Climate
of the Past

Revisiting carbonate chemistry controls on planktic foraminifera Mg / Ca: implications for sea surface temperature and hydrology shifts over the Paleocene–Eocene Thermal Maximum and Eocene–Oligocene transition

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Abstract. Much of our knowledge of past ocean temperatures comes from the foraminifera Mg / Ca palaeothermometer. Several nonthermal controls on foraminifera Mg incorporation have been identified, of which vital effects, salinity, and secular variation in seawater Mg / Ca are the most commonly considered. Ocean carbonate chemistry is also known to influence Mg / Ca, yet this is rarely examined as a source of uncertainty, either because (1) precise pH and $[CO_3^{2-}]$ reconstructions are sparse or (2) it is not clear from existing culture studies how a correction should be applied. We present new culture data of the relationship between carbonate chemistry and Mg / Ca for the surface-dwelling planktic species *Globigerinoides ruber* and compare our results to data compiled from existing studies. We find a coherent relationship between Mg / Ca and the carbonate system and argue that pH rather than $[CO_3^{2-}]$ is likely to be the dominant control. Applying these new calibrations to data sets for the Paleocene–Eocene Thermal Maximum (PETM) and Eocene–Oligocene transition (EOT) enables us to produce a more accurate picture of surface hydrology change for the former and a reassessment of the amount of subtropical precursor cooling for the latter. We show that pH-adjusted Mg / Ca and $\delta^{18}O$ data sets for the PETM are within error of no salinity change and that the amount of precursor cooling over the EOT has been previously underestimated by $\sim 2\,°C$ based on Mg / Ca. Finally, we present new laser-ablation data of EOT-age *Turborotalia ampliapertura* from St. Stephens Quarry (Alabama), for which a solution inductively coupled plasma mass spectrometry (ICPMS) Mg / Ca record is available (Wade et al., 2012). We show that the two data sets are in excellent agreement, demonstrating that fossil solution and laser-ablation data may be directly comparable. Together with an advancing understanding of the effect of Mg / Ca$_{sw}$, the coherent picture of the relationship between Mg / Ca and pH that we outline here represents a step towards producing accurate and quantitative palaeotemperatures using this proxy.

1 Introduction

The relationship between foraminifera Mg / Ca and temperature has been widely applied as a method of reconstructing the thermal evolution of the oceans across a range of timescales (see, e.g., Mashiotta et al., 1999; Lear et al., 2000; Sosdian and Rosenthal, 2009; Wade et al., 2012). Whilst

a substantial portion of our understanding of the response of ocean temperature, hydrology, and circulation to external forcing is derived from this proxy, several nonthermal controls have been identified (aside from the well-known vital effects), which complicate the translation of measured Mg / Ca ratios to temperature. Principal amongst these are dissolution (Regenberg et al., 2014), salinity (Kisakürek et al., 2008; Hönisch et al., 2013), and, deeper in geological time, bias derived from secular variation in seawater Mg / Ca (Evans and Müller, 2012; Evans et al., 2015). Finally, the effect of seawater carbonate chemistry on Mg incorporation has been investigated by several culture studies (Lea et al., 1999; Russell et al., 2004; Kisakürek et al., 2008). However, the potential effect of differential palaeo-carbonate chemistry on Mg / Ca-derived reconstructions is rarely noted for planktic foraminifera, although a carbonate ion correction is routinely applied to some benthic foraminifera species (Sosdian and Rosenthal, 2009; Yu and Broecker, 2010). All of these studies indicate that the relationship between pH or [CO_3^{2-}] and Mg / Ca is significant: on the order of a 30–60 % increase in Mg / Ca for a 0.4 unit pH decrease from 8.0 (total scale). This implies that absolute Mg / Ca-derived temperatures may be systematically biased when ocean pH or [CO_3^{2-}] was significantly different to modern values, and relative Mg / Ca-derived temperature shifts over climatic events associated with a large perturbation of the carbonate system may be inaccurate.

Here we focus on the implications of variable carbonate chemistry for Mg / Ca-derived sea surface temperature (SST) shifts across two key intervals of geologically rapid climatic change: the Paleocene–Eocene Thermal Maximum (PETM) and the Eocene–Oligocene transition (EOT). Both of these events are associated with a significant (0.1–0.3 unit) pH shift (Penman et al., 2014; Pearson et al., 2009); therefore, a reexamination of previously published records is warranted.

The PETM is characterised by a massive release of ^{13}C-depleted carbon over a geologically brief period of time (Kennett and Stott, 1991). The event is associated with a surface warming of several °C in most locations where this has been reconstructed, using TEX$_{86}$ or planktic foraminifera Mg / Ca and δ^{18}O (see, e.g., Sluijs et al., 2007; Zachos et al., 2003). Because there is evidence that the PETM was also associated with a shift in the hydrological cycle (Schmitz and Pujalte, 2007; John et al., 2008; D'haenens et al., 2012), δ^{18}O is frequently coupled with an independent temperature proxy in order to reconstruct surface ocean salinity change (Zachos et al., 2003; Tripati and Elderfield, 2004). Both these and the results of coupled climate models suggest that the hydrological response was complex and spatially variable (Sluijs et al., 2011; Winguth et al., 2010), indicating more saline surface waters in the (sub)tropical Pacific, whilst the subtropical Atlantic and coastal-proximal sites may have been characterised by increased freshwater flux to the surface ocean. These proxy reconstructions are sensitive to the control that pH exerts on foraminifera δ^{18}O (Uchikawa and Zeebe, 2010)

and also require revision in light of our analysis of the relationship between carbonate chemistry and Mg / Ca. Our data and reanalysis of existing records are timely given the recent publication of a high-resolution δ^{11}B record across the PETM (Penman et al., 2014).

The EOT is marked by a stepwise transition to a climate state characterised by a continental-scale ice sheet on Antarctica, as evidenced by δ^{18}O measurements of benthic foraminifera (Zachos et al., 1996; Katz et al., 2008; Coxall et al., 2005). Sequence stratigraphic studies and Mg / Ca-derived deep-ocean temperatures indicate that approximately 50 % of this shift can be attributed to temperature (Miller et al., 2008; Lear et al., 2008). A δ^{11}B-pH record is available (Pearson et al., 2009), which means that both planktic foraminiferal δ^{18}O and Mg / Ca may be corrected for the effects of a significant (~ 0.15 pH unit) shift in the ocean carbonate system associated with CO_2 drawdown. There are relatively few high-resolution SST records across the transition. In the subtropics, the St. Stephens Quarry (SSQ, Alabama) *Turborotalia ampliapertura* Mg / Ca record shows a large precursor cooling event beginning ~ 250 kyr before the Eocene–Oligocene boundary (Wade et al., 2012). In the Southern Hemisphere, a similar albeit smaller event has been reconstructed from Tanzania Drilling Project samples of the same species (Lear et al., 2008). Finally, several sites in the Southern Ocean show Mg / Ca cooling that occurs prior to the largest benthic foraminifera δ^{18}O shift, "Oi-1" (Bohaty et al., 2012). Whilst this indicates a spatially coherent picture of surface ocean cooling, a large portion of our current knowledge is derived from Mg / Ca analyses of planktic foraminifera, although biomarker-derived proxies have also been utilised (Liu et al., 2009). Therefore, improving the accuracy of these reconstructions is of critical importance to our understanding of this major climatic transition.

As well as examining the implications of this pH change on published Mg / Ca-derived subtropical SST across the EOT, we also present new laser-ablation inductively coupled plasma mass spectrometry (ICPMS) data of *Turborotalia ampliapertura* from SSQ, for which a solution ICPMS Mg / Ca record is already available (Wade et al., 2012). This provides a methodological comparison for deep-time fossil samples: laser ablation is spatially resolved (inter- and intra-chamber) and allows the exclusion of data from poorly preserved areas of the test, whilst samples crushed for solution analysis may be easier to clean.

In order to form the basis of more accurate Mg / Ca-derived absolute and relative temperature shifts throughout the Cenozoic, we present a compilation of new and previously published data of the relationship between Mg / Ca, pH, and [CO_3^{2-}] for planktic foraminifera. Whilst we use the PETM and EOT as examples of climatic events for which ignoring this effect may lead to substantial bias (as δ^{11}B-derived reconstructions of temporal changes in pH are available for both), our findings are applicable to any time period

with a non-modern and/or temporally variable surface ocean carbonate chemistry.

2   Materials and methods

We present new culture data of the relationship between Mg / Ca and carbonate system parameters for *Globigerinoides ruber* and a reanalysis and compilation of literature data for this species, *Globigerina bulloides*, and *Orbulina universa*. We utilise data from culture experiments of *G. ruber* grown at the Interuniversity Institute for Marine Science, Eilat, between January 2010 and November 2013. The primary purpose of these experiments was to determine the pH sensitivity of $\delta^{11}B$ in *G. ruber* for different $[B]_{sw}$ (with some of these cultures described in Henehan et al., 2013) and to examine the relationship between seawater Mg / Ca (Mg / Ca_{sw}) and shell Mg / Ca (Evans et al., 2016). Because Mg / Ca_{sw} was varied in the cultures of Evans et al. (2016), this enables the consistency of the relationship between carbonate chemistry and foraminifera Mg / Ca to be examined at below-modern Mg / Ca_{sw}.

For both new and previously published data, Mg / Ca is normalised to the ratio that would be expected at 26 °C and a salinity of 35 ‰, specific to each species. In order to account for different temperatures, salinities, and in one case Mg / Ca_{sw} between the cultures, all data were normalised to these conditions where they differed and/or where Mg / Ca_{sw} was not the same as in the modern ocean. For *G. ruber* this was achieved using the Mg / Ca–temperature calibration of Kisakürek et al. (2008), the Mg / Ca–salinity relationship of Hönisch et al. (2013), and the seawater-test Mg / Ca calibration of Evans et al. (2016). Between the three sets of *G. ruber* cultures, temperature varied between 26 and 27 °C and salinity varied between 35.0 and 37.2 ‰. For *G. bulloides* and *O. universa*, data were normalised to 26 °C assuming that both species are characterised by Mg / Ca–temperature relationships with an exponential coefficient of 0.09 in the modern ocean (Anand et al., 2003). Mg / Ca was then normalised to that of the culture(s) with modern seawater pH ($\sim$ 8.02 total scale) within the same study. No salinity correction was necessary as this was consistent within the studies of Russell et al. (2004) and Lea et al. (1999) and would therefore cancel out. Where measurements were not available, dissolved inorganic carbon (DIC) and $[CO_3^{2-}]$ were calculated using co2sys (Lewis and Wallace, 2006), based on the same constants as used by Raitzsch et al. (2010).

2.1   Laboratory culture calibration

Whilst a more detailed description of culturing methods is provided elsewhere (Henehan et al., 2013; Evans et al., 2016), a brief summary is given here. Foraminifera were towed from the Gulf of Eilat and cultured in individual 120 mL airtight flasks. Individuals were fed a juvenile brine shrimp every 1–2 days until gametogenesis took place or cal-

cification ceased, after which they were rinsed in deionised water, dried, and stored for analysis.

Within experiments intended for boron isotope measurement, the pH of flask solutions was measured at the beginning of each experiment and then every 2–3 days using an electrode calibrated against NBS buffers. At the end of experiments, the individual flask pH was measured and a composite sample of all flasks combined, measured, and then poisoned for DIC and total alkalinity (TA) analysis at the UKOARP, Southampton (see Henehan et al., 2013). For experiments designed around varying Mg / Ca_{sw} (Evans et al., 2016), pH was measured at the start of culture. Based on repeat measurements of the reservoir seawater used to fill the individual culture flasks, we apply a conservative pH uncertainty of ± 0.1 to these experiments. pH electrode measurements were corrected to total-scale pH via calibration against pHs derived from the analysis of multiple DIC and TA water samples.

2.1.1   Laser-ablation analysis

The cultures outlined in Evans et al. (2016) were analysed using the 193 nm RESOlution M50 laser-ablation system at Royal Holloway, University of London (Müller et al., 2009), as described previously (Evans et al., 2015). Briefly, foraminifera were cleaned in 10 % NaOCl, rinsed in deionised water, and mounted on carbon tape. Individual chambers were identified as those precipitated in culture if they were characterised by elevated $^{135}Ba/^{138}Ba$, as the seawater used in these experiments was spiked with 74 nM ^{135}Ba. NIST610 was used as a calibration standard for Mg, based on the NIST Mg value of Pearce et al. (1997), which results in a Mg / Ca accuracy $\sim$ 7 % better than the value of Jochum et al. (2012) on our system. Data reduction followed established procedures (Longerich et al., 1996) using in-house Matlab data reduction software. ^{43}Ca was used as an internal standard. Long-term Mg / Ca accuracy and precision is better than 5 % (2 SD) as assessed by standardising the MPI-DING komatiite glass GOR132 (Jochum et al., 2006) to NIST610.

2.1.2   Solution ICPMS

Prior to analysis, foraminifera were cleaned as described in Henehan et al. (2013). Foraminiferal culture samples of 1–3 mg (to permit boron isotope analysis on the same samples where possible) were lightly crushed between two clean glass slides, ultrasonicated, and rinsed repeatedly with Milli-Q ultrapure water (18.2 MΩ). Samples were subject to intensified oxidative cleaning (3×20–30 min treatments of 250–400 μL 1 % H_2O_2 in 0.1 M NH_4OH at 80 °C) to remove organic material, followed by a brief weak acid leach in 0.0005 M HNO_3 to remove any readsorbed contaminants. Finally, 200 μL of Milli-Q was added to each sample (to slow subsequent dissolution and reduce the likelihood of leaching

of B off any remnant contaminants) and 0.5 M HNO$_3$ (normally $< 300\,\mu$L) was added incrementally until the sample was fully dissolved. Samples were centrifuged for > 5 min at 1400 rpm and the supernatant removed to a clean vial, leaving the last $\sim 20\,\mu$L to be discarded.

Solution ICPMS measurements of Mg / Ca were performed on a Thermo Element ICPMS at the University of Southampton and the Bristol Isotope Group. Analysis of common consistency standards ensures that no bias exists between these two laboratories. Tuning is performed on a 0.1 ppb multielement tune solution to optimize sensitivity while minimising the presence of oxides (the ratio of m/z 248/232 was maintained below 7 %). During each analytical session, in-house consistency standards (Mg / Ca ratios of 1.277, 3.289, and 7.573 mmol mol^{-1}) were analysed at a range of concentrations (typically 0.5, 1, and 2 mM Ca) to monitor accuracy and precision. Reproducibility of element ratio measurements is optimised (following Yu et al., 2005) by matrix-matching samples and their bracketing standards (the in-house gravimetric standard BSGS). This is achieved by analysing for [Ca] in a dilute aliquot of each sample (typically 20 μL in 200 μL 0.5 M HNO$_3$) prior to full elemental determination. Samples are then diluted with 0.5 M HNO$_3$ to match standard [Ca] and analysed for the full trace metal suite. Long-term reproducibility of Mg / Ca ratio measurements is better than 3 % (2 SD), based on repeat measurements of in-house consistency standards.

Because foraminifera did not precipitate calcite exclusively in culture, final Mg / Ca ratios were obtained via mass-balance calculations. To determine this, initial pre-culture mass was estimated from the starting diameter using the calculated size–mass relationship from Henehan et al. (2013).

2.2 Fossil samples: St. Stephens Quarry

St. Stephens Quarry (Alabama) is a shallow water site characterised by a palaeodepth of 50–100 m (Miller et al., 2008) and exceptional foraminifera preservation (Wade et al., 2012). In order to compare laser-ablation-derived trace element data with the solution ICPMS Mg / Ca record of Wade et al. (2012), the planktic foraminifera *Turborotalia ampliapertura* was sampled from selected intervals across the Eocene–Oligocene transition. The laser-ablation analytical procedure differed from above only in that foraminifera were cleaned by ultrasonication for 1 min in acetone, 1 min in methanol, and 4 min in deionised water to maximise the removal of clay particles without damaging the specimens. Every chamber available for analysis was targeted. Mean element / Ca ratios for each foraminifer were calculated by taking the average of all measurements for that individual. Because laser-ablation depth profiling is a highly spatially resolved technique, poorly preserved areas of the test or those associated with clay mineral contamination could be excluded before the calculation of these means. We use the qualitative coherence of Mg / Ca and elements indicative of

diagenetic overgrowths (e.g. the rare earth elements (REE) which are present at very low concentrations in primary foraminifera calcite; see, e.g., Palmer, 1985). A sample-specific Al / Ca cut-off was used to exclude foraminifera that presumably contained clay minerals which were not removed during ultrasonication. This was either 2 or 4 mmol mol^{-1}, based on the point at which elevated Al / Ca coincided with elevated Mg / Ca.

3 Results

3.1 Carbonate chemistry control on foraminifera Mg / Ca

New and published Mg / Ca–carbonate-chemistry data are shown in Table 1. Our *G. ruber* culture data are shown in the context of a previous study examining the relationship between pH and Mg / Ca in this species (Kisakürek et al., 2008), as well as data compiled for *G. bulloides* and *O. universa* (Lea et al., 1999; Russell et al., 2004), in Fig. 1. Because it has been argued that there is a limited control on foraminifera Mg / Ca at high pH and/or [CO$_3^{2-}$] (Russell et al., 2004) and there is no relationship between pH and Mg / Ca below pH 7.8 for *G. ruber*, we fit regressions that capture the nonlinear aspects of the data. In pH space, *G. ruber* is characterised by a steeper slope between pH 7.8 and 8.1 (Fig. 1a), and we use this as justification for fitting logistic functions to the data. pH and [CO$_3^{2-}$] covaried both in our cultures and those previously published. Therefore, it is not possible to identify which is the controlling factor based on these data. For this reason, normalised Mg / Ca is also shown in [CO$_3^{2-}$] space in Fig. 1b. We fit power regressions to these data in order to capture the decreasing sensitivity of Mg / Ca to [CO$_3^{2-}$] at high values.

There are significant differences between the species-specific regressions. These may represent real differences in the varying ability of the different foraminifera to exclude Mg from the site of biomineralisation as seawater carbonate chemistry changes, or they may represent analytical and experimental noise, given the different culturing methods, locations, and necessary corrections we describe above. Whilst these calibrations should be used where these species have been utilised in the fossil record, in order to apply these relationships to reconstructions based on extinct species in the Paleogene, we combine all the data in order to derive a broad picture of the likely response of foraminifera Mg / Ca to carbonate system perturbations (Fig. 1c and d). The change in slope in the relationship between Mg / Ca and pH, with two inflection points, is also manifest in the combined data and is described by the following logistic function:

$$\text{Mg / Ca} = \frac{0.66}{1 + \exp(6.9 \times (\text{pH} - 8.0))} + 0.76, \qquad (1)$$

with $R^2 = 0.74$; $n = 27$. One outlier (the *G. bulloides* data point at pH 7.6) has been excluded as it has a greater than

Table 1. New and compiled foraminifera culture data of the relationship between shell Mg / Ca and seawater carbonate chemistry. Values are given to the precision originally reported.

Exp.	Ref.[1]	pH (total scale)	$[CO_3^{2-}]$ (µM)	DIC (µM)	T (°C)	Salinity (‰)	Mg / Ca (mmol mol^{-1})	Norm. Mg / Ca[2]
Globigerinoides ruber								
DE3-5-26	1	7.90 ± 0.1	134	2089	26.3	37	6.37 ± 0.25	1.23
DE3-3-26	1	7.98 ± 0.1	162	2137	26.3	37	4.38 ± 0.25	1.34
C1	2	8.18 ± 0.01	297	1957	26	37	4.99 ± 0.15	0.99
C2	2	7.90 ± 0.01	164	1954	26	37	6.92 ± 0.21	1.38
C3	2	7.56 ± 0.01	79	1942	26	37	7.05 ± 0.21	1.40
MH13-1	–	7.62 ± 0.02	94	2175	26	37	7.99 ± 0.24	1.59
MH13-2	–	7.93 ± 0.01	175	2092	26	37	5.21 ± 0.16	1.04
MH13-3	–	8.48 ± 0.00	526	2026	26	37	3.56 ± 0.11	0.71
BK3-7.9	3	7.77 ± 0.06	119	1881	27	35	7.5 ± 0.3	1.46
BK3-8.1R	3	7.95 ± 0.08	175	1885	27	35	4.2 ± 0.2	0.82
BK3-8.3R	3	8.13 ± 0.07	255	1893	27	35	4.2 ± 0.2	0.82
BK3-8.4R	3	8.29 ± 0.08	353	1920	27	35	3.1 ± 0.2	0.60
Globigerina bulloides								
BH1	4	8.17 ± 0.02	185	1996	22	33.6	4.23 ± 0.13	1.06
BH2	4	8.2 ± 0.02	197	1992	22	33.8	3.82 ± 0.11	0.96
BH3	4	7.74 ± 0.02	71	1974	22	33.7	7.75 ± 0.23	1.95
BH4	4	8.65 ± 0.02	469	1980	22	33.7	2.69 ± 0.08	0.68
–	5	7.47	51	1987	22	33	6.33 ± 0.13	1.33
–	5	8.37	282	1591	22	33	3.67 ± 0.07	0.77
Orbulina universa								
–	5	7.67	78	1927	22	33	10.12 ± 0.20	1.14
–	5	8.47	325	1523	22	33	6.15 ± 0.12	0.69
BH3	4	7.74 ± 0.03	72	1523	22	33.7	9.41 ± 0.9	1.36
BH6	4	7.93 ± 0.01	110	1974	22	33.7	7.92 ± 1.49	1.15
AR1	4	8.24 ± 0.02	213	1981	22	33.9	6.82 ± 0.27	0.99
AR3	4	8.41 ± 0.02	300	1977	22	33.8	6.68 ± 0.33	0.97
AR4	4	8.56 ± 0.01	399	1988	22	33.6	6.42 ± 0.46	0.93
AR5	4	8.66 ± 0.01	482	2004	22	33.6	6.49 ± 0.34	0.94
AR6	4	8.22 ± 0.01	170	2030	15	33.8	3.53 ± 0.11	0.96
AR27	4	8.17 ± 0.03	167	2029	18	33.7	5.02 ± 0.33	1.04
AR10	4	8.21 ± 0.01	217	1962	25	34.0	9.6 ± 0.39	1.06

[1] 1: Evans et al. (2016); 2: Henehan et al. (2013); 3: Kisakürek et al. (2008); 4: Russell et al. (2004); 5: Lea et al. (1999). [2] Normalised (ratioed) to Mg / Ca in mmol mol^{-1} expected at 26 °C, 35 ‰, and modern Mg / Ca$_{sw}$ for a given species.

critical Cook's distance and a high residual from the regressions. Whilst a logistic function is consistent with the empirical insensitivity of Mg / Ca to pH or $[CO_3^{2-}]$ at higher values, it is not possible to statistically exclude a simpler relationship. The corresponding linear regression through the data is

$$Mg / Ca = -0.70 \times pH + 6.7, \tag{2}$$

with $R^2 = 0.71$. Finally, because it is not possible to distinguish between a $[CO_3^{2-}]$ and pH control based on these data sets, the relationship between Mg / Ca and $[CO_3^{2-}]$ is best

described by a power function:

$$Mg / Ca = 8.1 \times \left[CO_3^{2-}\right]^{-0.068} - 4.6, \tag{3}$$

with $R^2 = 0.61$. The application of these calibrations to fossil samples implicitly assumes that they describe some fundamental characteristic of the efficacy of the biological processes within foraminifera that exclude Mg, i.e. that the location of typical modern surface pH midway between the two inflection points of the logistic function is coincidental and does not represent an evolutionary adaption to modern carbonate chemistry. This is important as, if a logistic function is indeed appropriate, perturbations to the carbonate system that do not shift pH outside of the range 8.2–8.6
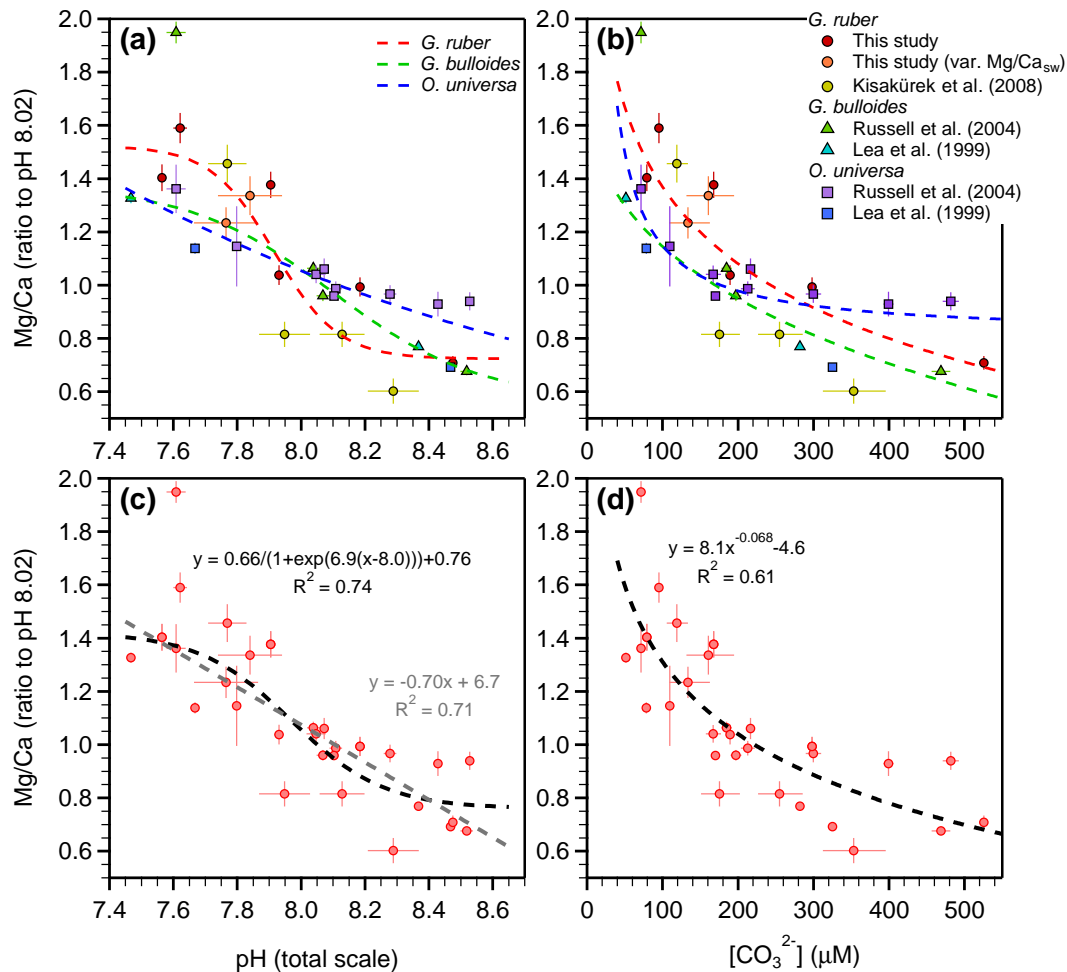
Figure 1. New and compiled planktic foraminifera Mg / Ca–carbonate-chemistry data. Mg / Ca is shown as a ratio to that at pH 8.02 ($\sim$ 8.15 on the NBS scale) for each species. Panel (**a**): species-specific Mg / Ca variation with pH. Panel (**b**): Mg / Ca variation with $[CO_3^{2-}]$. Panels (**c, d**) show the same data sets with regressions calculated from all data combined. Both logistic and linear relationships are shown between Mg / Ca and pH.

or 7.7–7.4 are unlikely to be associated with a large pH-derived shift in Mg / Ca$_{test}$. There is no relationship between foraminifera Mg / Ca and DIC (Fig. 2), and we eliminate secular changes in DIC as a potential control on foraminifera Mg / Ca through time.

Because a proxy that relates directly to pH is available (δ^{11}B), whereas $[CO_3^{2-}]$ cannot be reconstructed without another known carbonate system parameter (e.g. alkalinity, DIC), we base the implications for palaeotemperature reconstruction on the relationship between Mg / Ca and pH. Whilst we cannot eliminate $[CO_3^{2-}]$ as the primary control, we argue that pH is the most likely driver of carbonate-chemistry-related Mg / Ca shifts in Sect. 4.1. If this is incorrect and $[CO_3^{2-}]$ is found to exert the dominant control on Mg / Ca, then our results may require minor revision.

3.2 St. Stephens Quarry laser-ablation data

Laser-ablation data of *T. ampliapertura* from St. Stephens Quarry are characteristic of excellent foraminifera preservation. Mn/Ca ratios are typically $< 0.2\,\text{mmol}\,\text{mol}^{-1}$, suggesting little or no bias from diagenetic overgrowths. Interchamber profiles (Fig. 3a) show localised areas with elevated Al / Ca which likely result from remnant clay particles, which were discounted before calculating mean shell values. Four intervals were sampled for which solution ICPMS Mg / Ca data have already been published (Wade et al., 2012), as shown in Fig. 3b. Mg / Ca from both techniques are within error of each other for all intervals. Moreover, relative inter-sample differences in Mg / Ca are indistinguishable between the laser-ablation and solution Mg / Ca data. Whilst mean laser-ablation measurements (which represent the average of 10–30 individual chamber profiles) are offset to values $\sim 10\%$ higher, which would result in a 1 °C tem-
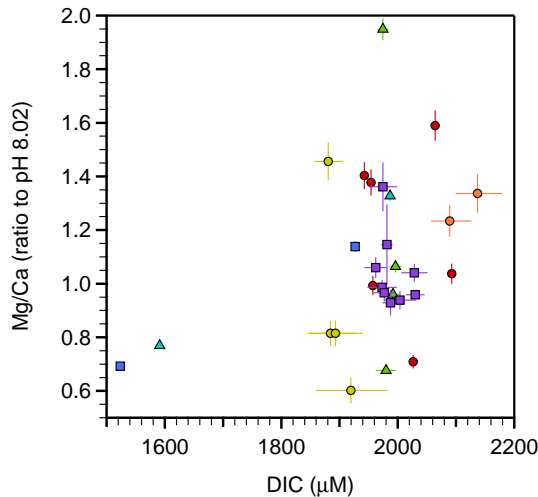
Figure 2. Foraminifera Mg / Ca variation with dissolved inorganic carbon. See Fig. 1a, b for legend.

Figure 3. Panel (**a**): an example laser-ablation profile trough a *Turborotalia ampliapertura* chamber. Sub-micrometre variations in element / Ca ratios are identifiable, enabling poorly preserved or contaminated areas of the test to be excluded from the calculation of mean values. Here, the inner and outer surfaces of the chamber are characterised by elevated Al / Ca, implying incomplete clay particle removal. Panel (**b**): a comparison of laser-ablation and solution ICPMS Mg / Ca data from the same intervals at St. Stephens Quarry. Solution data from Wade et al. (2012). Labels show the depth intervals of these samples. Solution ICPMS error bars are the long-term precision (relative standard deviation, RSD), whereas laser-ablation error bars are 2 SE of all analyses from each interval.

perature bias, this error is small compared to uncertainties derived from the complications we list below (see Sect. 4.4) and may be coincidental given the small number of samples that were analysed using both techniques. Based on these data, we infer that calibrations derived from solution analyses of planktic foraminifera are applicable to laser-ablation fossil data and vice versa.

4 Discussion

4.1 A mechanistic understanding of Mg / Ca variation with carbonate chemistry

Foraminifera are known to elevate the pH of vacuolised seawater by up to ~ 1 unit (Bentov et al., 2009; de Nooijer et al., 2009), and seawater vacuoles have been suggested to play a fundamental role in calcification (Erez, 2003; Bentov and Erez, 2006), although the importance of their role has been questioned (Nehrke et al., 2013). This implies that the [CO_3^{2-}] of the calcifying fluid is significantly higher than that of the vacuolised seawater, especially given the carbon-concentrating mechanism proposed by ter Kuile and Erez (1987) and modified by Bentov et al. (2009). If Mg is pumped out of seawater vacuoles by the vacuole–cytosol concentration gradient and membrane potential, as suggested by Bentov and Erez (2006), then the efficiency of Mg removal may be sensitive to pH. There are several reasons why this could be the case. When seawater pH is lower, then the foraminifer needs to work harder in order to elevate vacuolar pH. If this process is fundamentally linked to the ability of these organisms to remove Mg, whereby a lower pH makes it more difficult to precipitate calcite with low Mg / Ca, then a decreased pH would result in calcite with a higher Mg concentration. The observed dependence of shell Mg / Ca on pH may also be explicable if calcification proceeds through an intermedi-
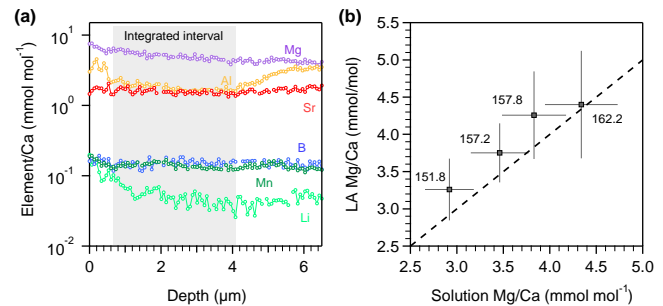
ate phase such as amorphous calcium carbonate (see, e.g., Politi et al., 2004), for which there may be a relationship between Mg and pH that is different to calcite (Burton and Walter, 1991). Alternatively, pH has been shown to significantly affect membrane potential in algae (Spanswick, 1972). If foraminifera use this gradient to pump Mg out of vacuolised seawater at some point in the calcification process, the Mg driving force would therefore also be sensitive to seawater pH.

It is more difficult to imagine a mechanistic control of seawater [CO_3^{2-}] on Mg / Ca$_{test}$ because foraminifera probably source a portion of the DIC required for calcification from metabolic CO_2 (ter Kuile et al., 1989; Bentov et al., 2009). Whilst lower pH or [CO_3^{2-}] is known to negatively affect calcification rates in several marine organisms (Ries et al., 2009) including *G. ruber* (Kisakürek et al., 2008; Henehan et al., 2013), in foraminifera it is more likely as a result of the reduced efficiency of the carbon-concentrating mechanism when vacuole pH is lower and not because fewer [CO_3^{2-}] ions are present in the endocytosed seawater (the two are related, but it is the pH of seawater that is the dominant control). However, until experiments are carried out with variable [CO_3^{2-}] (DIC) at constant pH, it will be difficult to disentangle the effects of each. It may be that both pH and [CO_3^{2-}] affect calcification rate and Mg / Ca in related but different ways. If pH were to be varied at constant [CO_3^{2-}], the efficiency of any carbon-concentrating mechanism would be affected, whereas variable [CO_3^{2-}] at constant pH would control calcite growth kinetics. Because it may be the relative rate of calcification and Mg removal from the calcifying fluid that controls shell Mg / Ca, we might expect both fac-

tors to exert an additive effect. Our model predicts that pH is more important because foraminifera modify vacuole pH to a value substantially exceeding that of seawater, although further culturing experiments are required to confirm this.

An alternative biomineralisation model has been proposed, wherein ions predominantly arrive at the site of calcification through channels (the transmembrane transport model), with a small proportion arriving as a result of seawater leakage from vacuoles (Nehrke et al., 2013). However, there is no clear reason that a lower ambient pH would result in greater seawater leakage and therefore a higher Mg / Ca$_{test}$, and this model may not be able to explain the observed relationship between seawater carbonate chemistry and Mg incorporation. In any case, these biomineralisation studies should be viewed with the caveat that observations derived from shallow-dwelling benthic foraminifera may not be directly applicable to planktic species.

4.2 Implications for reconstructing relative temperature shifts

Both transient and unidirectional temperature shifts are often associated with a change in ocean pH, as has been demonstrated for both the PETM (Penman et al., 2014) and the EOT (Pearson et al., 2009) based on δ^{11}B measurements of planktic foraminifera. It therefore follows that some portion of the observed foraminifera Mg / Ca shift over such events is not due to temperature but to changes in the pH of seawater. Figure 4 shows the extent to which relative temperature shifts would be overestimated as a result of assuming that temperature is the only dominant control on foraminifera Mg incorporation. The degree to which the associated temperature change may be biased is dependent on the magnitude of the pH shift and the type of regression used to describe Mg / Ca$_{test}$ change with pH. Using a logisitic relationship, Mg / Ca is most sensitive to pH change between 7.9 and 8.4, as the regression slope becomes less steep outside of this range. Of course, this is not the case for a linear Mg / Ca– pH relationship.

Correcting PETM records for pH change is therefore sensitive to the type of regression used if the pre-excursion pH was ≤ 7.8, as indicated by the reconstructions of Panchuk et al. (2008) and Zeebe et al. (2009). If a linear fit is more appropriate, and assuming no other bias on deep-time Mg / Ca-derived relative temperature shifts, then a 0.3 unit pH drop would cause an apparent change in foraminifera Mg / Ca equivalent to a 1.6–1.8 °C temperature shift, implying that a reconstruction of relative temperature change would be overestimated by this amount if the effect of pH is not accounted for. If the logistic function is applied to the data then the contribution of pH would cause the temperature shift to be overestimated by < 1 °C.

For the EOT, the Mg / Ca shift associated with the pH reconstructions of Pearson et al. (2009) is less uncertain. This is because the maximum pH over this interval was probably
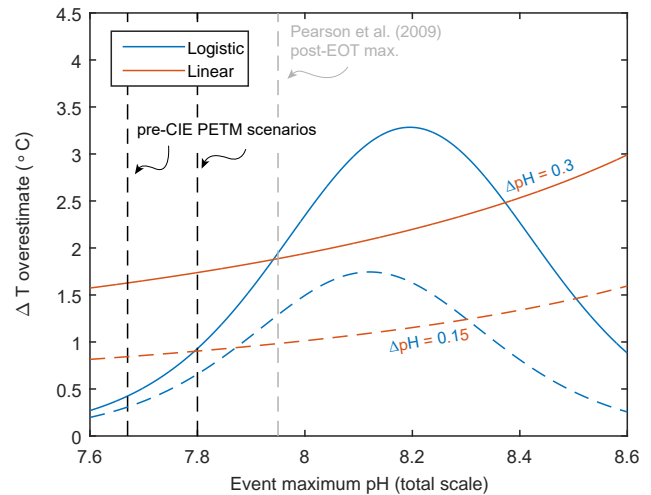

Figure 4. Temperature overestimate across climatic events if it is assumed that pH change exerts no control on foraminifera Mg / Ca. Overestimates derived from both a logistic and linear relationship between Mg / Ca and pH are shown for a 0.3 unit pH shift (solid lines) and a 0.15 unit pH shift (dashed lines). pH scenarios for both the PETM (Panchuk et al., 2008; Zeebe et al., 2009) and the EOT (Pearson et al., 2009) are overlaid.

higher than the background pH during the time of the early Eocene hyperthermals, and therefore there is a smaller difference between the pH-derived Mg shift between a logistic and linear function through the culture data (dashed lines in Fig. 4). If pH is unaccounted for in Mg / Ca-derived temperature reconstructions over the EOT (and again, assuming there are no other biases on Mg / Ca), then the relative temperature shift would be overestimated by 0.8–1.5 °C. This bias is not strongly controlled by the assumption of δ^{11}B$_{sw}$ (Pearson et al., 2009, report pH reconstructions based on δ^{11}B$_{sw} = 38 \pm 1$‰), as the pH-related temperature shift is reasonably insensitive to both pH and the choice of Mg / Ca– pH regression over the seawater pH range 7.75–7.95 for a pH change of this magnitude.

Whilst it is beyond the scope of this paper to discuss the implications across all climatic events with an associated shift in carbonate chemistry, aside from the intervals discussed here, this finding has particular relevance to glacial–interglacial SST reconstructions based on foraminifera Mg / Ca, which are typically viewed as being relatively robust as no Mg / Ca$_{sw}$ correction is necessary during the Pleistocene. Whilst glacial–interglacial surface ocean pH shifts were spatially variable (see, e.g., Foster, 2008; Martínez-Botí et al., 2015), a 0.1–0.15 unit change is typical (between ∼ 8.1 and 8.25), which may result in an overestimation of glacial–interglacial SST change on the order of 1–1.5 °C.

The relationship between pH and Mg / Ca means that relative temperature shifts in the past may have been overestimated. However, a further consideration is the recent finding

that the sensitivity of the relationship between Mg / Ca and temperature may not be constant at below-modern Mg / Ca$_{sw}$ (Evans et al., 2016). Figure 5 shows calibrated and modelled variation in the exponential coefficient (A) of a *G. ruber* Mg / Ca–temperature calibration with Mg / Ca$_{sw}$. The relationship between Mg / Ca and temperature is assumed to take the form Mg / Ca $= B \exp^{AT}$, where B and A vary according to an unknown function with respect to Mg / Ca$_{sw}$. At present, only the sensitivity in the modern ocean (see, e.g., Anand et al., 2003; Kisakürek et al., 2008) and at Mg / Ca$_{sw}$ = 3.4 mol mol^{-1} (Evans et al., 2016) is known, indicating a reduction in sensitivity from 9 to 7.4 % °C^{-1}. Further calibrations are required to constrain this sensitivity at Paleogene Mg / Ca$_{sw}$ ratios, which were reasonably invariant between 2.0 and 2.5 mol mol^{-1} (Dickson, 2004; Coggon et al., 2010; Evans et al., 2013). Six different model curves between the exponential coefficient (A) and Mg / Ca$_{sw}$ are shown in Fig. 5. These were derived by fitting both the observed sensitivity change as well as the calibrated nonlinear relationship between seawater-test Mg / Ca reported by Evans et al. (2016) for a variety of assumptions regarding the shape that this relationship should take (linear, power, exponential, quadratic). These curves are better constrained than they appear from the two data points available, as only specific models are capable of also capturing the upwards-convex seawater-test Mg / Ca relationship for *G. ruber*, which has also been observed in other foraminifera (Evans et al., 2015; Raitzsch et al., 2010). For example, a linear regression through the two data points implies a convex-down seawater-test Mg / Ca curve, the opposite of that for all species studied so far (see Evans and Müller, 2012), and can be immediately discounted. Nonetheless, the sensitivity of Mg / Ca to temperature is not yet precisely known for the Paleogene and may lie anywhere in the range 5.0–7.5 % °C^{-1} based on the data currently available.

The effect of pH and the shift in Mg / Ca–temperature sensitivity with Mg / Ca$_{sw}$ act in opposite directions on reconstructed relative temperature shifts, and these effects may – to some extent – cancel each other in the Paleogene when Mg / Ca$_{sw}$ was ∼ 50 % of modern. However, it should not be assumed that the two are balanced exactly, and at the very least both of these factors should be propagated into error estimates. This may be the case to a lesser extent for events that occurred within the last ∼ 20 Myr, when seawater chemistry was closer to that of today, and therefore the effect of pH dominates the correction applied. Finally, whilst both factors should be considered when reconstructing relative temperature shifts, the relationship between pH and foraminifera Mg / Ca is such that the reporting of absolute temperatures will be highly sensitive to differential carbonate chemistry throughout the Paleogene, as pH was probably broadly lower throughout this Period (Tyrrell and Zeebe, 2004). Absolute Mg / Ca-derived temperatures should not be reported without full consideration of the nonlinearity of the seawater-test
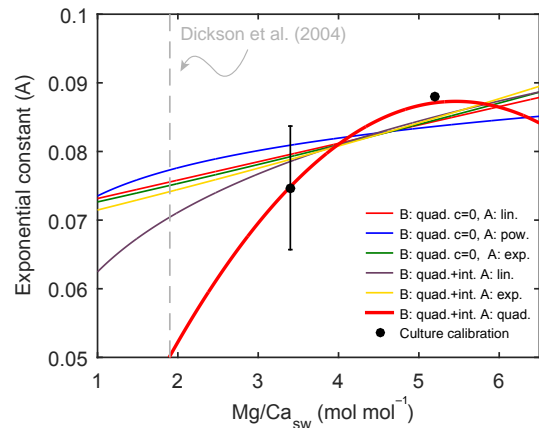

Figure 5. Variation in the sensitivity of the *G. ruber* Mg / Ca thermometer with seawater Mg / Ca, for a range of assumptions regarding the relationship between Mg / Ca$_{sw}$ and the coefficients of a Mg / Ca–temperature calibration of the form Mg / Ca $= B \exp^{AT}$. Data points are based on the cultures of Kisakürek et al. (2008, modern seawater) and Evans et al. (2016, Mg / Ca$_{sw}$ = 3.4 mol mol^{-1}). Lines are derived from least-squares modelling of these data sets as well as the seawater-shell Mg / Ca calibration of Evans et al. (2016). A range of model curves are shown based on different assumptions of the form the regression between the exponential coefficient of a Mg / Ca–temperature calibration and Mg / Ca$_{sw}$ should take, shown in the legend. For example, the thick red line assumes that both coefficients of a Mg / Ca–temperature equation vary quadratically with Mg / Ca$_{sw}$; the blue line assumes that the pre-exponential coefficient varies quadratically whilst the exponential coefficient varies with a power function with respect to Mg / Ca$_{sw}$. "quad. c = 0" are quadratic equations forced through the origin, whilst "quad.+int." are quadratic regressions with a y intercept. An estimate of early Eocene Mg / Ca$_{sw}$ (Dickson, 2004) is shown for comparison. These models suggest that the exponential coefficient of a Mg / Ca–temperature calibration may be reduced from 0.09 to 0.05–0.075 at this time.

Mg / Ca relationship and the seawater pH for the interval of interest.

We now apply these findings to the PETM and the EOT in detail, in order to better constrain SST and hydrological shifts over the former and to produce the first absolute Mg / Ca-derived temperatures across the EOT corrected for both Mg / Ca$_{sw}$ and pH.

4.3 Implications for SST and hydrological shifts over the PETM

Coupled Mg / Ca–δ^{18}O measurements of foraminifera have been used to derive both SST and hydrological change across the PETM. Based on this technique, Zachos et al. (2003) reconstruct a 1.0–2.6 ‰ positive salinity shift at Ocean Drilling Project (ODP) Site 1209 (North Pacific), implying a change to a more evaporative regime during peak warming. Similarly, this technique has been applied to ODP Site 865 (equatorial Pacific) and Deep Sea Drilling Project (DSDP) Site 527

(subtropical South Atlantic) (Tripati and Elderfield, 2004), with a more complex picture of hydrological change emerging. Uncorrected for pH, these data also imply enhanced evaporation in the Pacific (i.e. Mg / Ca shows a larger temperature shift than δ^{18}O), whereas the Atlantic site is characterised by a shift towards more negative δ^{18}O$_{sw}$ during the PETM. Finally, Zachos et al. (2006) reconstruct a negative δ^{18}O$_{sw}$ shift at the coastal proximal Wilson Lake (New Jersey), which may be related to increased freshwater runoff, given that the PETM is known to be associated with seasonally increased precipitation in at least some regions (e.g. the Pyrenees; Schmitz and Pujalte, 2007). All of these data sets require revision in light of the control that both pH and Mg / Ca$_{sw}$ exert on the reconstruction of relative temperature shifts. As an example, this is shown for ODP Site 1209 in Fig. 6.

The ~ 0.3 unit pH shift over the PETM (Penman et al., 2014) would result in a 15–20 % increase in foraminifera Mg / Ca using the pre-excursion pH scenario of 7.8. If it were the only previously unaccounted for source of error, this would result in a reduction in the reconstructed SST shift from 4.5 to 3 °C (Fig. 6). However, the potential shift in Mg / Ca–temperature sensitivity, or rather the large uncertainty in how this may have varied in the past, means that the maximum SST excursion may lie anywhere between 3–6 °C. This full range of error includes the pH correction that we outline and assumes that the exponential constant of a Mg / Ca–temperature calibration may lie anywhere between the modern value (0.09) and the lowest modelled value shown in Fig. 5 (0.05). Until this is further constrained, it should be considered as a source of error for relative temperature shifts. It is not possible to assess at present whether reported temperature shifts are overestimates or underestimates or fortuitously accurate.

The potential effect of seawater pH on foraminifera δ^{18}O has been previously recognised (Spero et al., 1997; Uchikawa and Zeebe, 2010) and has a mechanistic basis in oxygen isotope fractionation between carbonate species (Zeebe, 1999), i.e. this fractionation is also most appropriately causally ascribed to pH rather than [CO$_3^{2-}$]. *Orbulina universa* and *Globigerina bulloides* are characterised by cultured pH–δ^{18}O slopes of −0.89 and −2.51 per pH unit respectively, which means that a 0.3 unit pH shift over the PETM would result in underestimating the combined temperature and δ^{18}O$_{sw}$ component of the foraminifera δ^{18}O shift by 0.27–0.75 ‰ (i.e. temperature and pH act in opposite directions on a δ^{18}O$_{shell}$ record if the climatic event is characterised by a temperature increase and ocean pH decrease). This large inter-species difference in δ^{18}O–pH slopes is a further large source of uncertainty given that extinct species may be characterised by different slopes. Figure 6C shows a range of δ^{18}O$_{sw}$ shifts over the PETM based on different assumptions regarding the control that Mg / Ca$_{sw}$ and the relationship between pH, Mg / Ca, and δ^{18}O exert on this record. The blue line shows $\Delta\delta^{18}$O$_{sw}$ (δ^{18}O$_{sw}$ relative to the pre-
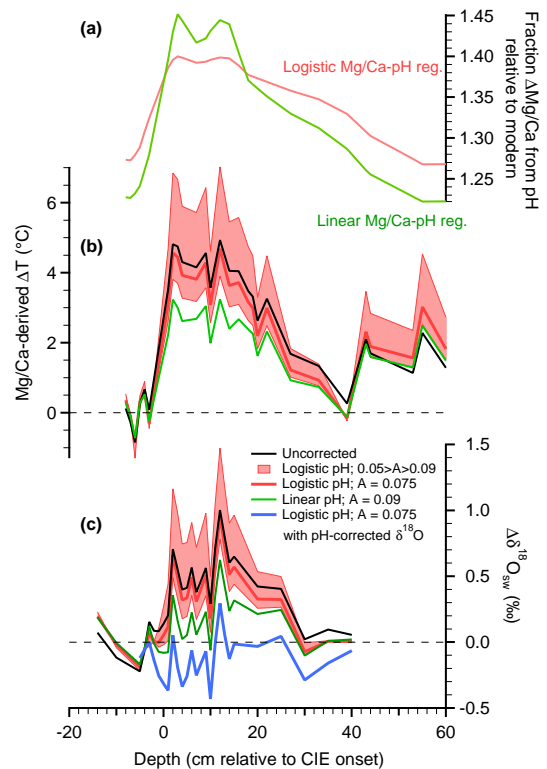

Figure 6. Panel (**a**): the fraction shift in Mg / Ca over the PETM based on the calibrations between Mg / Ca and pH shown in Fig. 1, and the pH reconstructions of Penman et al. (2014, assuming initial pH = 7.8). All data are shown relative to Mg / Ca at modern pH and display the relative change as a result of pH only. Panel (**b**): ODP Site 1209 *Morozovella* Mg / Ca-derived temperature shift across the PETM. The data are shown as originally reported and with various corrections for both pH and Mg / Ca$_{sw}$, relative to the pre-carbon isotope excursion (CIE) baseline. Panel (**c**): δ^{18}O$_{sw}$ shift from coupled Mg / Ca–δ^{18}O data, based on the range of transient temperature shifts shown in (**b**). Our preferred record (blue line), corrected for the pH effect on both foraminifera Mg / Ca and δ^{18}O, and accounting for the likely lower sensitivity of Mg / Ca to temperature in PETM seawater, implies little change in subtropical Pacific surface hydrology over the event. Data from Penman et al. (2014) and Zachos et al. (2003).

carbon isotope excursion (CIE) baseline) fully corrected for all of the effects described above, using our logistic Mg / Ca–pH relationship (Fig. 1), a reduced Mg / Ca–temperature sensitivity of 7.5 % °C^{-1} for the Paleogene (Fig. 5), and the pH–δ^{18}O relationship for *G. bulloides* (Spero et al., 1997). This fully corrected record is characterised by $\Delta\delta^{18}$O$_{sw}$ within ±0.25 ‰ of zero, implying relatively little surface hydrology change at ODP Site 1209 over the PETM if this set of corrections is indeed applicable to this extinct genus (*Morozovella*). For example, alternatively using the *O. universa* δ^{18}O–pH slope would result in a δ^{18}O$_{sw}$ anomaly 0.4–0.5 ‰ more positive. Therefore, the blue line in Fig. 5c is a best estimate based on the available data and calibrations and

by no means definitively demonstrates no hydrology regime change across the PETM but rather serves to highlight that (1) salinity anomalies were likely less extreme than previously suggested and (2) that such reconstructions are associated with large uncertainties.

Aside from those mentioned above, both $\delta^{18}O$ and Mg / Ca data are also available for DSDP Site 401 in the Bay of Biscay (Bornemann et al., 2014) and DSDP Site 277 in the southwest Pacific (Hollis et al., 2015). Furthermore, $\delta^{18}O$ and TEX$_{86}$ data are available for Bass River (Sluijs et al., 2007; John et al., 2008), ~ 50 km east of Wilson Lake. Compiling the data for these sites and applying the corrections that we detail above enables a more accurate picture of SST and hydrological shift over the PETM to be constructed. Figure 7 shows peak-PETM SST and $\Delta\delta^{18}O_{sw}$ relative to the pre-CIE baseline, with error bars that incorporate the full range of uncertainties that we discuss above. Temperature shows a broad relationship with palaeolatitude, with $< 2\,°C$ warming in the (sub)tropics and $2–7\,°C$ at higher latitudes. DSDP Site 401 does not conform to this. These Mg / Ca data are characterised by only a $0.3\,mmol\,mol^{-1}$ raw Mg / Ca change and therefore a corrected temperature shift of $0.2 \pm 0.1\,°C$. In contrast, the *Morozovella* $\delta^{18}O$ excursion at this site would imply an SST change of $5–7\,°C$ if interpreted purely in terms of temperature. Conversely, the oxygen isotope data may simply reflect freshwater flux, given that there is also evidence for an abrupt shift in hydrological regime from the style of clay deposition (Bornemann et al., 2014), although modelling results predict a substantial surface ocean warming in the northeast Atlantic (Jones et al., 2013). It is possible that the small Mg / Ca shift at DSDP Site 401 is a result of poor foraminifera preservation and/or drilling disturbance or dissolution. However, the raw ratios are not abnormal for this time interval, and the high clay content and relatively shallow palaeo-water depth of $1.5–2\,km$ (D'haenens et al., 2012) means that differential preservation or dissolution across the PETM is unlikely (Bornemann et al., 2014). Nonetheless, with the exception of this site, the broad relationship between the magnitude of the SST excursion and latitude is consistent with enhanced high-latitude warming compared to the tropics and a reduction in latitudinal temperature gradients with global warming (Bijl et al., 2009).

Compiled $\Delta\delta^{18}O_{sw}$ shifts over the PETM (Fig. 7b) are all within error of zero, with the exception of the northeast Atlantic (which is a result of the small Mg / Ca shift discussed above) and Wilson Lake. The difference between reconstructed hydrology at Wilson Lake and Bass River is not a GDGT calibration artefact, as Wilson Lake shows a larger raw TEX$_{86}$ shift across the PETM (Sluijs et al., 2007). It is more likely that $\delta^{18}O$ at Wilson Lake is affected to a greater extent by terrestrial freshwater input as it was located closer to the palaeo-shoreline, whilst Bass River essentially shows no shift in surface hydrology. Alternatively, because the temperature record at these sites is derived from different ma-
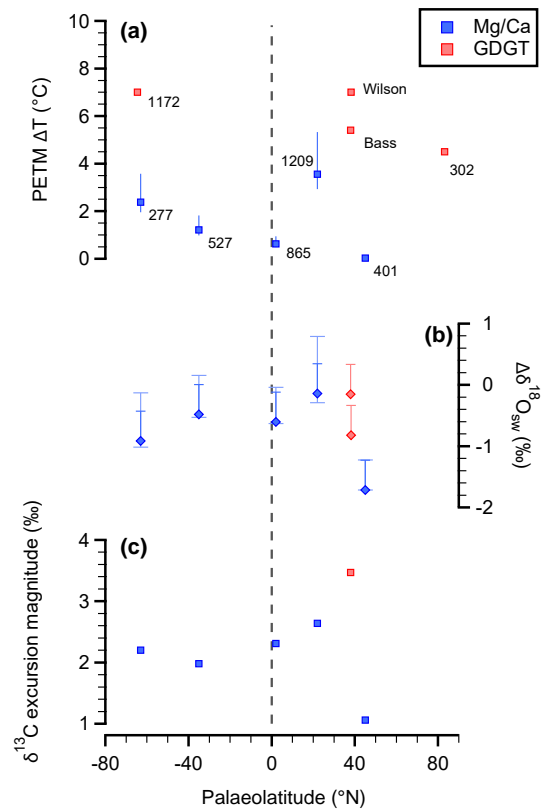

Figure 7. Compiled sea surface temperature and $\delta^{18}O_{sw}$ peak-PETM shifts relative to pre-CIE values. Panel (**a**): GDGT and Mg / Ca-derived warming as a function of latitude. Mg / Ca estimates are adjusted for both pH and the sensitivity of the Mg / Ca–temperature relationship in PETM seawater (see text for details) and are the average of estimates derived from the two surface-dwelling foraminifera genera *Morozovella* and *Acarinina*. Labels refer to ODP and DSDP site numbers or locality names. Panel (**b**): $\Delta\delta^{18}O_{sw}$ reconstructions based on foraminifera $\delta^{18}O$ coupled with either Mg / Ca or GDGT-derived sea surface temperature shifts. $\delta^{18}O$ was adjusted for pH following Uchikawa and Zeebe (2010). Inner error bars are the uncertainty relating to the $\delta^{18}O$–pH slope (data points use the $\delta^{18}O$–pH slope of *G. bulloides*, whilst the inner positive error bar shows where the data would lie if the slope of *O. universa* were to be used); outer error bars also include the uncertainty relating to the pH and sensitivity corrections applied to the Mg / Ca data. Data not specifically discussed in the main text are from Sluijs et al. (2006) and Sluijs et al. (2011). Panel (**c**): the magnitude of the carbon isotope excursion at each site in *Acarinina*, with the exception of DSDP Site 401 (*Morozovella*).

terial, it is possible that a seasonal bias in foraminifera or GDGT production could impact the accuracy of hydrology reconstructions. Furthermore, microanalytical approaches to proxy extraction from foraminifera shells are becoming more common (e.g. Kozdon et al., 2013; Evans et al., 2015). As a result, the impact of diagenesis on planktic species from sites previously thought to be well-preserved are becoming more apparent. The relatively large negative $\Delta\delta^{18}O_{sw}$ shift

that we reconstruct for the equatorial Pacific (ODP Site 865, Fig. 7) is in part because we use the new spatially resolved $\delta^{18}O$ data of Kozdon et al. (2013), which are characterised by a larger shift in raw $\delta^{18}O$ than the multiple whole-shell analyses of Tripati and Elderfield (2004). If other sites are similarly diagenetically compromised, then it is possible that current data sets do not accurately portray temperature and hydrology change during the CIE.

Although some sites may be biased in these respects, or are likely influenced by near-coastal processes, applying these corrections overall implies a slight freshening of surface waters during the peak CIE. At distal sites, this can only result from a change in hydrology towards relatively more precipitation. Although the detail of hydrological change across the full PETM interval is evidently more temporally complex, particularly when differences between surface and thermocline water are considered (see, e.g., Tripati and Elderfield, 2004), this suggests that most areas for which records are available were characterised by a salinity decrease. A salinity increase associated with the peak-CIE PETM interval is only possible at sites other than ODP Site 1209 if the pH–$\delta^{18}O$ slope of *Morozovella* and *Acarinina* was substantially lower than that of the extant species for which this relationship has been calibrated (Spero et al., 1997) and/or (1) if the reduction in the exponential coefficient of the Mg / Ca–temperature calibration was greater than shown in Fig. 5 and/or (2) the pH–Mg / Ca relationship was steeper for these extinct species than shown in Fig. 1. Whilst some of these issues will be challenging to address, we highlight that all of these factors should be considered as sources of error, and applying corrections for both pH and Mg / Ca$_{sw}$ gives a current best estimate of no surface hydrological change to a slight freshening at any site distal from the coast, with the possible exception of ODP Site 1209. Further calibration of the pH–$\delta^{18}O$ relationship in both symbiont-bearing and asymbiotic foraminifera would enable the likely inter-species variability of this relationship for extinct foraminifera with more confidence. An additional consideration is the impact of diagenesis on these geochemical records.

Finally, because a drilling disturbance at DSDP Site 401 and dissolution at other sites cannot be ruled out, we also show the magnitude of the $\delta^{13}C$ excursion in Fig. 7c (based on the same foraminifera as the $\Delta\delta^{18}O_{sw}$ data) as an indicator of sites where this may be an issue. Reconstructions from sites with smaller CIEs should be regarded as not necessarily representing peak-PETM conditions. This should be viewed with the caveat that other processes may affect the magnitude of the $\delta^{13}C$ shift at a given site as recorded in planktic foraminifera. Within a given site all reconstructions are based on coeval material; however, this does leave the possibility that some sites record post-maximum CIE conditions (e.g. DSDP Site 401), whilst those with the largest CIEs inform us of peak-PETM hydrology.

We do not apply a salinity correction to the Mg / Ca data as most sites are within error of no salinity change and because

such a correction requires some assumption regarding the salinity–$\delta^{18}O_{sw}$ relationship at the time. However, if robust evidence for salinity change is shown then this additional factor should be accounted for. Using the Mg / Ca–salinity slopes of Hönisch et al. (2013), a PETM salinity change of 1 ‰ would impact ΔT reconstructions by 0.15–0.5 °C.

4.4 Towards accurate absolute Mg / Ca-derived temperatures: the EOT as an example

Mg / Ca-derived reconstructions of the thermal evolution of the surface ocean across the Eocene–Oligocene climate transition is known from only a handful of sites: the Tanzania Drilling Project (Lear et al., 2008), St. Stephens Quarry, Alabama (Wade et al., 2012), and four locations in the Southern Ocean (Bohaty et al., 2012). Planktic foraminifera boron isotope measurements indicate that the transition was associated with a 0.1–0.15 unit positive pH shift from a pre-event pH of 7.8–8.0 (Pearson et al., 2009). As for the PETM, the Mg / Ca shift over the EOT resulting from this pH change is counteracted to some extent by the reduced sensitivity of the relationship between Mg / Ca and temperature, as Mg / Ca$_{sw}$ reconstructions based on three independent proxies within a few million years of the transition are 2.0–2.4 mol mol^{-1} (Horita et al., 2002; Coggon et al., 2010; Evans et al., 2013). However, the pH change over this interval is characterised by a reversal to more acidic conditions between 33.6 and 33.4 Ma (Pearson et al., 2009), which means that this will impact relative temperature reconstructions across the EOT irrespective of the reduced sensitivity in Mg / Ca temperature. As the pH record has a far lower resolution than the Mg / Ca data, it is possible that there are unavoidable inaccuracies derived from linearly interpolating between data points.

In order to reconstruct absolute temperature (as well as relative shifts) from Mg / Ca before the Pleistocene, two additional pieces of information are required: (1) a Mg / Ca$_{sw}$ reconstruction for the time interval of interest, in order to revise the coefficients of the Mg / Ca–temperature calibration, and (2) a pH record in order to adjust the Mg / Ca data according to Eqs. (1) or (2). As before, this assumes that the pH–Mg / Ca relationship that we present is broadly characteristic of all foraminifera and that the *G. ruber* calibrations of the nonlinearity of the Mg / Ca$_{test}$-Mg / Ca$_{sw}$–temperature surface of Evans et al. (2016) are applicable to other species. Whilst not all foraminifera are characterised by the same pre-exponential Mg / Ca–temperature coefficient in the modern ocean (see, e.g., Anand et al., 2003), this may be difficult to assess for extinct species. The curvature of a seawater-test Mg / Ca calibration and the reduced sensitivity of the relationship between Mg / Ca and temperature, although now known for *G. ruber* (Evans et al., 2016), should be calibrated in other extant foraminifera in order to see to what degree of certainty these equations may be applied in deep time. Nonetheless, now that the necessary calibrations are available for at least one species it is possible to recon-

struct appropriately corrected absolute Mg / Ca temperatures for the Paleogene for the first time, with the caveat that doing so assumes that these calibrations are applicable to the extinct species on which the existing records are based. This is shown in Fig. 8 for St. Stephens Quarry (see Wade et al., 2012). We use this EOT data set as an example of how these corrections should be applied, noting that the absolute temperatures are likely to shift as further pH reconstructions, seawater Mg / Ca estimates, and foraminifera seawater-shell Mg / Ca calibrations become available. For example, a pH record is currently only available from Tanzania, which, although based on the same species as the St. Stephens Quarry Mg / Ca record (*T. ampliapertura*), may not necessarily reflect the detail of carbonate chemistry changes at this site. Realistic Mg / Ca errors for this time are $\pm 4\,^\circ$C, of which $2\,^\circ$C is derived from the uncertainty in Mg / Ca$_{sw}$ ($\pm 0.4\,\mathrm{mol\,mol^{-1}}$), $1.5\,^\circ$C results from a 1 ‰ uncertainty in δ^{11}B$_{sw}$ at this temperature, and $\sim 0.5\,^\circ$C from the uncertainty in extrapolating the seawater-shell Mg / Ca calibrations to Paleogene Mg / Ca$_{sw}$ (Fig. 5). Within the assumptions stated above (i.e. that these calibrations are applicable to extinct foraminifera), reducing uncertainty in Mg / Ca$_{sw}$ reconstructions is clearly a priority in order to improve the precision of absolute Mg / Ca-derived ocean temperatures before the Pleistocene.

Although the absolute temperatures shown in Fig. 8 could shift in either direction by $\sim 4\,^\circ$C as a result of these uncertainties, the Mg / Ca record from SSQ remains in good agreement with TEX$_{86}$ from the same site (Wade et al., 2012); the two proxies do not deviate by more than $2\,^\circ$C where (approximately) coeval samples have been measured. TEX$_{86}$ temperatures are associated with an error of a similar magnitude to Mg / Ca (Tierney and Tingley, 2014). Therefore, it would be coincidental if not impossible if both proxies were offset from the true value by approximately the same amount and in the same direction. However, because the effect of pH and temperature acts in the opposite direction on Mg / Ca$_{test}$, it is possible to arrive at the "right" values by any combination of incorrect assumptions regarding pH and seawater chemistry. For this reason, apparent proxy agreement with Mg / Ca should be viewed with caution (including agreement in relative temperature shifts), unless both a precise and accurate Mg / Ca$_{sw}$ and pH record are available.

At St. Stephens Quarry (Fig. 8b), the magnitude of the precursor cooling described by Wade et al. (2012) is sensitive to the corrections that we detail. Because it was not known otherwise at the time, the published $3.9\,^\circ$C temperature shift used 0.09 as the exponential coefficient (*A*) of a Mg / Ca–temperature calibration and is uncorrected for pH change. Correcting for the difference in modern-EOT Mg / Ca–temperature sensitivity, shown by the orange dashed line in Fig. 8b, results in temperatures far higher than those from TEX$_{86}$ and a precursor cooling of $6.3\,^\circ$C. Finally, applying a pH correction brings the absolute temperatures back into good agreement with those derived from
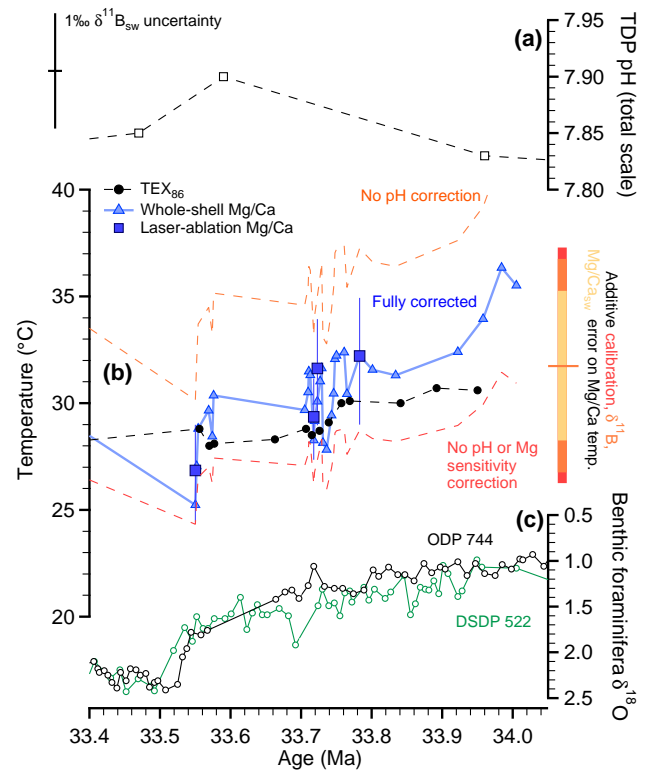

Figure 8. Panel **(a)**: EOT pH reconstruction from Pearson et al. (2009) based on Tanzania Drilling Project samples. The error bar is derived from an uncertainty in δ^{11}B$_{sw}$ of ± 1‰. Panel **(b)**: subtropical sea surface temperature from Mg / Ca and TEX$_{86}$. These absolute Mg / Ca temperatures are the first to be adjusted for both the pH effect on Mg incorporation and the nonlinear relationship between seawater-shell Mg / Ca and temperature. St. Stephens Quarry Mg / Ca data from both solution ICPMS (Wade et al., 2012) and laser ablation (this study) are shown. The combined Mg / Ca error estimate is that due to uncertainty in the Mg / Ca$_{sw}$ ratio ($\pm 0.5\,\mathrm{mol\,mol^{-1}}$), δ^{11}B$_{sw}$, and in the calibration regressions of Evans et al. (2016). The corrected Mg / Ca data imply $\sim 6\,^\circ$C of precursor cooling at ~ 33.9 Ma. Panel **(c)**: ODP Site 744 and DSDP Site 522 benthic foraminifera δ^{18}O (Zachos et al., 1996). Note that the inter-interval Mg / Ca and δ^{11}B$_{sw}$ error (i.e. the error in relative changes) is far smaller than shown by the bars.

TEX$_{86}$ and results in a slightly smaller precursor cooling of $5.9\,^\circ$C (albeit higher than that originally reported), as $0.4\,^\circ$C of apparent cooling can be ascribed to the ~ 0.05 pH change over this 200 kyr interval. This further highlights how these factors may have a significant effect on both absolute and relative Mg / Ca temperature shifts. Given the stability of tropical SST at one site throughout the Eocene (Pearson et al., 2007), this event may represent unprecedented subtropical cooling compared to the earlier Paleogene. The corrected records that we present highlight that global cooling markedly greater than previously thought is likely to have occurred several 100 kyr prior to the onset of major Antarctic glaciation, given that it is observed at several widely

distributed sites. A subtropical SST shift of almost 6 °C is greater than the change reconstructed for most of the subtropics between the present day and the Last Glacial Maximum (LGM), although it is interesting to note that the LGM–Recent temperature difference for this region is of the same magnitude (Waelbroeck et al., 2009), which may imply that this region was similarly sensitive to global climate change in the Paleogene.

The excellent agreement between the published solution data and our new laser-ablation analyses (Figs. 3b and 8b) not only demonstrates that the SSQ Mg / Ca data of Wade et al. (2012) are robust but also provides good evidence that laser-ablation and solution ICPMS results are directly comparable. It is not possible to assess whether the laser-ablation data we present here are more accurate than the solution analyses, as the two are within error of each other (Fig. 3). It is possible that the laser-ablation data are offset to higher Mg / Ca because it is more challenging to remove clay minerals from whole specimens, although given that we exclude all areas of the test with elevated Al / Ca this is unlikely. The offset could alternatively have its roots in the necessity to standardise laser-ablation data to glasses in the absence of a homogeneous carbonate material (see, e.g., Hathorne et al., 2008). However, we note that inter-laboratory comparison studies of solution data are themselves not always within 10 % agreement (Rosenthal et al., 2004); these data do not necessarily highlight an issue with standardising carbonate Mg using the NIST glasses. Given the recent proliferation of Paleogene laser-ablation-derived trace element data (see, e.g., Creech et al., 2010; Evans et al., 2013; Hollis et al., 2015), the consistency that we observe between data sets (Fig. 3b) is encouraging.

5   Conclusions

Using a combination of new and compiled data on the relationship between foraminifera Mg / Ca and seawater carbonate chemistry, we show that pH exerts a large control on Mg incorporation into planktic foraminiferal calcite. Using these data, we present new calibrations of how differential modern and ancient pH may be corrected for. This correction is on the order of 5–20 % per 0.1 unit pH shift between pH 7.7 and 8.3 (total scale), and has the implication that both absolute and relative Mg / Ca-derived temperature changes are likely to be inaccurate and imprecise if secular variation in carbonate chemistry is unaccounted for. We apply these findings to the PETM and EOT. Over the PETM, the ∼ 0.3 unit pH shift (Penman et al., 2014) may be counteracted to an extent by the recent finding that the sensitivity of the relationship between Mg / Ca and temperature was likely lower in the Paleogene (Evans et al., 2016), although the uncertainty in relative temperature and hydrology change is substantially greater than previously thought. However, coupled with the effect that pH exerts on foraminifera $\delta^{18}O$ (Spero

et al., 1997), we show that at most sites peak-PETM sea surface hydrology was likely characterised by a shift to less saline conditions relative to the pre-onset baseline. In contrast, the broadly unidirectional pH shift over the EOT means that relative Mg / Ca-derived temperature shifts have been previously underestimated, as the reduced sensitivity of this thermometer at this time dominates the correction. We report the first pH-corrected absolute Mg / Ca temperatures for the Paleogene that take into account palaeo-Mg / Ca$_{sw}$, the differential modern deep-time Mg / Ca–temperature sensitivity, and pH.

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