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## Geology

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# Extreme warming of tropical waters during the Paleocene–Eocene Thermal Maximum

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## ABSTRACT

**The Paleocene–Eocene Thermal Maximum (PETM), ca. 56 Ma, was a major global environmental perturbation attributed to a rapid rise in the concentration of greenhouse gases in the atmosphere. Geochemical records of tropical sea-surface temperatures (SSTs) from the PETM are rare and are typically affected by post-depositional diagenesis. To circumvent this issue, we have analyzed oxygen isotope ratios ( $\delta^{18}\text{O}$ ) of single specimens of exceptionally well-preserved planktonic foraminifera from the PETM in Tanzania (~19°S paleolatitude), which yield extremely low  $\delta^{18}\text{O}$ , down to <−5‰. After accounting for changes in seawater chemistry and pH, we estimate from the foraminifer  $\delta^{18}\text{O}$  that tropical SSTs rose by >3 °C during the PETM and may have exceeded 40 °C. Calcareous plankton are absent from a large part of the Tanzania PETM record; extreme environmental change may have temporarily caused foraminiferal exclusion.**

## INTRODUCTION

During the Paleocene–Eocene Thermal Maximum (PETM), >2000 Gt of isotopically light carbon was released into the atmosphere in <60 k.y., possibly by the destabilization of deep-sea methane hydrates (Dickens, 2011) or soil organic carbon within permafrost (DeConto et al., 2012). The carbon release caused a substantial negative carbon isotope ( $\delta^{13}\text{C}$ ) excursion (CIE), the magnitude of which remains uncertain (e.g., Zachos et al., 2007). The PETM was associated with globally averaged warming estimated to be >5 °C (Dunkley Jones et al., 2013). The absorption of such large quantities of carbon into the ocean resulted in a lowering of oceanic pH and a shoaling of the calcium carbonate compensation depth (Zachos et al., 2005). Records of tropical sea-surface temperatures (SSTs) from calcareous organisms are rare, as deep-sea sediments commonly have poor microfossil preservation (Zachos et al., 2007). Here we report new geochemical and faunal data from an expanded section from the continental margin of East Africa that provides information about the PETM in the tropics.

## STUDY SECTION

Tanzania Drilling Project Site 14 (TDP-14) (9°16′59.89″S, 39°30′45.04″E) (Nicholas et al.,

2006) comprises two ~30 m holes drilled 1 m apart in late Paleocene–early Eocene hemipelagic sediment. The site was at ~19°S paleolatitude in an outer shelf to slope bathyal environment, estimated at water depths of >300 m (Nicholas et al., 2006). The principal lithologies are claystone and siltstone, with excellent microfossil preservation (e.g., Bown and Pearson, 2009). The site’s proximity to the continent (~70 km to the paleoshoreline; Kent et al., 1971) and shallow burial history mean that TDP-14 contains abundant well-preserved organic biomarkers (van Dongen et al., 2006).

## METHODS

Planktonic foraminifer assemblage count samples were sieved at 63  $\mu\text{m}$ , dried, and split. The first 300 (if present) specimens were counted from the 125–600  $\mu\text{m}$  fraction. Calcareous nanofossils were viewed as smear slides (Bown and Young, 1998), using microscopy in cross-polarized and phase-contrast light on rock surfaces using scanning electron microscopy (Lees et al., 2004). Count data were from more than five fields of view until ~400 specimens were counted.

Species of the genera *Acarinina*, *Morozovella*, and *Subbotina* from the 300–355  $\mu\text{m}$  fraction were screened for preservation quality and

infilling. Individuals with excellent preservation (see the GSA Data Repository<sup>1</sup>) were analyzed as single specimens for carbon and oxygen isotope composition ( $\delta^{13}\text{C}_{\text{foram}}$  and  $\delta^{18}\text{O}_{\text{foram}}$ ), augmenting multiple-specimen *Subbotina* data published by Handley et al. (2008). Specimens were analyzed using an IsoPrime mass spectrometer, and data are reported to the Vienna Pee Dee belemnite scale.

For  $\delta^{13}\text{C}$  analyses of  $\text{C}_{25}\text{--}\text{C}_{31}$  *n*-alkanes ( $\delta^{13}\text{C}_{\text{alk}}$ ), 40–75 g of sediment was solvent extracted and separated into an alkane fraction by alumina flash column chromatography and urea adduction. Analyses were performed on a ThermoFinnigan Delta<sup>plus</sup>XP coupled to a Trace 2000 GC via a GC-C III interface.

The abundances of organic carbon and calcium carbonate were measured from aliquots of sediment powders using a LECO CNS-2000 elemental analyzer. Decarbonated sample powders were also analyzed for their organic carbon isotope composition ( $\delta^{13}\text{C}_{\text{org}}$ ) using a Thermo Flash HT elemental analyzer coupled to a ThermoFinnigan MAT 253 mass spectrometer (see the Data Repository for reproducibility and uncertainties of our methods).

## RESULTS

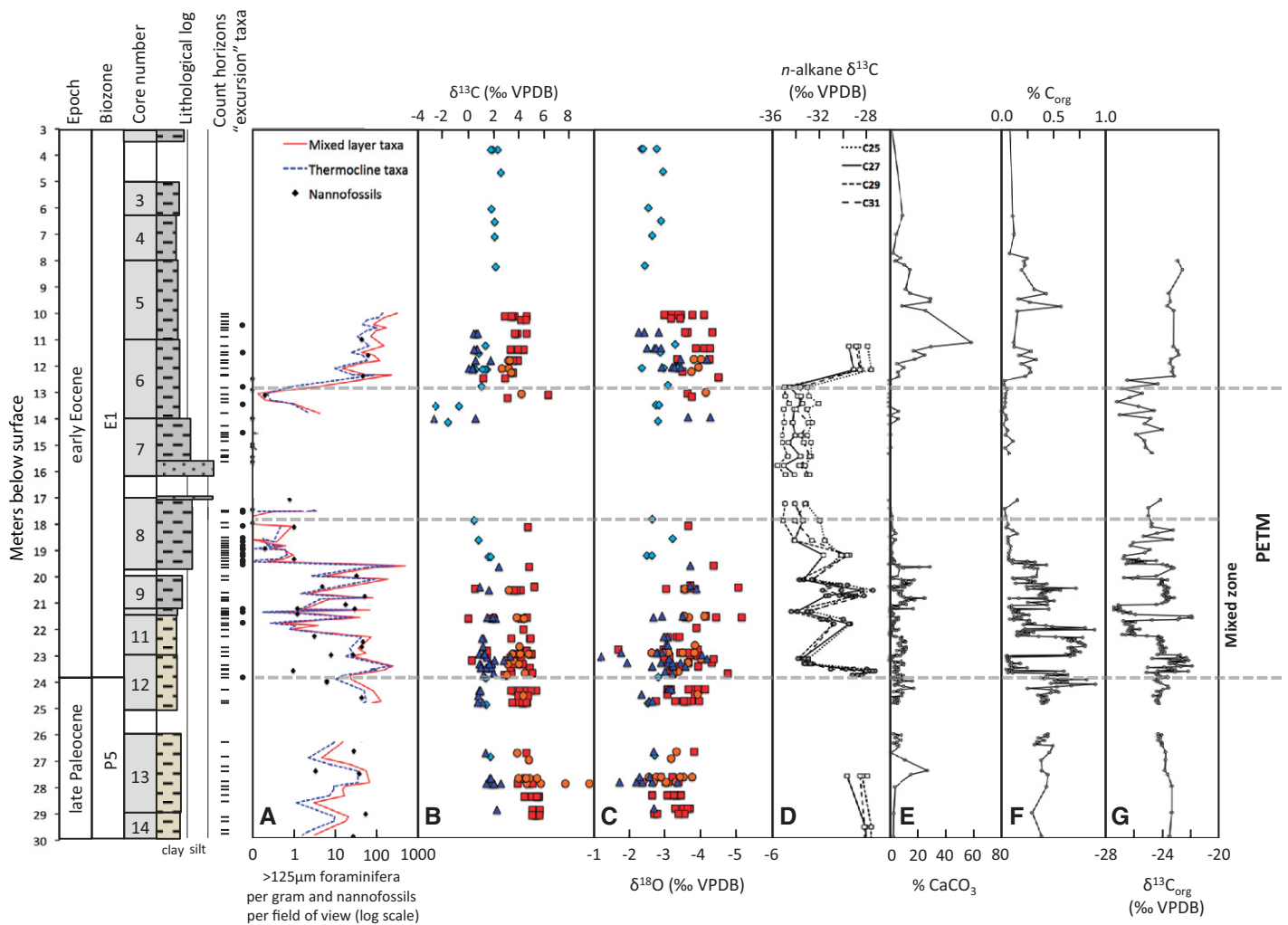
### Sedimentological and Biotic Records

Deposits of the PETM in TDP-14 are ~11 m thick. The base of the PETM interval is ~24 m below surface (mbs), as defined by the first occurrence of the excursion taxon *Acarinina africana* and a negative shift in  $\delta^{13}\text{C}_{\text{alk}}$ , along with some lower  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in single specimens of planktonic foraminifera (Fig. 1). The lower part of the PETM interval is sedimentologically complex, with fluctuating abundances of organic carbon and  $\delta^{13}\text{C}_{\text{org}}$  that likely reflect changes in the relative abundance of distinct sources of

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<sup>1</sup>GSA Data Repository item 2014272, raw data and further details of methods, and oxygen isotope paleotemperature conversion tool (.xls file), is available online at [www.geosociety.org/pubs/ft2014.htm](http://www.geosociety.org/pubs/ft2014.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 1.** Stratigraphic log of Tanzania Drilling Project Site 14 (TDP-14) with geochemical and biotic records of the Paleocene–Eocene Thermal Maximum (PETM). Log records epoch, planktonic foraminiferal biozone (Berggren and Pearson, 2005), lithological variation (dashed gray is clay and silty clay, dotted gray is fine-grained sandstone), horizons sampled for assemblage analysis (dashes), and horizons containing “excursion taxa” (black circles). **A:** Assemblage data of mixed layer (red)– and thermocline (blue)–dwelling planktonic foraminifera and calcareous nannofossils (black diamonds) on a log scale from TDP-14B. **B:** Planktonic foraminifera  $\delta^{13}\text{C}$  from single specimens of the mixed-layer genera *Morozovella* (red squares) and *Acarinina* (orange circles) and thermocline genus *Subbotina* (light blue diamonds); also included are the multiple-specimen *Subbotina* data (blue triangles) from Handley et al. (2008) from TDP-14B (VPDB–Vienna Pee Dee belemnite). **C:** Planktonic foraminifera  $\delta^{18}\text{O}$  (symbols as in B). **D:** *n*-alkane  $\delta^{13}\text{C}$  data from TDP-14A (Handley et al., 2008) (open squares) and new data from this study between ~20 m and 24 m (gray circles). **E:** Bulk sediment weight percent  $\text{CaCO}_3$ . **F:** Bulk sediment weight percent organic carbon. **G:** Bulk sediment  $\delta^{13}\text{C}$  of organic carbon. Gray dashed lines at 24 m to ~13 m denote PETM interval, with mixed interval highlighted between 24 m and ~18 m. For further details of lithology of TDP-14, see Handley et al. (2012).

organic matter (Fig. 1). No mass transport features were observed in the core (Nicholas et al., 2006), but reworking, switching sources, or sediment mixing may account for this complexity. The pre-excursion sediments and reworked packets contain an abundant open-ocean planktonic foraminifer assemblage comprising more than 40 species (see the Data Repository). Stratigraphic horizons containing excursion taxa commonly have low abundance (commonly <1 foraminifer/g) and diversity of planktonic foraminifera. Between ~24 and 18 mbs, planktonic foraminifer abundances fluctuate between pre-excursion levels and very low abundances, with a near complete absence of calcareous microfossils between ~18 and 13 mbs. Where planktonic foraminifer abundances are lowest, the  $\text{CaCO}_3$

content drops to near zero (Fig. 1). Between 24 and 19 mbs (“mixed zone” in Fig. 1), levels with higher microfossil abundances and  $\delta^{13}\text{C}_{\text{foram}}$  are interpreted as dominated by transported pre-PETM sediments. The top of the PETM section is truncated by a hiatus (~13 mbs), and a rich and diverse microfossil assemblage returns higher in the core (13–10 mbs).

#### Geochemical Records

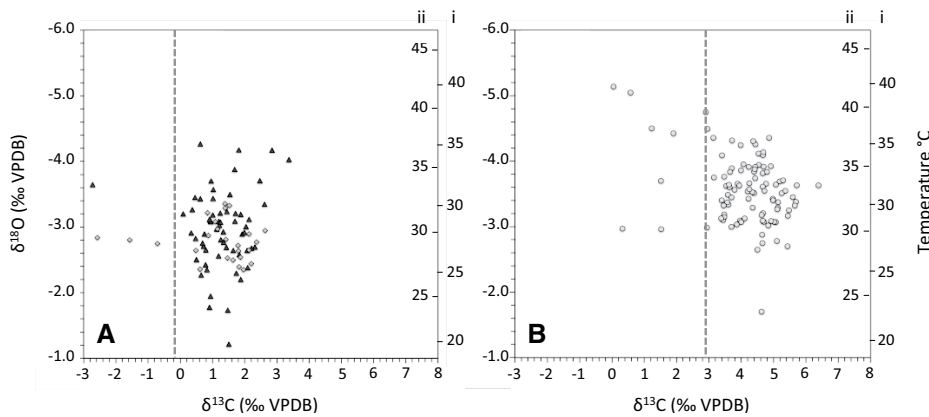
Single-specimen pre-PETM  $\delta^{13}\text{C}_{\text{foram}}$  values for mixed layer– and thermocline-dwelling species are typically  $\sim 4.9\text{‰}$  ( $\pm 1.94\text{‰}$ , 2 standard deviations [SD]) and  $1.5\text{‰}$  ( $\pm 1.11\text{‰}$ , 2 SD), respectively (Figs. 1 and 2). Mean pre-PETM  $\delta^{18}\text{O}_{\text{foram}}$  values are  $-3.3\text{‰}$  for mixed layer– and  $-2.7\text{‰}$  for thermocline-dwelling species (Figs. 1

and 2). Two *Morozovella* specimens from within the CIE exhibit  $\delta^{18}\text{O}_{\text{foram}}$  lower than  $-5\text{‰}$ . However, not all specimens that exhibit the lowest  $\delta^{13}\text{C}_{\text{foram}}$  also record the lowest  $\delta^{18}\text{O}_{\text{foram}}$  (see the Data Repository). Due to the complex stratigraphy at TDP-14, PETM and pre-PETM specimens occur in the same stratigraphic intervals, which makes an estimation of the true magnitude of the CIE from foraminiferal calcite problematic.

#### DISCUSSION

##### Sea-Surface Temperatures

To quantify paleo-SSTs, we explore variables that can impact estimates including (1) seawater  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O}_{\text{sw}}$ ), (2) pH, and (3) the paleotemperature equation.



**Figure 2.**  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  cross-plot of single- and multiple-specimen planktonic foraminifer isotope data from Tanzania Drilling Project Site 14 (TDP-14) (VPDB—Vienna Peedee belemnite). **A:** Single-specimen (dark gray triangles) and multiple-specimen (light gray diamonds) data of thermocline genus *Subbotina*. **B:** Single-specimen data of mixed-layer genus *Morozovella*. Points to left of dashed gray lines in A and B are  $>3$  standard deviations outside mean background value for  $\delta^{13}\text{C}$ , and are regarded as specimens that most likely represent peak carbon isotope excursion (CIE) values. Third axis displays temperatures inferred from  $\delta^{18}\text{O}$  based on Kim and O’Neil (1997), with paleolatitude (Zachos et al., 1994) and pH corrections (Uchikawa and Zeebe, 2010) using the end-member values of Paleocene–Eocene Thermal Maximum pH change suggested by Hönisch et al. (2012) of (i)  $-0.25$  and (ii)  $-0.45$

### Seawater $\delta^{18}\text{O}$

Large continental ice sheets are unlikely to have been present during the Paleocene–Eocene transition (e.g., Sluijs et al., 2008), so all SSTs are estimated using a global  $\delta^{18}\text{O}_{\text{sw}}$  correction of  $-1.0\text{‰}$  (Cramer et al., 2011). Zachos et al. (1994) produced a correction factor for modern latitudinal variations in  $\delta^{18}\text{O}_{\text{sw}}$  as a function of the transport of water vapor from the low to high latitudes, giving SSTs that are up to  $\sim 4^\circ\text{C}$  higher than uncorrected values (because the latitude of TDP-14 is one of net evaporation). Local hydrological cycle changes may have influenced the input of meteoric waters to the surface ocean near the continental margin during the PETM, affecting the  $\delta^{18}\text{O}_{\text{sw}}$ . Deuterium enrichment of *n*-alkanes from TDP-14 implies that regional conditions during the PETM were hotter and more arid than today, punctuated by intense seasonal precipitation events (Handley et al., 2012). The effect of adding meteoric wa-

ters to the surface ocean directly or via rivers is small ( $-0.06\text{‰}$   $\delta^{18}\text{O}$  change for a  $1\text{‰}$  decrease in salinity) (Damassa et al., 2006), therefore a major drop in salinity sufficient to lower the local  $\delta^{18}\text{O}_{\text{sw}}$  seems unlikely; if anything, more arid conditions during the PETM in this region would make the  $\delta^{18}\text{O}_{\text{foram}}$  SSTs slight underestimates. For these reasons we have not corrected for local  $\delta^{18}\text{O}$  variability.

### pH

The changing carbonate ion concentration and decrease in pH associated with elevated  $\text{CO}_2$  levels during the PETM may have resulted in higher  $\delta^{13}\text{C}_{\text{foram}}$  and  $\delta^{18}\text{O}_{\text{foram}}$  because of the “pH effect” (e.g., Spero et al., 1997). We have corrected for changes in the isotopic fractionation of oxygen due to potential pH shifts (Uchikawa and Zeebe, 2010) using the end-member values of pH decline for the PETM ( $-0.25$  to  $-0.45$ ) (cf. Hönisch et al., 2012) to inform our pH correc-

tion, resulting in SSTs that are higher by up to  $\sim 1.5^\circ\text{C}$  than uncorrected values.

### Paleotemperature Equations

The paleotemperature equation of Kim and O’Neil (1997) is favored because it is the only one that is calibrated above  $30^\circ\text{C}$ . For comparison, we have also applied the foraminifera equations of Erez and Luz (1983) and Bemis et al. (1998) (Table 1).

To explore the effects of the paleotemperature assumptions and equations outlined above, we calculated SSTs from single-specimen  $\delta^{18}\text{O}_{\text{foram}}$  of the mixed-layer planktonic foraminifer genus *Morozovella* using the mean pre-PETM, mean PETM, and lowest recorded PETM  $\delta^{18}\text{O}_{\text{foram}}$  (Table 1). Resulting PETM SSTs from TDP-14 range from  $\sim 28^\circ\text{C}$  to  $43^\circ\text{C}$ . Model simulations suggest that PETM tropical SSTs could have reached  $\sim 35^\circ\text{C}$  (Huber and Caballero, 2011), but following corrections for both paleolatitude and ocean acidification, PETM SSTs at this site most likely reached between  $\sim 36^\circ\text{C}$  and  $43^\circ\text{C}$  (Table 1; Fig. 2; see the Data Repository). The calculations suggest that prior to the CIE, SSTs were warmer than modern SSTs at equivalent latitudes, and that during the PETM, SSTs were significantly higher. The change in temperature using the mean background and mean CIE  $\delta^{18}\text{O}_{\text{foram}}$  is  $\sim +3^\circ\text{C}$  ( $\pm 0.5^\circ\text{C}$ ). The lowest  $\delta^{18}\text{O}_{\text{foram}}$  values likely reflect maxima in seasonal warmth on a background of already high temperatures; this may explain the absence of significant temperature change recorded by thermocline species that were living at greater depths.

### Plankton Assemblage Changes

The absence of calcareous plankton from much of the main PETM interval at TDP-14 may be due to dissolution, exclusion due to environmental stress (e.g., Kelly et al., 1996), or sedimentary dilution. Dissolution effects are unlikely as there is no increase in planktonic foraminifer fragmentation (Hemleben et al., 1989) prior to their

**TABLE 1. PETM SEA-SURFACE TEMPERATURE ( $^\circ\text{C}$ ) ESTIMATES FROM TDP-14 BASED ON SINGLE-SPECIMEN MOROZOVELLA PLANKTONIC FORAMINIFERA  $\delta^{18}\text{O}$  VALUES**

$\delta^{18}\text{O}$ temperature correction factors	Bemis et al. (1998)			Erez and Luz (1983)			Kim and O’Neil (1997)		
	Pre-PETM	PETM	Lowest $\delta^{18}\text{O}$	Pre-PETM	PETM	Lowest $\delta^{18}\text{O}$	Pre-PETM	PETM	Lowest $\delta^{18}\text{O}$
	$\delta^{18}\text{O} -3.38\text{‰}$	$\delta^{18}\text{O} -4.04\text{‰}$	$\delta^{18}\text{O} -5.14\text{‰}$	$\delta^{18}\text{O} -3.38\text{‰}$	$\delta^{18}\text{O} -4.04\text{‰}$	$\delta^{18}\text{O} -5.14\text{‰}$	$\delta^{18}\text{O} -3.38\text{‰}$	$\delta^{18}\text{O} -4.04\text{‰}$	$\delta^{18}\text{O} -5.14\text{‰}$
No latitude or pH correction	25.0	28.2	33.5	26.9	30.0	35.2	26.3	29.6	35.4
Latitude correction, no pH correction	29.0	32.2	37.5	30.8	33.9	39.1	30.5	34.0	39.9
Latitude correction, pH correction $-0.25$	N/A	33.9	39.2	N/A	35.6	40.9	N/A	35.9	41.9
Latitude correction, pH correction $-0.45$	N/A	35.2	40.5	N/A	36.9	42.2	N/A	37.4	43.4

*Note:* PETM—Paleocene–Eocene Thermal Maximum; TDP-14—Tanzania Drilling Project Site 14. The oxygen isotope fractionation equations of Bemis et al. (1998) (*Orbulina universa* high light), Erez and Luz (1983) (*Globigerinoides sacculifer*), and Kim and O’Neil (1997) (inorganic calcite) are used. Each equation is applied to the mean background  $\delta^{18}\text{O}$  value ( $-3.38\text{‰}$ ), the mean PETM  $\delta^{18}\text{O}$  value ( $-4.04\text{‰}$ ), and the lowest recorded PETM  $\delta^{18}\text{O}$  ( $-5.14\text{‰}$ ). Data are left uncorrected in row 1, corrected for paleolatitude in row 2 (Zachos et al., 1994), and corrected for paleolatitude and a pH shift (Uchikawa and Zeebe, 2010) of  $-0.25$  and  $-0.45$  in rows 3 and 4, respectively. The PETM pH corrections are not applied to the pre-PETM mean value.

disappearance, and where present, diminutive and fragile nannofossils are exceptionally well-preserved (Bown and Pearson, 2009).

Shelf PETM sections show increased sedimentation rates related to hydrological cycle changes (e.g., Sluijs et al., 2008), and this likely also happened in Tanzania (Handley et al., 2012) leading to decreased calcareous plankton concentrations. The complex stratigraphy and short core length hinder development of an age model that could determine whether the decline in calcareous plankton abundance is the result of sediment dilution. However, the reduction in planktonic foraminifer specimens per gram (s/g) before (average = 86 s/g) and during the peak of the CIE (average = 1 s/g) (Fig. 1) would require sedimentation rates to increase by a factor of ~80, whereas marine biomarker concentrations indicate a sedimentation increase by an order of magnitude less (~6; Handley et al., 2012). Hence, we suggest that the declines in foraminifer abundances represent exclusion due to environmental pressure in combination with sedimentary dilution. As “tropical” foraminifer assemblages appear in higher latitudes during the PETM (Kelly, 2002) and culture experiments demonstrate upper temperature tolerances of ~33 °C (Hemleben et al., 1989), extreme temperatures are likely to have been the principal environmental agent driving the ecological changes captured at TDP-14. The most extreme ecological conditions and the calcareous plankton exclusion occur higher in the core than the geochemical and biostratigraphic evidence for the onset of the CIE. This may reflect a slow response to the initial forcing, whereby plankton populations were able to tolerate environmental change for a significant period of time before tolerance thresholds were breached.

## SUMMARY

TDP-14 contains exceptionally well-preserved calcareous plankton, and although the stratigraphy is complex, a number of biotic and geochemical records document the environmental perturbation and biotic responses of the PETM at low latitudes.  $\delta^{18}\text{O}$  from some single-specimen planktonic foraminifera display low values (~–5‰) and yield paleotemperatures in excess of 40 °C when corrected for paleolatitude and pH effects. A major decline in calcareous plankton abundance throughout the PETM interval likely represents exclusion due to environmental pressure in combination with sedimentary dilution. It is possible that SSTs near TDP-14 may have been even higher than have been inferred during the intervals of the PETM when foraminifera were absent.

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