/Ca ratios

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1078 Table S7. Microfossil and carbon isotope datums

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